

INDUSTRIAL USES OF WATER

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PART I.

WATER.

CHAPTER I.

CHEMICAL ACTION OF WATER IN NATURE AND IN INDUSTRIAL USE.

THE chemical action of water in nature and the phenomena of hydrochemical activity observed in a large number of industrial operations are so closely related that their study will help to determine the causes of difficulties with water, and assist at the same time to a discovery of the necessary remedies.

If water actually were what its chemical formula represents it to be, simply a compound of hydrogen and oxygen, the difficulties and troubles which arise when it is put to industrial uses could not arise. From this consideration it is evident that the distillation of water is in itself a preventive against the various accidents liable to arise from the use of ordinary water, in which is held in solution a variety of matters prejudicial to manufacturing processes.

These injurious influences at work vary not only according to the nature of the process to which the water is applied, but also according to the quantity and nature of the matter held in solution in the water. Water that in nature produces the chemical phenomena of corrosion and detrition not infrequently reproduces the like phenomena in the processes of manufacture, occasioning serious accidents, such as boiler explosions.

As water forms it seizes hold of the various constituents of the air with which it comes in contact, and charges itself with them. In this way carbonic acid, nitrogen and oxygen, ammonia and nitrites enter into its composition.

Charged thus with these constituents of the atmosphere, the water falls on to the rock of the earth's crust, where its chemical

action, exerted on the different bodies of which that envelope is composed, is the cause of various phenomena of transformation and disintegration.

It is owing to the presence of these gases, and more especially to the further supply of carbonic acid which it takes up in its passage over the earth's crust, that the water is able to penetrate the rocks and exercise its powers of destruction and decomposition on even the hardest of them.

This carbonic acid is produced by the decomposition of organic matter, as shown by Boussingault, or is the effect of the oxidation of combustible matter, or of the action of acids on limestone rock. The different substances in solution which have this destructive power on rock are likewise the cause of corrosion in steam-boilers and of iron generally.

It is easy to understand that, if water is capable of such vigorous action in nature, it must necessarily display similar energy in industrial use, and even be able to get the better of substances endowed with a maximum of resisting power. Charged with oxygen and carbonic acid and with organic matter in its action on the rocks water can convert anhydrous bodies into hydrates, dissolve mineral matter, produce carbonates, and separate the metals from the substances combined with them.

The solution of combined metals effected by water proceeds according to the co-efficient of their solubility and in virtue of special considerations relating to their decomposition.

As these salts are soluble water often contains calcium sulphate and calcium carbonate, which are injurious to most manufacturing processes; but the proportion of the latter is found to vary considerably, according to the amount of carbonic acid present.

As calcium carbonate is soluble in water which holds carbonic acid in solution, calcium bicarbonate is formed; so also with magnesium carbonate, which yields even more readily to carbonic acid.

In the case of water containing calcium carbonate and magnesium carbonate in solution, according to the excess of carbonic acid present, this water, which readily absorbs this acid, will often just as readily release it.

In nature this liberation of the carbonic acid occurs either as the result of its action on other rocks, or through the action of marine organisms, and the final outcome is a deposit of carbonate of lime.

In industrial operations it has been observed that the giving off of carbonic acid through the boiling of water causes injurious

deposits of calcium carbonate in the form of scale, and that, in bleaching, troublesome reactions occur through the hydrates of metals of the alkaline earths being fixed by the fatty acids of the soap used for scouring, resulting in an insoluble calcareous compound entailing a great waste of soap.

In dyeing, the formation of lakes when water is charged with calcic carbonate furnishes us with another example of this release of carbonic acid and isolation of calcium carbonate, the result in this case being wasteful precipitation of the colouring matter.

Having instanced some of the effects associated with the use of water, and shown the reason of these effects both in nature and in the industrial arts, we proceed by deduction to determine the remedies necessary to counteract them.

To begin with, care must be taken not to use water containing lime salts in any considerable quantity, if vexatious troubles are to be avoided in the workshop and the factory. If a calcareous water must be used it must first be softened.

This preliminary correction consists in eliminating the carbonic acid by bringing the water to the boiling-point in a special apparatus, or by precipitation of the carbonic acid in a vessel containing milk of lime or some other chemical reagent possessed of the same property.

Precipitation similar to that of calcium carbonate takes place in the case of water impregnated with iron, such as mineral waters. This has been sufficiently demonstrated by M. Riban in the learned treatise laid by him before the Academie des Sciences. The same may apply to iron precipitates which cause difficulties in certain industrial operations.

Calcium sulphate induces deposits as the result of molecular transformation and also in terms of the co-efficient of its solubility. These deposits are troublesome in proportion as they are hard and adherent.

Calcium sulphate, in presence of other bodies, frequently forms calcareous combinations detrimental to industrial processes. In nature, calcium sulphate is formed by the sulphuric acid of pyritic rocks being absorbed by the adjacent limestone.

The oxygen of the air held in solution in water has an oxidising effect on the pyrites, apparent in surface transformations that gradually extend in depth.

Thus we obtain the different sulphates of iron ; thus also is basic sulphate of iron formed, which precipitates on the rock, and likewise normal ferric sulphate, which dissolves in water.

The sulphuric acid disengaged by this reaction acts on limestone,

aluminous and magnesian rocks, and combines with the metallic elements and the alkaline earths to produce sulphates.

In nature these sulphates find substances on which to exert their reducing powers; and so also in industrial processes, where as a consequence of the use of water containing sulphates similar phenomena are liable to occur.

In boilers reduction of the ferric salts takes place at the expense of the iron plates, and this is as liable to occur with sulphate of aluminium as with ferric sulphate. As a result of reduction of the sulphates by organic matter, sulphides are formed; this transformation takes place in nature, and likewise in industrial operations, where it is an evidence of similar action.

As for the chlorides, sodium chloride in particular is rapidly dissolved when water passes over beds of rock salt. Were it not that these rocks are protected by impermeable beds of clay, they would soon be carried off altogether by the water.

Sodium chloride is readily diffused through the rocks, which in contact with water yield the salt in solution, and some spring waters owe their saline character to infiltration of sea water.

Sodium chloride operates on the rocks within reach, its action being frequently assisted by the presence of silica. In this way the different elements of the rocks become impregnated with chloride, and eventually the water is found to contain chlorides of sodium, of potassium, of magnesium, of calcium and others. These chlorides are the cause of trouble and damage in the industrial arts, as we shall have occasion to observe, for example in tanning hides, and in other crafts troubles arise from the corrosive effects of the chlorides on metals.

On the other hand, in certain industrial operations distilled water is not always preferable to water containing specific matters in solution. For instance, in dyeing, a calcareous water is an advantage in the application of alizarine colours.

Again, in brewing, the process of mashing is improved by the use of a gypseous water.

Further we shall note in the course of this work, that phenomena of chemical activity in nature arising from the action of microbes recur in the industries, frequently with serious consequences. Certain phenomena of iron corrosion induced by nitrous and nitric ferments may be instanced, and likewise certain troubles in breweries and other places where the process of fermentation is carried out.

CHAPTER II.

COMPOSITION OF WATERS—ORIGIN OF THE SUBSTANCES THEY CONTAIN.

IN a general way, all water is impure.

Pure water—that is to say, water with a composition answering to the scientific formula H_2O , or a combination of two volumes of hydrogen with one volume of oxygen, without admixture of even a trace of any other substance—is not met with in nature.

Distilled water is the typical pure water obtained by condensing steam. Although a simple one, the process requires care.

All waters contain foreign substances, such as nitrogen, carbonic acid, nitrites, nitrates, sulphates, chlorides, carbonates; salts of potassium, sodium, calcium, and magnesium; ferrous and ferric salts, silicates and salts of aluminium—the nature, association and proportion of which enable us to distinguish between the different waters and to ascertain their origin.

The origin of any water may thus be determined by its composition.

We may classify the different kinds of water as follows :—

1. Rain, snow, hail, etc.
2. Ordinary water : well and spring waters ; running waters : calcareous and selenitic waters.¹
3. Sea water.
4. Deep well waters.
5. Mineral waters.
6. Distilled water.

From the industrial point of view it is important that the composition of different waters and the origin of the substances they contain should be known ; as in many cases this knowledge will enable the manufacturer to foresee the troubles their use will cause,

¹ The author uses the term "calcareous" to signify water containing carbonate of lime, and "selenitic" to signify water containing sulphate of lime. In English, at any rate, this terminology is objectionable, and in future we have called them simply "carbonate" and "sulphate" waters.—TR.

and he will be in a position to apply the necessary remedies in a methodical manner.

1. RAIN, SNOW, HAIL, ETC.

The water on the surface of the earth is subject to continual evaporation, rendering the air more or less humid. Hence the atmosphere contains aqueous vapour, but in quantities varying greatly, according to a condition of the atmosphere known as its hygrometric state.

This hygrometric condition is the ratio between the pressure of water-vapour and the temperature of the atmosphere.

The air can only contain a certain definite quantity of moisture or of water-vapour at a given temperature and pressure. The humidity of the atmosphere is therefore limited, and when that limit is reached the air is said to be saturated.

At this point the surplus is condensed and falls back in the form of rain, to undergo anew the process of evaporation; and the drier the air and the stronger the wind the more rapidly does this evaporation take place. As a result we have the formation of mist and clouds, and these become visible the moment the relative humidity of the air has fallen below the point of saturation.

In the case of clouds this condensation of the vapour is caused either by the cooling of the atmosphere, or by the combination of cold volumes of air driven by the wind with warm air charged with moisture.

The condensation of aqueous vapour in the atmosphere may also be caused by the proximity of mountains, whose low temperature cools the volumes of damp air that sweep over them.

If the clouds are neither kept up by ascending currents nor are in a drier atmosphere, condensation takes place and rain is formed.

When the temperature of the air is below zero, instead of rain a crystalline substance usually falls, which we call snow; and gradually as the temperature falls the downfall of snow diminishes in proportion.

Snow continues to fall until the temperature reaches about -20° C. Under these conditions its formation may be assisted by the wind, but it is very scant. Below -20° C. snow is of rare occurrence.

Verglas (a mere glaze of ice) is caused by rain at a temperature verging on zero falling upon a colder soil.

Water crystallises in forms belonging to the rhombohedral system. Snow is composed of a certain number of small crystals

usually in the form of six-rayed stars, in the centre of which is sometimes seen a small brilliant crystal, hexagonal in shape.

The specific gravity of snow may be stated as 0.10 when newly formed. The results of examinations made by different authors vary as much as 100 per cent., but everything depends on the condition of the snow at the time of examination.

But whatever the form of the aqueous meteors,¹ be it rain or snow, notwithstanding that they are the purest water, they contain gases of atmospheric origin. This is owing to the solvent power of the water, and the amount of such gases held in solution must vary with the composition of the air and the conditions of the atmosphere as regards pressure and temperature, and with the season.

Among the gases found in solution in rain water are oxygen, nitrogen and carbonic acid.

In addition to these gases meteoric waters contain salts, such as the carbonate, nitrate and chloride of ammonia, sodium chloride,



FIG. 1.—Snow crystals.

the proportion of which is very appreciable in waters found near the sea, sodium sulphate and calcium salts.

In proximity to the sea meteoric waters also contain iodides and bromides.

Finally, the organic matter which is always found in the air is carried down by rain, and, as in the case of compounds of ammonia, the quantity of this organic matter is greater in the vicinity of centres of population, such as large cities.

From the investigations conducted by Chatin we may conclude :—

1. That at Paris, when the wind blows in from the sea, chlorides are found in greater proportion in rain water than in the water of the Seine: they abound in rain water near the sea.

2. That the rain water of Central France and of Paris contains a considerable amount of sulphates, more so generally than the river waters. As a rule rain water is not as heavily charged with chlorides as river water.

¹ Henceforth the author uses this poetic expression, but we have translated it "rain," and this must be taken to include all forms of water from the skies.—TR.

3. That the salts of calcium and sodium are found in quite appreciable quantities in rain water.

4. That rain water is found to contain some nitrogenous organic matter which may be considered a mixture of ammonia ultimate and ulmic acid. This organic matter abounds in the lower layers of the atmosphere, and rain water contains as much as 0.05 gramme per litre.

		Water collected at the Paris Observatory. On the terrace. On the level. (Grammes per cubic metre.)	
Nitrogen		6.397	7.939
Ammonia		3.334	2.769
Nitric acid		14.069	21.800
Chlorine		2.801	1.946
Lime		6.220	5.397
Magnesium		2.100	2.300

Analyses of rain water when collected at the Paris Observatory made by M. Barral show a residuum of 0.0228 gramme per litre.

The presence of organic matter makes it extremely difficult to preserve rain water, because of the objectionable transformation such matter undergoes. As the result such water may be rendered unfit for domestic purposes, and injurious even in industrial operations. This is frequently the case with rain water collected without necessary precautions in ill-kept cisterns, when it is liable to absorb disease germs, under which circumstances it is not fit for consumption.

Rain water, generally speaking, is the purest of all natural waters, and it will be found advantageous to use it in the place of any other water which may have proved detrimental to industrial processes.

Rain water is often used instead of distilled water in the preparation of most of the baths required in photography.

2. ORDINARY WATER.

(a) **Well and Spring Waters.**—Owing to the porous nature of the rocks of the earth's crust, and to the cracks and faults occurring in them, the water falling on the surface of the earth is able to penetrate into the ground.

This water, charged with carbonic-acid gas and oxygen, has a powerful disintegrating action on the material of the rocks, some of whose constituents are chemically attached and carried away in solution. In this way the hardest rocks are worn away.

By reason of the principle by virtue of which water always seeks the lowest level, these waters in their passage into the depths of the earth absorb more and more carbonic-acid gas, from the abundant supply afforded by organic matter.

The water being thus strengthened by this fresh accession of carbonic gas, the phenomena of chemical activity become more marked.

As a consequence of the phenomena of oxidation, carbonation and decomposition produced by the excess of carbonic acid, the water loses more and more of the gases, especially the carbonic acid, which dissolves the limestone rocks with the greatest ease.

The permeation of the different geological strata by the water is arrested when it comes in contact with an impervious bed, and it here collects and forms subterranean pools.

These underground reservoirs, which sometimes are of a capacity sufficient to form regular lakes and subterranean rivers, feed the springs and wells.

A spring therefore is produced by an underground flow of water emerging from the ground. The direction of this flow may be ascertained by determining the bearings of the geological strata.

These underground bodies of water are therefore retained by an impervious stratum.

By sinking a shaft in the ground down to the water-line a well is formed.

If the spot at which the boring is made is at a level considerably lower than that of the highest point of the water-containing stratum, by virtue of the principle illustrated in the syphon the water thus compressed strives to reach the highest water-mark, and spurts out as an artesian well.

In sinking wells through the different strata consecutive sheets of water are frequently met with. Thus, when boring the well for the railway station at Saint-Ouen, M. Flachet came across five at depths of 36, 45, 51, 59 and 66 metres respectively.

That these artesian wells are sometimes of great depth and furnish a considerable yield is shown by the following table :—

Location of well.	Depth in metres.	Yield per minute. Litres.
Grenelle	548	800
Tours	140	1,100
Bages, near Perpignan	140	2,000
Saint-Ouen Railway Station	66	2,000

The greater the depth of the well the higher is the temperature of the water. The ratio of increase has been ascertained to be 1° per 25 metres ; but this temperature is independent of the atmosphere above ground.

Water rising from deep wells has a temperature higher than that of the locality in which it issues from the ground.

Thus at Paris the mean temperature at the surface of the ground is $10\cdot6^{\circ}\text{C}$., while that of the well at Grenelle is 27°C ., and that of the well at Saint-Ouen is $12\cdot9^{\circ}\text{C}$.

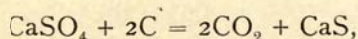
As a rule also, the greater the depth the greater the pureness of the artesian water. This is sufficiently proved by the proportion of suspended matter found in it. Thus at Saint-Ouen M. O. Henry found $0\cdot734$ gramme of solids at a depth of 49 metres, and only $0\cdot267$ gramme at 65 metres.

The composition of spring water varies according to the distance traversed and according to the nature of the strata it has percolated through. Thus water obtained from the granitic stratum is purer than that derived from the secondary strata, the latter being more or less calcareous.

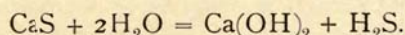
Ordinary well water frequently contains a considerable quantity of calcium carbonate and calcium sulphate, which render it unsuitable for industrial and domestic purposes.

In the case of shallow wells the water often gives off a marked odour of sulphuretted hydrogen, arising from the formation of sulphur by the reduction of calcium sulphate in the presence of the organic matter in the water:—

We have first:—



and then,



These reactions show first of all this reduction, the organic matter being represented by C; and next the decomposition of the sulphur converted into sulphuretted hydrogen, for calcium sulphide is very unstable.

When this organic matter has become nitrogenised it is liable to be transformed, under the influence of certain ferments, into compounds of nitrogen, such as nitrites, nitrates and ammonia.

Salts of potassium are found in artesian well water, as also in waters derived from granitic and feldspathic strata; but they occur only in extremely minute quantities in river water.

(b) **Running Waters.**—After forming subterranean reservoirs and issuing from the ground in the form of springs, the water has not yet reached the end of its journey. It now pursues its way over the surface of the earth, wearing it down little by little, and carrying off by the sheer mechanical action of its current the material of which that surface is composed.

The streamlets thus formed meet and develop into brooks, and these in turn swell into rivers, which eventually run into the sea,

sweeping along with them the detritus collected throughout their course.

In the working of the chemical activity exerted by underground waters, their solvent power enables them to take up a variety of substances in solution, and the quantity of these at the point of outlet varies greatly, and decreases more and more the farther we move from the spring.

When the water has passed through granitic strata only and pursues its course over silicious ground, the quantity of matter held in solution will be small, and in its onward progress it will liberate a portion of the salts thus held.

The operation may be described as one of exchange: the water, after robbing the underground rocks of their constituents—either directly by the exercise of its solvent power, or after subjecting them to certain transformations—on reaching the surface liberates a portion of the substances with which it has become charged.

Thus carbonic acid, which enables water to dissolve limestone readily and facilitates the solution of certain salts, is disengaged; consequently the lime and salts are no longer capable of being held in solution and are precipitated.

In addition to the spring waters which assist to make the streamlets, rain water contributes materially to the solvent action of water flowing over the surface of the land.

Rain, being loaded with carbonic acid, serves to reinforce the supply of this acid remaining in this water; hence renewed energy accrues to the solvent power of the water over the rocks through which it passes, while the salts are maintained in solution.

Notwithstanding this, there ensues a marked decrease in the amount of mineral matter held in solution; so that a much larger quantity of this substance is found in streamlets near their source than in brooks, and, in the same way, a far greater quantity in brooks than in rivers.

Calcium carbonate is one of the salts which are most rapidly reduced; still running waters always contain a certain quantity of it and to this they owe their distinctive taste.

The proportion of calcium carbonate present in running water decreases according to the distance travelled from its source and the nearer its approach to the sea. Thus tributaries contain a larger quantity of calcium carbonate than the large rivers, and brooks more than the tributaries.

The solvent action of water diminishes in proportion to the amount of carbonic gas disengaged in its course. Its energy is then exerted on the more easily dissolved rocks, composed of alkaline salts.

The farther water travels from its source towards the sea, the more does it become charged with salts of potassium and sodium, and more especially with chloride of lime.

Spring waters contain large quantities of carbonic acid, and little oxygen; streams, on the other hand, are more highly aerated.

If spring water is clear, not so river water, which collects the rain which in its flow carries along organic and silicious matter, such as clay, sand and earth.

This matter remains in suspension in the water, and the mud-diness thus occasioned is generally more noticeable when the waters are in flood.

In the Hydrometric Service of the basin of the Seine the degree of transparency of the water is determined as follows:—

A white object, one decimetre square, is immersed to a depth of 30 centimetres in the water to be tested.

If the object is distinctly visible the water is clear.

If the object is indistinctly visible the water is considered doubtful.

If the object is invisible the water is turbid.

The gentler the slope—in other words, the slower the current—the more readily is the suspended matter in the water deposited.

This deposit constitutes the slime, and the organic matter of which it is composed combines with silicious substances, with salts of calcium, with aluminium and with oxide of iron.

The series of tests of Seine water made by M. Hervé Mangon at Port-à-l'Anglais, and extending over a period of three years, gave an average of 39'660 grammes of slime per cubic metre; the maximum weight of slime per cubic metre stood at 626'12 grammes, and the minimum at 1'350 grammes.

Analysis of the slime yielded the following proportions of mineral matter:—

	Per cent.
Carbonate of lime	9'84 to 29'68
Peroxide of iron and of aluminium	3'88 to 16'52

Water described as clear, following the practice of the Hydrometric Service, must contain less than 10 grammes of slime per cubic metre.

The proportion of slime present in water varies considerably in different rivers, thus the Durance at Merundol contains an average of 1'454 grammes of slime per cubic metre, while the Var at La Gaude contains 3'577 grammes.

Seeing that the nature and amount of the suspended matter in the water is so variable, it stands to reason that the composition of the slime differs as widely.

There is no need to dwell on the formation of nitrites and ammonia, the latter combining, in particular, with carbonic acid to yield ammonium carbonate.

Sulphides are also met with as a consequence of the reduction of sulphates in the presence of organic matter.

It is worth noting that if river water contains nitrates, sea water is free from them at a distance from the shore.

(c) **Carbonate and Sulphate Waters.**—According to the nature of the ground they have passed through, spring, well and running waters contain a greater or less quantity of salts of calcium in solution.

Such waters are known as sulphate waters when the proportion of calcium sulphate present is considerable, say over 0.20 gramme per litre.

This calcium sulphate has entered into the composition of the water through the solvent action of the latter on gypseous beds, and its frequent occurrence is explained by the wide distribution of this kind of strata.

The Seine at certain points is very rich in sulphate, for instance in the gypsiferous country between Meulan and Chateau-Thierry, where springs are numerous. Beyond this district the Seine contains barely 0.01 gramme of calcium sulphate per litre.

The greater the quantity of calcium sulphate in water the more unsuitable is it for industrial and general domestic uses.

Well water is frequently rich in sulphate, as for instance within the area of the Paris basin, where the wells have been sunk in gypsiferous strata.

Sulphate waters do not liberate calcium sulphate in contact with the air, and require to undergo special purification before being used.

The calcium carbonate which is found in water is attributable to the solvent action of the carbonic acid in the water on limestone rocks. The freedom with which this action is exerted is in inverse proportion to the degree of crystallisation of the calcium carbonate.

Not only does water dissolve limestone and crystalline rocks, such as arragonite, but also rocks composed of compound carbonates, such as dolomite, which is a double carbonate of calcium and magnesium.

If the quantity of calcium carbonate held in solution in the water exceeds 0.5 gramme per litre, the water is said to be a carbonate water.

The readiness with which any excess of carbonic acid is liberated, with a consequent precipitation of the calcium carbonate, forbids the use of carbonate waters in many industries.

Salts of lime are prejudicial to nearly every industrial process, and every precaution must be taken to guard against them.

We will examine, in separate chapters, the effects produced by these waters in the industrial arts, and the remedies to be applied.

3. SEA WATER.

The composition of sea water varies greatly, and the results of analyses differ according as the sample is taken off the shore or at a distance from land, from the surface or from the bottom, in one region or in another.

Sea water contains a large number of substances—chlorides, sulphates, bromides, iodides, etc., but the salt that predominates is chloride of sodium.

The quantity of chlorine in a litre of sea water is never less than 200 grammes.

This chlorine is in combination with the alkali metals potassium and sodium, and with the metals of the alkaline earths magnesium and calcium.

Magnesium chloride plays an important part in the phenomena of corrosion set up by sea water.

The salinity of the sea is the sum total of the salts it contains, and is determined by their total weight. As a rule they aggregate 35 to 36 grammes per litre, chloride of sodium accounting for about 30 grammes, while salts of magnesium—to which sea water in a great measure owes its taste—amount to one-sixth or so of the total weight of saline matter.

The degree of salinity of sea water varies greatly, being higher in the tropical regions near the Equator than in the polar circles.

The temperature of the sea is far from being uniform, and it is lower at a depth than at the surface.

The mean annual surface temperature of the Mediterranean Sea is about the same as that of the atmosphere.

But the temperature of the sea varies also with the seasons, the mean temperature of the Mediterranean in summer and spring being lower, while on the other hand in autumn and winter it is higher, than that of the atmosphere.

Calcium sulphate, which is a constituent of fresh water, is also found in sea water; the same remark applies to calcium carbonate.

The constant accession of water charged with calcium carbonate would speedily saturate the ocean with that salt, were it not that marine organisms—such as the coral insect, molluscs, foraminifera, and echinoderms—secrete it.

We gather from the observations of J. Davy that calcium carbonate is found particularly in the neighbourhood of the poles.

The high degree of salinity of sea water and the diversity of the salts present in it give rise to most harmful reactions when it is used for manufacturing purposes.

It is therefore impossible to utilise this kind of water in industrial operations without removing the greater part of its salts and utterly eliminating those which are specially detrimental.

Later on we will consider the effects produced by sea water under various conditions, and the methods of purification that may be recommended.

4. DEEP WELL WATERS.

Deep well waters are the outcome of percolation through the different strata of the earth's crust.

In this somewhat slow process the rocks are scoured by the water, which effects a disintegration of their principal minerals.

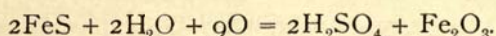
It follows, as a matter of course, that the composition of these deep waters must vary considerably; but in any event it must be closely in keeping with the character of the ground in the vicinity.

In these waters it is usual to meet with salts of calcium—calcium carbonate, calcium sulphate and calcium chloride; with ferrous, barium, sodium and potassium sulphates; with various mineral sulphates and with ferrous carbonate, etc.

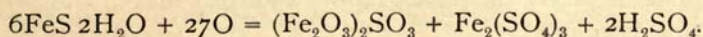
Water passing through pyritic strata takes up sulphates consequent on certain transformations taking place.

In the slate quarries of Angers M. Lechatelier has assured himself that deep waters do not contain the least trace of free sulphuric acid.

After certain special phenomena of oxidation have taken place in the rocks beneath the surface, the pyrites or sulphides are changed by means of oxygen into sulphate of iron:—

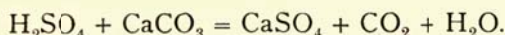


This oxidation of pyrites which takes place in the presence of water charged with air eventually results in the production of basic ferric sulphate, which precipitates on the adjacent rocks normal ferric sulphate and free sulphuric acid, which the water carries off in solution:—



The sulphuric acid produced as a result of this reaction attacks the adjacent rocks, particularly limestone, forming calcium sulphate,

and in this way we account for the presence of this last substance in deep waters :—



In addition to normal ferric sulphate, we also find in solution sulphate of aluminium, cupric sulphate, etc.

By dint of exercising their solvent powers deep waters are finally saturated with mineral substances, which they subsequently deposit on the ground.

Deep waters are injurious in manufacture. Their use requires extraordinary precautions if serious harm is to be avoided. We will treat of these later on under special headings.

5. NATURAL MINERAL WATERS.

By this term we understand waters that at their source have as a rule a high temperature with varying odour, and contain certain fixed or volatile elements in solution in greater or less quantity, which elements impart to them medicinal properties.

Mineral waters may, according to their chemical composition, be divided into five groups :—

1. Chlorinated waters.
2. Bicarbonated waters.
3. Sulphuretted waters.
4. Ferruginous or chalybeate waters.
5. Sulphated waters.

We do not propose to dwell further on this subject, which is a by-branch of the subject-matter of the work.

6. DISTILLED WATER.

No matter what the origin of water in nature may be, it always holds matter either in solution or in suspension.

As we have seen, rain water, which is the purest form of natural water, contains air, oxygen and hydrogen compounds, nitrogen and various salts.

Some surface waters hold so great a proportion of substances in solution as to render them unsuitable for manufacturing purposes, and to disqualify them, *a fortiori*, for the delicate and exact preparations required in photography and pharmacy, and in the chemical laboratory.

All foreign matter held in solution in water may be eliminated, without the introduction of any other substance, by means of

evaporation and condensation of the vapour, which yields distilled water, the vehicle or medium of all delicate preparations.

Distillation is carried out by the aid of an apparatus known as a still (fig. 2), which is composed of a retort A, fitted with a head C, communicating through a beak with a worm or coiled tube S, which is immersed in a stream of cold water in the refrigerator.

To proceed to distillation, water is introduced into the retort, the fire is lighted, and the worm is kept cold by turning on the cold water from the main.

In a few moments the water-vapour rises into the head, where it throws off any foreign matter that may have been borne up by mechanical action.

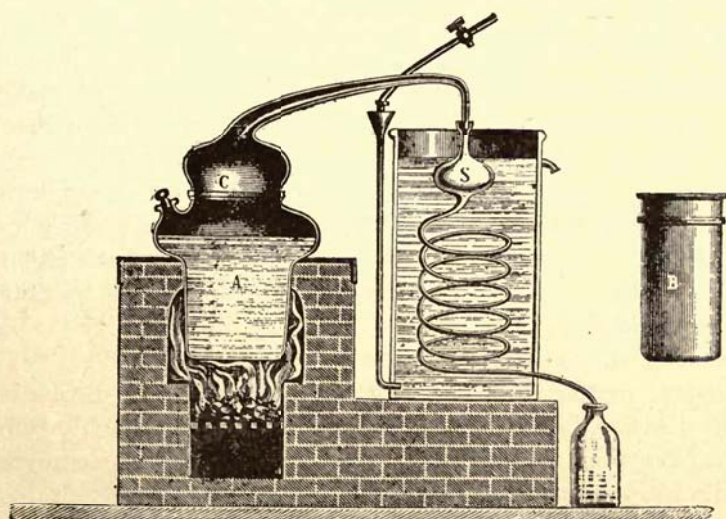


FIG. 2.—Still.

It then passes into the worm, where, as the result of refrigeration, it is condensed and yields distilled water, which should be collected in perfectly clean vessels.

Easy as the operation is, it requires to be conducted with a certain amount of precaution to ensure a product of the requisite pureness.

To begin with, the water should be tested as soon as it issues from the still, and the collection of it deferred so long as it is found to contain foreign matter.

The water to be distilled may contain volatile substances, such as carbonic acid and ammonia. This is especially the case with waters passing through large towns, like those of the Seine and the Rhône. These bodies are evaporated in the still, and are found in

the first portion of the distillate. For all practical purposes, therefore, this should be rejected.

Owing to the instability of salts of ammonium and of magnesium chloride, water charged with these substances is liable to yield, consequent on their decomposition, a distillate impregnated with ammonia and hydrochloric acid.

As a first precaution the operation should not be carried out to a finality, and the amount of distillate collected should only equal three-fourths of the original volume of water; in other words, the last portion of the water in the retort should be thrown away.

Another method is to add to the water in the retort, before applying heat, some substance that will have the effect of reducing the instability of these various objectionable compounds.

Thus, in the case of water charged with ammonia, the ammonia is fixed by the addition, before distillation, of magnesium phosphate, while in the case of water containing carbonic acid milk of lime is substituted.

Frequently laboratory-distilled water is found to be acid, owing to the hydrochloric acid produced by the decomposition of chloride of magnesium. In this case it is well to render the water slightly alkaline by the addition of sodium or potassium, so as to obtain double chlorides of magnesium and of the metal of the alkali, which are far more stable than the simple chlorides.

Organic matter is also liable to be carried over in distillation. It will therefore be advisable to clean the retort thoroughly before commencing work, especially if in the preceding operation empyreumatic substances have been distilled.

If the water contains organic matter, distillation should cease when three-fourths of the amount has been evaporated. Also potassium permanganate may be added in the retort.

By closely following these instructions distilled water is obtained that will be found suitable for all ordinary purposes; but should water of an extreme degree of pureness be required for some special purpose, the operation must be carried out as follows:—

A strongly acid solution of potassium permanganate must be added to the water and the distillate must be redistilled with an admixture of aluminium sulphate.

As a result of this treatment the distillate will be free from all trace of ammonia, of chloride and of organic matter. More often than not the distilled water used in manufacture has not been specially prepared, but consists of the water obtained by condensing the steam from the boilers that serve to drive machinery.

This water, which is equally a product of distillation, is liable to the same objections arising from mechanical agency which we have had occasion to notice in connection with distilled water properly so called; that is to say, hydrochloric acid and ammonia are just as often found in it.

It is important to bear in mind that preparations intended to counteract calcareous deposits are frequently introduced into steam boilers.

These preparations, which are often bought of the manufacturer without any information as to their composition, occasion decomposition of one form or another, and the resultant matter is carried into the condensed vapour, so much so indeed that the distilled water is rendered unfit for manufacturing purposes.

Fatty matters are also frequently carried over. These arise from grease or oil accidentally dropped into the boiler or driven into it from about the lubricated parts of the engine, such as the cylinder, the slide-valve chest, and so forth. Vegetable and animal grease and oils, characterised by saponifiable fatty acids, are particularly detrimental to water obtained by condensation. This kind of water therefore should be carefully tested before use.

Any fatty or saponifiable matter may, however, be eliminated by fixing its fatty acid with milk of lime.

For consumption on board ship sea water is passed through the still. In former times a ship might be obliged to carry a supply of drinking water equal to three months' requirement, which of course was a heavy tax on the storage capacity of the vessel.

Nowadays a very limited supply of potable water is carried, as the vessel is fitted with special distilling apparatus.

As a rule distillation is carried out on board ship by means of a special device, by which the steam from the boilers driving the engines is collected and condensed.

In 1868 the Perroy distilling apparatus was adopted in the French navy. In this arrangement the steam from the boilers passes through a series of tubes surrounded by a metal cold-water jacket. The steam is condensed, and the distilled water is collected in special receivers.

Of course for a water to be potable it is necessary that it should be well aerated. To ensure this, the water, on passing into the apparatus, flows through a species of injector on the principle of the Giffard patent, the function of which is to inject air into the liquid.

Sometimes the distilling apparatus on board ship consists of a

still in which the heating power is supplied by the waste steam of the engines. Under these circumstances the water introduced into the retort to be distilled is sea water pure and simple.

By this plan the carrying over of fatty matter is absolutely obviated; but the retort must be cleared of solid matter at regular and frequent intervals.

CHAPTER III.

SOLUBILITY OF CERTAIN SALTS IN WATER CONSIDERED FROM THE INDUSTRIAL POINT OF VIEW.—EFFECTS ON THE BOILING OF WATER.

I. SOLUBILITY OF CERTAIN SALTS IN WATER.

ANALYSIS has established the fact that all water contains certain bodies in solution in greater or less quantity.

When water is boiled gases are liberated that may readily be identified. Among these are oxygen, nitrogen and carbonic acid.

These gases are not all absorbed in the same way by the water, and it is found that the air in solution in water is, as a rule, richer in oxygen than the air of the atmosphere.

This peculiarity arises from the difference in the co-efficient of absorption of these gases for the water ; or, more simply expressed, it depends entirely on their co-efficient of solution. Thus oxygen is far more readily dissolved by water than is nitrogen ; in other words, the co-efficient of solution of oxygen for water is greater than that of nitrogen.

On referring to the results obtained by Peligot, we find that analysis of a litre of fresh water yielded twenty-three cubic centimetres of gas, made up as follows :—

Nitrogen	68.0
Oxygen	32.0
Carbonic acid	2.4

The laws governing the solution of gases have been clearly established by Henry and Dalton.

The first of these laws refers solely to gases and liquids which do not react chemically on each other.

First Law.—At a given temperature any liquid will always dissolve the same volume of a gas ; whatever the atmospheric pressure of the gas, the volume dissolved is proportional to that pressure.

Second Law.—When several gases are mixed together each is absorbed in the same manner as if it were by itself.

From experiments verified by Bunsen, it follows that the co-efficient of absorption in the case of most gases varies with the

temperature. Hydrogen, however, has a co-efficient of solution which remains constant at all temperatures.

Taking K as the co-efficient of solution of a gas, that is to say, the volume of that gas dissolved by one litre of water at the atmospheric pressure, and t as the corresponding temperature, we obtain the following relations as found by Bunsen for the subjoined gases:—

Nitrogen	$K = 0.020346 - 0.00053887t + 0.000011156t_2$
Oxygen	$K = 0.04115 - 0.0011907t + 0.000022577t_2$
Carbonic acid	$K = 1.7967 - 0.07761t + 0.0016724t_2$
Hydrogen	$K = 0.0193$

Another conclusion arrived at as a result of Bunsen's experiments is that Dalton's law applies only in the presence of low pressure.

The figures in the following table, from the calculations made by Bunsen and Carius, show that the co-efficient of solution of a gas diminishes in proportion as the temperature of the water increases.

Tempera- ture.	Oxygen.	Nitrogen.	Air.	Carbonic Acid.	Hydrogen.	Ammonia.
0	0.04114	0.02035	0.02471	1.7967	0.01930	1049.6
1	0.04007	0.01981	0.02406	1.7207	"	1020.8
2	0.03907	0.01932	0.02345	1.6481	"	993.3
3	0.03810	0.01884	0.02287	1.5787	"	967.0
4	0.03717	0.01838	0.02237	1.5126	"	941.9
5	0.03628	0.01794	0.02179	1.4497	"	917.9
6	0.03544	0.01752	0.02128	1.3901	"	895.0
7	0.03465	0.01713	0.02080	1.3339	"	873.1
8	0.03389	0.01675	0.02034	1.2809	"	852.1
9	0.03317	0.01640	0.01992	1.2311	"	832.0
10	0.03250	0.01607	0.01953	1.1847	"	812.8
11	0.03189	0.01577	0.01916	1.1416	"	794.3
12	0.03133	0.01549	0.01882	1.1018	"	776.3
13	0.03082	0.01523	0.01851	1.0653	"	759.6
14	0.03034	0.01500	0.01822	1.0321	"	743.1
15	0.02989	0.01478	0.01795	1.0020	"	727.2
16	0.02949	0.01458	0.01771	0.9753	"	711.8
17	0.02914	0.01441	0.01750	0.9519	"	696.9
18	0.02884	0.01426	0.01732	0.9319	"	682.3
19	0.02858	0.01413	0.01717	0.9150	"	668.0
20	0.02838	0.01403	0.01704	0.9014	"	654.0

The question of the solubility of salts has an important bearing on the influence of water in industries.

Salts such as calcium carbonate, magnesium carbonate, calcium sulphate and magnesium chloride, which are of frequent occurrence in water and show their presence by reactions peculiar to them, require to be studied from the point of view of their solution.

If, in considering the solubility of certain solids capable of

combining with water, we describe a curve to represent the solubility of these salts, with the abscissæ representing the temperature and the ordinates the weight of salt dissolved per kilogramme of liquid, we have a figure that is concave towards the positive co-ordinates.

In seeking to ascertain the solubility of salts at a temperature at which hydrates are incapable of existing, it follows from the observations of M. Etard that the line of solubility of the salt is represented by a straight line, and its co-efficient of solubility is a linear function of the temperature, which increases with the temperature.

This function is thus expressed :—

$$K = a + bt,$$

K standing for the co-efficient of solubility.

According to Gay-Lussac, the co-efficient of solubility of solids is the weight of substance dissolved in 100 grammes of the solvent at a given temperature, when the solution is saturated at that temperature.

This definition, though faulty, is still accepted. It would be more rational to adopt Etard's definition, which gives the co-efficient of solubility of a solid in a liquid at a given temperature as the weight (calculated in grammes) of that solid dissolved in 100 grammes of the solution when saturated at that temperature.

Thus this co-efficient of solubility varies according to the temperature, and it nearly always increases with the temperature and in proportion with its variations.

The solution of solids is attended with certain external changes. In the case of a solid being dissolved in water, as it assumes the liquid condition it absorbs a certain quantity of heat, and of course a fall takes place in the temperature of the solution.

The reverse may be the case if the solid to be dissolved gives rise to chemical action in the liquid solvent, then a rise of temperature occurs.

The following may be said to be the laws that govern solution :—

First Law.—The quantity of a solid that is capable of being dissolved in a liquid is strictly limited, and is always the same at the same temperature.

Second Law.—A liquid saturated by the solution of one solid is capable of dissolving another.

Third Law.—The solubility of a solid increases with the temperature.

This last law is not absolute, as there are many exceptions to it.

Calcium Carbonate.—Calcium carbonate is very readily soluble in water charged with carbonic acid. A solution saturated with carbonic acid will dissolve 0.70 gramme of carbonate of lime per litre at 0° C., and 0.88 gramme at 10° C. This power of solution increases with the temperature.

It is generally accepted that the carbonic acid of water and the neutral carbonate produce bicarbonate of lime, or an acid carbonate, which is readily soluble. Bineau recognises the solubility of calcium carbonate in presence of carbonic acid as the result of simple solution.

If water containing calcium carbonate in solution is boiled, the whole of the neutral carbonate of calcium is not precipitated; and we shall see, when we deal with analysis, that Boutron and Boudet did not lose sight of this point in formulating their hydrotimetric system, and that they correct the results of their tests accordingly.

Hofmann found that 0.034 gramme of calcium carbonate remained in solution per litre of water, while Cruss fixed the amount at 0.036 gramme. This remaining carbonate of lime is not precipitated by lime-water, which goes to prove that it is unmistakably neutral and is not dissolved by carbonic acid.

It may be well to remember, with regard to the solubility of carbonic acid in water, that it is far more readily soluble in water containing calcium carbonate than in pure water.

Magnesium Carbonate.—Magnesium carbonate is more readily soluble than calcium carbonate in presence of carbonic acid.

Merkel has demonstrated that the solubility of magnesium carbonate in water varies, like that of carbonic acid, according to the temperature and not according to the pressure.

By varying the pressure on a water charged with carbonic acid he obtained the following results:—

One part of Mg CO_3 is dissolved:—

At 1 atmosphere in 761.0 parts of water charged with CO_2 .

2 atmospheres in	744.0	"	"	"
3	134.0	"	"	"
4	110.7	"	"	"
5	110.0	"	"	"
6	76.0	"	"	"

Engel and J. Ville have ascertained that temperature has a marked influence on the solubility of magnesium carbonate in water charged with carbonic acid.

In determining the solubility of neutral carbonate of magnesium at different pressures the following results were arrived at:—

Pressure in atmospheres.	Temperature. Degrees C.	Grammes of magnesium carbonate dissolved per litre of water.
1.0	19.5	25.8
2.2	19.5	33.1
3.2	17.7	37.3
4.7	19.0	43.5
5.6	19.2	46.2
6.2	19.2	48.5
7.5	19.5	51.2
9.0	18.7	56.6

At 13.4° C. and ordinary pressure water charged with carbonic gas would dissolve 28.45 grammes of neutral carbonate of magnesium per litre; but at 90° C. the amount dissolved is only 2.4 grammes.

Calcium Sulphate.—MM. Poggiale, Marignac and Lecoq de Boisbaudran have made numerous experiments with a view to determine the solubility of calcium sulphate in water, but the results they have obtained do not always correspond.

According to Lecoq de Boisbaudran it takes 500 grammes of water at 12.5° C. to dissolve 1 gramme of anhydrous calcium sulphate, but he recognises in a general way that his results are too low, and those of M. Marignac too high. In his opinion the correct results would be somewhere between M. Marignac's and his own.

From the experiments of M. Poggiale it would appear that the salt attains its maximum of solubility at 35° C., and that at 100° C. its solubility is almost the same as at 5° C.

The line of solubility of calcium sulphate would therefore be similar to that described by Gay-Lussac for sodium sulphate, and the curve would be formed of two lines having their point of retrogression at 35° C., as is the case with sodium sulphate; but the point of retrogression of calcium sulphate is graphically less accentuated.

Solubility of Sulphate of Lime.

Temperature. Degrees C.	Solubility of anhydrous sulphate of lime in grammes.
0	0.205
5	0.219
12	0.233
20	0.241
30	0.249
35 (maximum)	0.254
40	0.252
50	0.251
60	0.248
70	0.244
80	0.239
90	0.231
100	0.217

Marignac contends that the degree of solubility given by Poggiale at 20° C. is opposed to the conclusions of every other analyst. He is of opinion, speaking generally, that his results are too high, and that he must have been led astray by certain phenomena of supersaturation which, at the time that he conducted his tests, were not as well understood as they are now.

Like Poggiale, he was able to fix the maximum of solubility between 30° C. and 40° C.

For one part of anhydrite (anhydrous sulphate of lime) there would be required:—

Degrees C.	Parts of water.
0	525
18	488
24	479
32	470
38	466
41	468
53	474
72	495
86	528
99	571

If boiling water containing calcium sulphate in solution is carried to a high temperature, it is found that at 140° C. small and very hard crystals of that salt are precipitated of the formula $2\text{CaSO}_4\text{H}_2\text{O}$. We will presently see the important part calcium sulphate plays in steam boilers.

The solubility of calcium sulphate is materially affected by other salts. Thus alkaline chlorides and nitrates and magnesium chloride increase the solubility of calcium sulphate, and the more concentrated the liquid the greater the solubility.

Of all the chlorides ammonia chloride is the one that increases its solubility most; nitrates, on the other hand, exercise a more powerful solvent action than chlorides, while sulphates do not increase the solubility of calcium sulphate at all.

From the experiments made by M. Haver-Brœze it would appear that in order to dissolve one gramme of gypsum we require

162 cubic centimetres of a saturated solution of				KCl at 8.0° C.
147	"	"	"	NaCl " 8.5° "
93	"	"	"	NH_4Cl " 12.5° "
94	"	"	"	KNO_3 " 13.5° "
92	"	"	"	NaNO_3 " 8.5° "
320	"	"	"	NH_4NO_3 " 8.5° "
54	"	"	"	NH_4NO_3 " 13.5° "

Glycerine also adds greatly to the solubility of calcium sulphate..

Asselin has ascertained that it will dissolve in the cold state one per cent. of that sulphate.

On the other hand, according to Church, the solubility of calcium sulphate is reduced in the presence of carbonic acid. Sodium chloride would have the same effect.

Lime.—It is important that we should consider the solubility of lime, for this oxide is constantly used in water purification, and not infrequently it is the residuum from different operations dependent on the use of water.

Dalton discovered the fact that lime is far less soluble in hot than in cold water, and that its solubility is twice as great at 0° C. as at 100° C.; while, on the other hand, calcium sulphate and sodium sulphate are far less soluble at 0° C. than at 100° C.

The following are the figures given by Dalton for the solubility of lime :—

Temperature. Degrees C.	Anhydrous lime dissolved in 100 parts of water.
15.6	$\frac{100}{778} = 0.1285$
54.4	$\frac{100}{972} = 0.1002$
100.0	$\frac{100}{1270} = 0.0787$

Subsequent experiments by Richard Phillips led to similar conclusions, and this scientist ascribed the reduced solubility of lime occasioned by the rise of temperature to an increased molecular cohesion set up in the lime by the action of heat.

In the course of his investigations connected with saccharine juices Lamy paid particular attention to the subject of the solubility of lime, and found that a multitude of circumstances affect it.

The following considerations are to be taken into account: the nature and quality of the lime, the method of preparation, the temperature at which it was burnt, the degree of molecular cohesion, the degree of temperature to which the milk of lime was brought, the filtration of the milk of lime in order to obtain a clear solution, the recalcination of the calcium hydrate, and finally the contact action of the water with the lime.

These several points were all taken into consideration by Lamy in determining the conditions under which he carried out his experiments with lime obtained (1) from precipitated calcium carbonate; (2) from marble (carbonate of lime); and (3) from calcium hydrate.

He found that 100 parts of solution contain in the form of anhydrous lime :—

At degrees C.	Parts of CaO of pre- cipitated CaCO_3 .	Parts of lime from marble.	Parts of slaked lime.
0	1'362	1'381	1'430
10	1'311	1'342	1'384
15	1'277	1'299	1'348
30	1'142	1'162	1'195
45	0'996	1'005	1'035
60	0'884	0'868	0'885
100	0'562	0'576	0'584

At 60° C. calcium hydrate (crystals) has for formula $\text{Ca}(\text{OH})_2$; so has also the product obtained by crystallisation at a low temperature.

In preparing a reagent for lime in the purification of water for industrial purposes the solubility of lime is generally estimated at from 1'25 gramme to 1'30 gramme per litre.

Calcium Chloride.—Calcium chloride is one of the salts most readily soluble in water. The proportion dissolved is large, and the operation is attended by a considerable fall of temperature, which makes it specially useful for the manufacture of refrigerating mixtures.

On account of its hygroscopicity, calcium chloride is much used in laboratories as a drying agent; 25 per cent. of water is sufficient to dissolve it.

Unlike the crystalline salt, the solution of anhydrous calcium chloride in water produces a rise in temperature.

Hammerl has fixed the degree of solubility of calcium chloride at between -22°C. and $+29\cdot53^\circ \text{C.}$, and from his investigations it appears that 100 parts of saturated solution contain:—

At degrees C.	Parts of CaCl_2 .
- 22'00	32'24
0'00	36'91
+ 7'39	38'77
13'86	41'03
19'35	42'50
24'47	45'33
27'71	46'30
29'53	50'67

The formula of calcium chloride crystals is $\text{CaCl}_2 + 6\text{H}_2\text{O}$, and it is the form of hexagonal prisms terminating in pyramids. On drying these in a vacuum a hydrate is obtained of the formula $\text{CaCl}_2 + 2\text{H}_2\text{O}$.

By successive fusion and solidification of the hydrate $\text{CaCl}_2 + 6\text{H}_2\text{O}$ Hammerl obtained a hydrate of the formula $\text{CaCl}_2 + 4\text{H}_2\text{O}$.

Magnesium Chloride.—Magnesium chloride is a deliquescent salt, and therefore very ready soluble in water. As a matter of fact water dissolves from 130 per cent. of it cold to 366 per cent. at boiling-point.

In the presence of alkaline chlorides it readily forms double

chlorides, such as sodium-magnesium chloride, potassium-magnesium chloride and ammonium-magnesium chloride.

These double chlorides are far more stable than the simple magnesium chloride. A double chloride is found at Stassfurt, *viz.*, the double chloride of magnesium and calcium, which forms tachydrite in rounded deliquescent masses with the formula $2\text{MgCl}_2\text{CaCl}_2 + 12\text{H}_2\text{O}$.

The double chloride of magnesium and ammonium forms orthorhombical crystals $\text{MgCl}_2\text{NH}_4\text{Cl} + 6\text{H}_2\text{O}$. It is isomorphous with Stassfurt carnalite, with the formula MgCl_2KCl ; but the double salt of sodium crystallises only with $2\text{H}_2\text{O}$, yielding $\text{MgCl}_2\text{NaCl} + 2\text{H}_2\text{O}$.

When magnesium chloride is in the presence of magnesium carbonate in solution in water, oxychloride of magnesium is produced, of the formula $\text{MgCl}_2 + 10\text{MgO} + 18\text{H}_2\text{O}$, which crystallises in the form of microscopical needles.

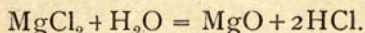
In taking the temperature at which anhydrous magnesium chloride, MgCl_2 , is dissolved, J. Thomsen found it to be equivalent to 35,900 units of heat, and for hydrated magnesium chloride, $\text{MgCl}_2 + 6\text{H}_2\text{O}$, equal to 2,950 units of heat. In the case of anhydrous magnesium chloride, for one molecule of water absorbed about + 5,495 units of heat are liberated.

This salt, magnesium chloride, is found in large quantities in sea water, varying with the locality of origin. Thus water from the Mediterranean is far more heavily charged with it than ocean water.

This peculiarity is readily detected by the marked bitter taste that distinguishes salt extracted from the saline marshes of the Mediterranean, which is not found in salt derived from the ocean.

By concentrating a solution of magnesium chloride colourless needles or extremely deliquescent orthorhombical crystals are obtained, of the formula $\text{MgCl}_2 + 6\text{H}_2\text{O}$.

On heating these needles of hydrated magnesium chloride to 106°C . dissociation into hydrochloric acid takes place, and at 119°C . fusion :—



Pelouze suggested the manufacture of hydrochloric acid by simple calcination of magnesium chloride.

The dissociation of magnesium chloride into hydrochloric acid is attended with injurious consequences in industrial operations, a striking instance being the corrosion of steam boilers.

Water containing magnesium chloride in solution produces corrosion more or less extensive according to the quantity of that salt present.

We have also had an opportunity of verifying this assertion

with water from the Mediterranean, which exerts a far more energetic corrosive action on iron than water taken from the ocean.

It is important to note that magnesium chloride may be produced, as the result of a double decomposition, if magnesium sulphate is in presence of other chlorides in water.

Sodium Chloride.—Owing to the large quantity of sodium chloride in sea water the question of the solubility of this salt is of the utmost importance, and has to be taken into account in the use of sea water on board steamers.

Steam boilers fed with sea water require special precautions to avoid the accumulation of saline scale, which would soon impede the regular working of the machinery and otherwise injure it. For this reason a special extractive method of treatment is adopted, which will be fully considered later on.

The solubility of sodium chloride varies little with changes of temperature.

Gay-Lussac found that one part of the salt was dissolved in

2·78 parts of water at	14° C.
2·70 "	60° "
2·48 "	109·7° "

In making a cold solution Page and Keightley found that at 15° C. 100 parts of it contained 26·34 parts of salt, and on making a hot solution and then letting it cool again down to 15° C. the quantity contained amounted to 26·61 parts.

Fuchs contends that sodium chloride is equally soluble in cold and in hot water, that, no matter what the temperature, 100 parts of water will dissolve 37 parts of sodium chloride. As for the conclusions arrived at by Gay-Lussac, they must, in his opinion, be erroneous, owing to the defective conditions under which his experiments were conducted, in which he cannot have completely eliminated the magnesium chloride.

Later on Poggiale resumed his tests of the solubility of sodium chloride, keeping in view the observations of Fuchs and working with sodium chloride free from all trace of calcium chloride and of magnesium chloride, with the results that his conclusions approximated to those of Gay-Lussac, thus proving Fuchs' criticism to have been ill-founded.

Now Gay-Lussac found that 100 parts of water will dissolve :—

35·81 parts of sodium chloride at	13·89° C.
35·88 "	16·90° "
35·14 "	59·93° "
40·38 "	109·73° "

He also found that at zero the solubility was greater than at 13·89° C.

Poggiale's figures for the solubility of anhydrous sodium chloride are as follows :—

Temperature. Degrees C.	Solubility of anhydrous sodium chloride per cent.
- 15	32'73
- 10	33'49
- 5	34'22
0	35'52
+ 5	35'63
9	35'74
14	35'87
25	36'13
40	36'64
50	36'98
60	37'25
70	37'88
80	38'22
90	38'87
100	39'61
109'7	40'31

The solution when saturated with this salt contains 26'4 per cent. of it, and has a density of 1'2043.

The density of the solution corresponding to the various quantities per cent. of sodium chloride at 15° C. is as follows :—

Quantity of salt per cent.	Quantity of sodium chloride at 15 degrees C.
1	1'0072
2	1'0145
3	1'0217
4	1'0290
5	1'0362
6	1'0436
7	1'0511
8	1'0585
9	1'0659
10	1'0733
11	1'0810
12	1'0886
13	1'0962
14	1'1038
15	1'1115
16	1'1194
17	1'1270
18	1'1352
19	1'1431
20	1'1511
21	1'1593
22	1'1675
23	1'1758
24	1'1840
25	1'1923
26	1'2010
26'4	1'2043 (saturation)

In connection with the use of sea water, this table will serve for carrying out the "extractive method," the application of which is based on the density of the saline solution.

2. EFFECTS ON THE BOILING OF WATER.

When a liquid is heated to the degree required to produce vapour of the same tension as that of the liquid itself it begins to boil; bubbles of vapour are then formed in the interior of the liquid, they rise and burst on the surface.

Any transformation of a liquid into vapour is called vaporisation, evaporation being distinguished by the formation of steam on the surface.

The phenomena of ebullition are subject to certain laws.

1. Throughout the period of boiling of a liquid the temperature is constant, and this degree of temperature is known as the boiling-point.

2. The boiling temperature of a liquid corresponds to that which must be reached in order that the liquid may throw off vapour having a pressure equal to the pressure on its surface.

3. The conversion of a liquid into vapour is attended by a certain absorption of heat.

If we consider the second of these laws we perceive at once the important bearing that the pressure on the surface of a liquid has on its boiling-point.

If the pressure on its surface is increased the boiling-point of the liquid is raised, and all the more so the greater the pressure.

The Papin Kier, which consists of a metal cylinder closed by a screw lid in which is a safety valve, admits of water being heated to the highest temperature without being brought to the boil.

On opening the valve the steam escapes with a considerable pressure, and is utilised for the production of power in the steam engine.

The dissolving property of water is markedly increased when it is kept liquid at temperatures above 100° C.

D'Arcet, by means of a kier, which is a modified form of that of Papin, has succeeded in converting the osseine of bones into gelatine.

Subjoined is a table showing the temperature of aqueous vapour for tensions of 1 to 50 atmospheres.

Elastic force in atmospheres.	Pressure in kilograms per square centi- metre.	Corresponding temperature. Degrees C.	Elastic force in atmospheres.	Pressure in kilograms per square centi- metre.	Corresponding temperature. Degrees C.
1	1'033	100	13	13'429	193'7
1½	1'549	112'2	14	14'462	197'19
2	2'066	121'4	15	15'495	200'48
2½	2'582	128'8	16	16'528	203'60
3	3'099	135'1	17	17'561	206'57
3½	3'615	140'6	18	18'594	209'4
4	4'132	145'4	19	19'627	212'1
4½	4'648	149'06	20	20'660	214'7
5	5'165	153'08	21	21'693	217'2
5½	5'681	155'8	22	22'726	219'6
6	6'198	160'2	23	23'759	221'9
6½	6'714	163'48	24	24'792	224'2
7	7'231	166'5	25	25'825	226'3
7½	7'747	169'37	30	30'990	236'2
8	8'264	172'1	35	36'155	244'85
9	9'297	177'1	40	41'320	252'55
10	10'330	181'6	45	46'485	259'52
11	10'363	185'03	50	51'650	265'89
12	12'396	190			

The boiling-point of liquids is absolutely variable, according to the nature of the vessel used, and according to the substances they hold in solution.

With glass vessels the boiling-point of water rises from 101° to 101'25° C., while with metal it is 100° C.

Gay-Lussac thought this phenomenon might be explained by the adhesion of the liquid to the walls of the vessel, which would then prevent it being converted into vapour.

As the result of further experiments, Gay-Lussac proved beyond a doubt that in a glass utensil covered with a coating of shellac the boiling-point of water is reached at a lower temperature than in a metal vessel; also that if iron filings are placed in the latter the boiling temperature becomes normal.

The gases contained in solution in water have a marked effect on its boiling-point: they promote ebullition.

A liquid that has already been boiled has lost the greater portion of the gases it held in solution. On being reboiled, ebullition is only reached at a temperature considerably higher than at its first boiling.

The vapour formed in the interior of the liquid is produced by the aid of the gas bubbles.

It follows that the presence of such bodies as coal, pumice-stone, sand or metal waste, promotes ebullition, since they always carry gas bubbles with them.

The experiments conducted by Gernez enable us to demonstrate that the ebullition of a liquid is greatly promoted by the gases con-

tained within it. This is done by introducing into a liquid, the boiling of which has been arrested, some air by means of a small glass bell: the moment the bell comes in contact with the liquid it recommences to boil.

Matter held in suspension in a liquid—say in water—does not alter its boiling-point; on the other hand, if the matter is contained in solution, the boiling-point of the water is retarded. But it does not follow *a priori* that the vapour given off contains the matter dissolved.

The greater the saline concentration of the liquid the longer is the ebullition retarded; thus, in the case of the salt of sea water, the boiling-point of the solution rises in proportion with its salinity.

Boiling-point of—

							Degrees C.
Pure water	100°0
Water containing 5 per cent. of sodium chloride	101°5
" " 10 "	"	"	"	"	"	"	103°0
" " 15 "	"	"	"	"	"	"	104°6
" " 20 "	"	"	"	"	"	"	106°3
" " 25 "	"	"	"	"	"	"	107°9

Apart from the variation of the boiling-point according to the degree of concentration, a liquid boils at different temperatures according to the substances it contains in solution.

The boiling-point of a saturated solution must be taken, when the temperature remains constant, while the precipitation of the salt is taking place; any indications based on the temperature when precipitation of the salt commences would be misleading.

Experiments conducted by M. Legrand in connection with the boiling of saturated saline solutions have yielded interesting results

Name of salt.	Weight of salt per 100 of water.	Boiling-point. Degrees C.
Sodium chloride	41°2	108°4
Potassium chloride	59°4	108°3
Calcium chloride	325°0	179°5
Ammonium chloride	88°9	114°2
Barium chloride	60°1	104°4
Strontium chloride	117°5	117°8
Sodium nitrate	224°8	121°0
Ammonium nitrate	2°0	180°0
Calcium nitrate	362°0	151°0
Sodium carbonate	48°5	104°6
Potassium carbonate	205°0	135°0
Sodium phosphate	112°6	106°6
Potassium chlorate	61°5	104°2

A solution containing 30 per cent. of magnesium chloride boils at 115°6° C.

When different bodies less volatile than water are held in solution in it, without reacting chemically on each other, the water evaporates and eventually, by concentration of the liquid mass, leaves a sediment consisting of the substances originally in a state of solution.

These deposits are left by ordinary water on its being heated, for instance, in steam boilers, and we will now turn our attention to the various effects produced in boilers according to the nature of the water used.

PART II.

EFFECTS OF WATER IN THE INDUSTRIES—DIFFICULTIES WITH WATER—APPROPRIATE REMEDIES.

WE will now proceed to a consideration of the various industries in which water is largely used and consequently its effects are of importance.

At the same time that we study the effects resulting from the use of water we shall also determine the causes that produce them, and ascertain the remedies to be applied apart from the preliminary general chemical purification, which will form the subject-matter of the third part of this volume.

In following out this plan we propose to consider one by one the different stages in each of the several industries dealt with.

The large number of accidents and the inordinate consumption of fuel necessitated by the use of steam boilers in every branch of industry impel us to investigate thoroughly the phenomena arising from the use of the large variety of waters to which every user of boilers is exposed. It is a question, therefore, of vital interest to the boiler-user.

We will thus have occasion to deal with waters producing scale (carbonate and sulphate waters), with waters causing corrosion or both scale and corrosion (sea water and deep well waters), and with oily or fatty waters.

The remedies to be applied will be discussed as we arrive at them, remembering the economical side of the question on the basis of chemical reaction and calculating the amount of correction needed, and without losing sight of any secondary reactions that may possibly occur. The preliminary subjecting of the water to the action of steam will also be fully considered.

The important part played by water in dye, print and bleach works has induced us to devote a separate chapter to this branch of our subject in order to study thoroughly the phenomena arising from the presence of matter in solution in the water, as well as of the means by which the consequent inconveniences may be obviated.

In the same way separate chapters will be allocated to the important problem of the use of water in the manufacture and finishing of textile fabrics, in soap-works, in laundries and wash-houses, in tanning, and in the preparation of tanning and dye-wood extracts.

A separate study of water will likewise be made in connection with paper-making. So also with photography, the importance of which, as one of the industrial arts, is daily growing by reason of the many fresh uses to which it is being applied. This branch of industry is exposed to a multiplicity of troubles contingent on the character of the water used, but the causes whereof unfortunately but too frequently escape detection. We propose therefore to review the different preparations affected, such as the preparation of the emulsion, the developing of the negatives, the washing of the plates and also of the prints. Nor will the agricultural industries be overlooked, since the satisfactory working of the operations involved is largely dependent on the character of the water used.

After discussing the water question in connection with sugar refining, we shall consider it in relation to the manufacture of ice and of beverages, a matter of prime interest as affecting health and public hygiene.

In cider making also, and more particularly in brewing, the quality of the product depends in great measure on that of the water. We shall, therefore, consider in detail the whole process of brewing, dealing with every salt frequently met with in water. The presence of particular salts in the water is often at the root of the popularity enjoyed by certain beers in high repute. On the other hand, the pernicious effects of certain waters and the troubles likely to ensue from their use will receive equally close attention, with a view to their avoidance.

In dealing with the water used in the distillery we shall extend our investigations not only to the action of water in malting, but likewise to the more recent aseptic treatment with *amylomyces* and the *mucor* β .

CHAPTER IV.

FEED WATER FOR BOILERS.

THE huge daily consumption of feed water for boilers and the many troubles which its quality may cause make the subject one of the greatest importance.

It is possible to ascertain the nature of a water by analysing it, and thus data may be obtained which allow the harmful effects it may cause to be obviated.

For use in steam generation waters may be classified as :—

1. Scale-producing water.
2. Corrosive or corrosive and scale-producing waters.

These will be considered under separate headings. We shall examine the effects produced, consider the cause and nature of the incrustations, and then proceed to study the corrective measures to be adopted.

The heavy expense, the troubles and the numerous accidents which are the consequence of scale in the boiler have led to the invention of many processes to obviate the formation of incrustation, but unfortunately these processes are far from being radical remedies.

We shall class the processes of the treatment of feed water for boilers in three categories :—

1. By the addition of substances to the water in the boiler acting (a) mechanically, (b) chemically.
2. By preliminary treatment with steam in special apparatus.
3. By preliminary chemical treatment of the water.

The examination of the treatment of water in this chapter relates to the first two categories which apply more particularly to feed water for steam production.

The third category applies not only to feed water for boilers but also to all the industries in which the water used must be first freed from harmful constituents without having recourse to steam.

In the third part of this work we shall consider specially the preliminary chemical treatment of water, and the apparatus in-

tended for this purpose which tend to wider and wider employment by the manufacturing world.

I. SCALE-FORMING WATERS—INCRUSTATION IN GENERAL.

Certain phenomena affecting the solubility of salts arise from the physical influences, elevation of temperature, ebullition, vaporisation, concentration and pressure, to which the water in the boiler is subjected.

After a prolonged boiling a natural water throws down a deposit in more or less abundance according to the nature of the water.

Water in its passage through the various geological strata meets with the mineral elements and becomes charged with them in proportion to their abundance and to the physical conditions under which it acts upon them.

Deposits form therefore according to the hydrotimetric number and according to the influences brought to bear on the solubility of the salts.

These deposits are formed by the substances in solution in the water, and compounds of lime, magnesia, iron, etc., are obtained which vary in homogeneity, permanence and adherence according to the composition of the water.

We find, therefore, in steam boilers :—

1. Skum, floating on the top of the water, drying after a time and turning into dust.
2. Saline agglomeration, soft to the touch and with a want of stability which causes it to be liable to decomposition.
3. Hard and solid deposits adhering to the sides of the boiler.

These hard adhesive deposits are known as scale, and are formed mainly of salts of lime and magnesia, but have a very variable composition.

Carbonate waters hold carbonate of lime in solution by reason of their excess of carbonic acid. When they are boiled this excess of carbonic-acid gas is driven off and the carbonate of lime, robbed of its solvent, deposits. This applies also to carbonate of magnesium. In sulphate waters the temperature exerts a considerable influence on the sulphate of calcium in solution, at about 140° C. The sulphate is transformed into another with the formula $2\text{CaSO}_4 + \text{H}_2\text{O}$ and this is deposited in crystals. With carbonate waters the deposits formed are amorphous and dust-like. With sulphate waters the deposits are hard, adherent and stratified. Usually the waters contain both salts of lime, the sulphate and the carbonate, and of course the deposits contain both also.

From the point of view of analysis these incrustations vary widely. The variations depend not only on the composition of the water but also on physical influences such as temperature and pressure which affect the solubility and decomposition of the salts. Deposited on the sides of the boiler they are subjected to a very high temperature and this again tends to modify them.

Nevertheless by the results of the hydrotimetric test the nature of the scale can be foreseen and an approximate idea of its formation may be gathered. The carbonate of lime itself is found almost integrally in the incrustation, but the other salts are more subject to variations in their solubility, and this leads to differences between the contents of these salts in the water and in the incrustations formed by it.

Not only does the scale vary in thickness, structure, composition, hardness and adherence in different boilers, or in the same boiler fed with different waters, but it varies even in a boiler supplied always from the same source. The deposit formed nearest the fire usually contains more carbonate and that farthest off more sulphate. If the water is heated rapidly the deposit tends to take the form of sludge.

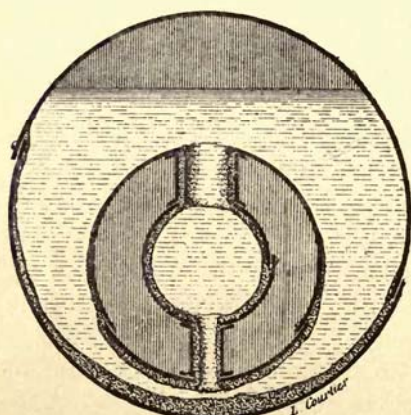


FIG. 3.—Scale in a boiler at Cornouailles (transverse section).

case of a long boiler, may lead to differences of expansion of the metal and cause breaks.

Moreover the dust-like substances may be carried into the working parts of the machinery and cause trouble, especially when the cylinders are lubricated with vegetable or animal fats with which the lime will combine to form very harmful compounds. In fact these calcareous combinations are often mixed with unsaponified oils and greases which facilitate the overheating of the boiler-plates. Generally speaking the formation of these deposits should be prevented, and later we shall consider the different treatments to which water can be subjected with this object in view.

Three important considerations lead the manufacturer to guard against incrustations. To begin with they turn up the coal bill, as the scale is an extremely poor conductor of heat, the conductivity

varying with its composition. According to the experiments of Rogers the average conductivity of scale is $\frac{1}{37}$ that of iron. This bad quality leads therefore to an extravagant use of fuel in converting water into steam and also retards the process.

To obtain an exact idea of the bad conductivity of scale we must first know exactly the composition of those experimented upon. It is not rare to see this bad conductivity represented by a waste of 50 to 60 per cent. of fuel in the case of a scale only 6 to 10 millimetres thick. Apart from this loss, when the boiler is scaled the operation is very difficult, especially in the case of sulphate waters. The scale must be cleared off with the aid of a hammer

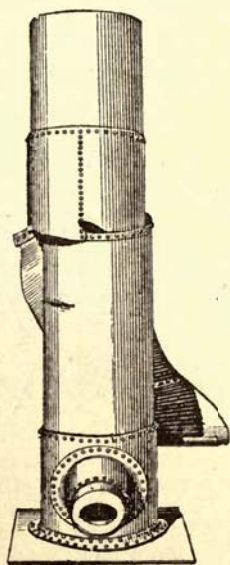


FIG. 4.—Explosion of a vertical boiler (front).

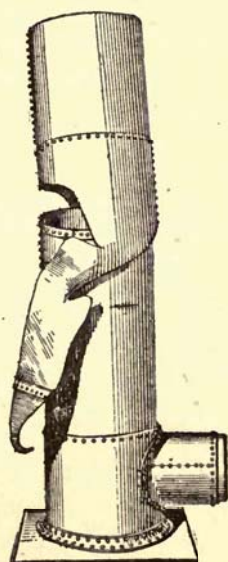


FIG. 5.—Explosion of a vertical boiler (side).

and chisel. This necessitates skilled labour and is always attended by injury to the boiler-plates.

Sometimes, to assist the operation, the scale is drenched with water acidulated with hydrochloric acid, but this has to be done very cautiously in order to avoid corrosion of the boiler-plates. Finally, the scale deteriorates the boiler and leads to accidents. The bad conductivity and want of homogeneity of the incrustation expands the plates unequally, producing cracks and fissures, and starts the rivets, thus parting the plates.

Sometimes even the plates are brought to red-heat, and thus submitted to the action of the furnace on the one hand and to the

pressure of steam on the other quickly bulge, cave in, burst and lead to terrible accidents.

It often happens that a break in the scale causes explosions. The badly conductive scale causes the plates to be overheated. A part of it cracks and breaks away. The water comes in contact with the overheated metal, instantly resolves into huge volumes of steam, and in a few seconds the enormous pressure leads to an explosion.

The crystalline incrustation of sulphates has the tendency to detach itself from the sides as it forms by reason of the great heat of the plates. It is then carried off by the steam and deposited at the bottom of the boiler in a heap, damaging the boiler and preventing the regular production of steam. This heap can be got rid of by providing the boiler with a mud-cock. These incrustations are especially harmful in quick steaming boilers, the tubes of which

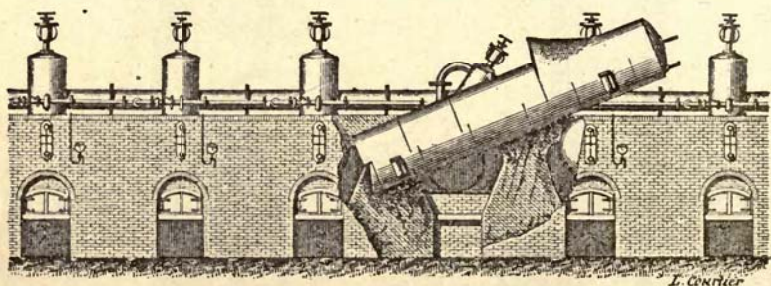


FIG. 6.—Explosion of a horizontal boiler.

are quickly choked, and this, apart from wear and tear, frequently leads to a stoppage of work.

2. TREATMENT OF SCALE-FORMING WATERS BY THE INTRODUCTION OF SUBSTANCES TO THE WATER IN THE BOILER.

We will first consider the additions which act mechanically and next those which have a chemical action on the substances in the water. We can divide the chemical reagents into two categories, organic and mineral.

(a) Substances acting mechanically.

Few of the agents introduced into the boiling water to prevent scale have a purely chemical action. If we seek for the causes of the action they exert we often find that it is both physical and chemical, transforming the original substance contained in the water into another substance, modified in its composition, which acts in a totally different manner to the original substance. The transforma-

tions of the original substances must be noted in order to understand the action exercised.

Purely mechanical action is based upon the introduction of inert substances into the boilers. These mingle with the particles of scale-forming matters and prevent them from forming a compact adherent mass. But if these additions, by the aid of the currents in the boiler, prevent the agglomeration of the particles of matter and are thus beneficial, they are the source of troubles outside the boiler.

In this way the introduction of inert substances is harmful, as they are often carried by the steam into the working parts of the machine with a subsequent rapid wear and tear. Amongst the inert matters usually employed are clay, ground glass, zinc scraps and starchy matters.

Clay.—The use of clay was suggested by Pelouze. This addition exposes the boiler to the risk of overheating, especially if the clay is not well steeped to begin with and added very gradually according to requirements. If these precautions are taken the deposit of the clay in too large quantities is avoided. This is a fairly good scale preventer, but there is always a danger of the particles of clay finding their way into the working parts of the machinery, as we have already noted in speaking of inert matter in general.

Zinc.—Zinc is of special service in the case of corrosive water or water which is both corrosive and scale-forming. It acts electro-mechanically, setting up an electric current [in contact with the iron-plates of the boiler.

Other substances such as talc, chips of wood and starchy matters have been proposed.

Talc.—Aragon recommends the use of talc in the proportion of $\frac{1}{10}$ the weight of earthy matters in the water; in other words, a number of grammes of talc is added equal to the hydrotimetric degrees found in testing the water. The action of the talc is explained by the general principle of the action of inert matters, but talc certainly exercises also a chemical action similar to that of the alkaline silicates which will be studied later.

Ground Glass.—Like talc and the silicates ground glass is dissolved to some extent by the steam under pressure, and enters into chemical combination with the salts of the alkaline earths. Ground glass, of course, has the drawback already mentioned as inherent to the inert matters.

Fats.—The use of fats, alone or mixed with other bodies, has been proposed to prevent incrustation. This method has found the most favour in other countries, and its adoption has serious inconveniences. When fat is put into the boiler a coat of grease spreads

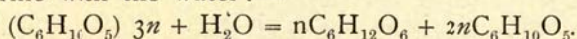
over the interior between the water and the plates and, being a bad conductor of heat, leads to overheating and the danger of explosions. In Belgium it has long been the practice to rub the interior of boilers with a mixture of tallow and plumbago.

This is an old expedient, and Sibbad in 1854 used a mixture of equal parts of tallow, graphite and wood charcoal for the same purpose. Some mechanics rub the interior of the boiler every month with a mixture of 1 part of tar and 5 parts of any kind of oil.

Others put into the boiler about 30 grammes of rosin per horse-power once a month. Whatever sort of fat is used it has the serious drawbacks we have noted above. Floury bran which is sometimes used leads to harmful deposit of calcined matters.

Starchy Matters.—Starchy matters such as artichokes and potatoes are often used by manufacturers. Their efficacy depends upon their transformation into a substance which envelops the salts of the alkaline earths precipitated from the water. By the interposition of this substance the particles of incrusting matter slide one over the other and are prevented from forming solid adherent masses.

Thus the potato fecula and diverse starchy matters under the influence of heat and pressure in the boiler form cyanodextrine and dextrine with the water:—



The proportion of potato or artichoke to be used is from 1 litre to $1\frac{1}{2}$ litres per horse-power per month. At the end of every month the boiler should be examined and cleaned.

(b) Substances acting chemically:—

I. ORGANIC MATTERS.

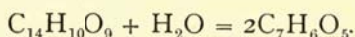
We have noted that certain substances, such as the starchy bodies, outside their purely mechanical intervention are transformed in combination with the water into cyanodextrine and dextrine which, in their turn, act mechanically. In addition to these bodies others, such as dye-wood extracts, have a chemical action which may be taken advantage of for the purpose, although so far the writers on the subject have not mentioned it.

The tannins and tannic compounds in these woods set up complex reactions often hardly understood in consequence of the variety of the tannins and the special conditions of pressure. The wood shavings employed, such as logwood, oak, fustic, lignum-vitæ, mahogany and quercitron, act not only as preventatives of the agglomeration of the particles of incrusting matter but their extracts also form lakes with the salts of the alkaline earths. All the woods

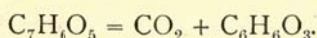
we have noted above are efficacious in preventing scale, but they are specially useful in the case of waters containing the carbonate of the alkaline earths. With the waters containing sulphates the scale is more difficult to deal with.

Various Woods.—The colouring matter in the woods form lakes with the calcic salts and these are precipitated. Moreover, the tannins they contain, such as catechin, catechutannic acid and morintannic acid or maclurin, produce calcic compounds which will not agglomerate. Each wood then acts by virtue of its special tannins, thus fustic contains morintannic and moric acids which combine with the calcic salts in water, and in the case of cutch the reagent is catechutannic acid.

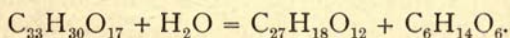
Tannins.—Ordinary tannin or tannic acid, whether free or combined with an alkaline metal, is hydrated in the presence of water and is converted into gallic acid, thus:—



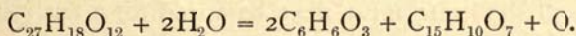
By prolonged boiling the gallic acid thus formed splits up into carbonic acid and pyrogallic acid:—



The introduction of ordinary tannin into the boiler brings about the precipitation of tannates, gallates, and hydrogallates of calcium and magnesium. When quercitron is boiled in water under pressure it is converted into quercetin and isodulcite, a species of sugar:—



Another reaction takes place after a prolonged boiling of the quercetin, which is then split up into phloroglucin and quercetic acid:—



The reaction is aided by the alkalis, and they are often added to anti-scale mixtures without a knowledge of the way they act, but recognising that they do good.

Wood Extracts.—Many products extracted from wood are on the market. In the case of logwood a dose amounting from 500 to 600 grammes per horse-power per month is sufficient for the water as a rule. In the case of the other woods the proportion is about the same, but it is a good thing to keep to the exact quantity determined by practice as suitable for the particular water. Of the anti-scale preparations on the market Constant's "tartriphage" is one of those which depend on the action of wood extracts. Its action

is complex, by reason of the large number of organic bodies it contains, and is both mechanical and chemical.

To make it mix together :—

50 kilos.	oak-bark	boiled in 30 litres water.
5	„ cutch	„ „ 15 „ „
5	„ lignum-vitæ	„ „ 15 „ „
5	„ logwood extract	„ „ 10 „ „
10	„ molasses	„ „ 10 „ „
10	„ strong glue	„ „ 15 „ „

Finally, 10 litres of a soapy wash of glycerine and margarine decoction are added. According to A. Mallet, in the case of a 5 horse-power boiler 1 litre of tarttriphage is used every eight days.

The use of extracts is much better than putting chips or raspings into the boilers. There is less exposure to the risk of agglutinous masses forming at the bottom of the boiler and there calcining, leading to a great waste of fuel. After examining the effects of wood extracts and considering their causes the author prepared a product composed of organic matters only, and found that this method was an efficacious remedy. To prepare it, boil 2 kilogrammes of oak sawdust for an hour at least in 10 litres of water, then add 3 kilogrammes of molasses. A kilogramme of this per horse-power per week is sufficient, and with some waters this dose is sufficient for several weeks.

Alkaline Tannates.—In the same order of things as the preceding another product is proposed, based on the solubility of the alkaline tannates and the formation of compounds of the alkaline earths, which will not adhere to the boiler-plates. To prepare this make an extract of cutch. This will contain catechutannic acid and catechin. Take 4 litres of water and boil 800 grammes of cutch in it for twenty minutes, then decant and filter the liquid obtained. The filtrate must next be boiled for a few minutes, and a weight of carbonate of soda added corresponding to 200 grammes of anhydrous carbonate. Various acids are formed, rubinic and japonic, and compounds of tannic acids with the soda. After solution, allow the mixture to cool.

A kilogramme of this per horse-power per week may be used with success and this dose may last longer with some waters.

Sugar.—The use of substances containing sugar in preventing scale depends on the increase of solubility of the lime.

By this addition considerable quantities of the salts of lime are dissolved, the deposit is retarded, and when formed has no adhesive powers. Let us examine the chemical action. A monocalcic sucrate with the formula $C_{12}H_{22}O_{11}CaO$, very soluble in water, is

formed. This may, moreover, be precipitated with alcohol and falls down in a white brittle mass. In the boilers the heat and pressure splits up the monocalcic sucrate and two other sucates are produced, the sesquicalcic sucrate $2C_{12}H_{22}O_{11}3CaO$ and the tricalcic sucate $C_{12}H_{22}O_{11}3CaO$. This latter is less soluble in hot water than in cold water, consequently the water in the boiler in cooling redissolves it.

In this method of preventing scale from 800 to 900 grammes of molasses per horse-power are used per month. The salts of lime are dissolved in such a quantity that a volume of water equal to that in the boiler can be evaporated several times, resulting in the formation under the influences of heat and pressure of glucate and apoglucate. A bronze powder consisting largely of ulmic acid is deposited and this is inflammable to some extent.

If too large quantities of water are evaporated without the addition of more molasses scale will then form. Fresh additions of molasses must therefore be made as required and the boiler should be cleaned once a month.

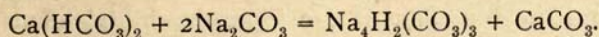
Glycerine.—The use of glycerine recommended by Asselin and P. Videt depends upon the great solubility of the calcic salts in this agent. When the water by continued evaporation contains too great a quantity of calcic salts for the glycerine salts, the salts of the alkaline earths instead of forming adhesive scale take a gelatinous form and will not adhere to the boiler-plates.

2. MINERAL SUBSTANCES.

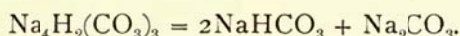
Not only the organic bodies increase the solubility of the salts of the alkaline earths, certain mineral substances, among others hyposulphite of soda and chloride of ammonium, greatly augment this solubility. Scale may be prevented not only by increasing the solubility of the incrusting salts but also by forming from them by double decomposition other salts with no adhesive properties. Certain salts may be used to this end, for instance carbonate of soda, chloride of barium, oxalate of sodium, the oxides of the alkalis (soda and potash) and of the alkaline earths (lime and magnesia).

We will review briefly the action of these salts in the boiler and shall return to some of them in considering the preliminary purification of the water.

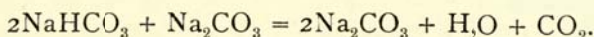
Carbonate of Soda.—Sodium carbonate, first suggested by Kuhlmann, precipitates the calcium carbonate in solution in the water. Precipitated calcium carbonate and sesquicarbonate of sodium are obtained:—



The sesquicarbonate is decomposed in its turn and gives bicarbonate of sodium :—

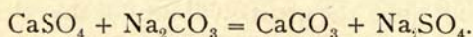


When the water boils the bicarbonate in solution gives off a part of its carbonic acid and becomes the neutral carbonate of sodium.

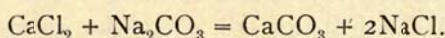


This final reaction shows that two molecules of neutral carbonate of sodium are obtained which remain in solution ready to recommence the cyclic reaction thus set up. If the water contains only carbonate of calcium in solution a minimum quantity of carbonate of sodium is sufficient to precipitate considerable quantities of the carbonate of calcium.

If however the water contains other salts, as it generally does, the sulphate and chloride of magnesium and the sulphate of magnesium, the soluble sulphate of sodium is obtained and carbonate of calcium is precipitated :—



The chloride of calcium also reacts with the carbonate of sodium giving soluble chloride of sodium and carbonate of calcium :—



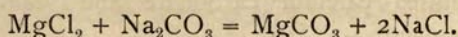
The sulphate of magnesium reacts in a similar way to sulphate of calcium :—



As shown in this equation the magnesium sulphate is transformed into insoluble magnesium carbonate.

It will be seen that the quantity of the sulphates present affect the proportion of the reagent to be employed. The more sulphates present the greater quantity of carbonate of soda is needed. Water as a rule contains hardly any sulphate of calcium, and, putting aside exceptions to the rule, about 100 grammes per horse-power per month of sodium carbonate is sufficient. If however the water contains sulphate of calcium an additional dose of about 78 grammes of carbonate of soda for each 100 grammes of sulphate of calcium, calculated as anhydrite, contained in the water is necessary.

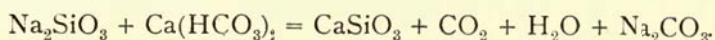
Like sulphate of magnesium chloride of magnesium reacts with carbonate of soda and is precipitated as carbonate of magnesium :—



This reaction is useful as it transforms the chloride of magnesium,

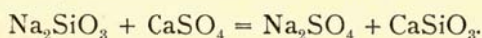
which is very unstable and highly corrosive, into a soluble salt. It is advantageous to use carbonate of soda in just sufficient quantities to precipitate the salts in the water in order to avoid corrosion of the boiler-plates.

Alkaline Silicates.—Sodium silicate, which has been proposed as a scale preventative, is transformed in the presence of the carbonate of calcium in the water into silicate of calcium and falls down in a white gelatinous precipitate:—



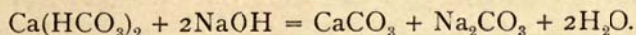
Carbonate of soda is thus obtained and is ready to set up the cycle of reactions which we have just described in the presence of a fresh quantity of a soluble salt, bicarbonate of calcium, and on the other hand the reactions with the other salts of calcium and magnesium are produced.

We have still to consider the direct reactions between the silicate of sodium and the soluble salts, sulphate of calcium and sulphate of magnesium. The sulphate of calcium gives a precipitate of silicate of calcium and sulphate of sodium enters into solution:—



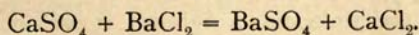
Sulphate of sodium enters into solution and silicate of magnesium is thrown down. With ordinary waters scale can be prevented by the addition of 600 grammes of silicate of sodium solution of 35° B. per horse-power per month. It is evident that the more sulphate the water contains the more silicate of sodium will be required. It is advantageous to calculate the necessary amount exactly according to the proportion of salts in the water.

Caustic Soda and Potash.—The caustic alkalis are still used, but it is more difficult to precipitate the calcium of carbonate with them than with carbonate of sodium, and their employment exposes the boiler-plates to the risk of corrosion if the precaution is not taken to introduce exactly the required quantity in small doses. When caustic soda is added the bicarbonate of calcium in solution in the water reacts with it as follow:—



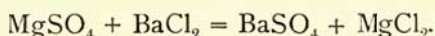
The carbonate of sodium thus obtained reacts in its turn upon the sulphates of the alkaline earths within a certain limit. When this limit is exceeded another reagent must be employed.

Chloride of Barium.—In using chloride of barium the sulphate of calcium which forms a hard scale is transformed into sulphate of barium which has no incrusting properties:—



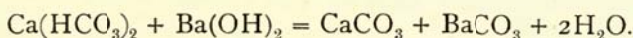
Soluble chloride of calcium is also obtained by the reaction.

Sulphate of magnesium reacts in a similar manner to sulphate of calcium :—



The formation of magnesium chloride however is harmful, as we shall see later on. Chloride of barium costs less than caustic baryta (barium hydrate), but this latter is often used with calcareous waters.

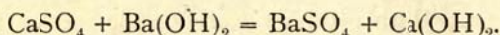
Barium Hydrate.—By using this reagent calcium carbonate is thrown down :—



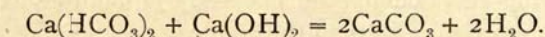
The carbonate of barium obtained is not very soluble in water, it in turn acts on the sulphates in the water and sulphate of barium is precipitated :—



This reaction takes place slowly as the carbonate of barium acts with difficulty on the sulphate of calcium. Outside this secondary reaction the barium hydrate may have a direct action on the sulphate of calcium and in this case sulphate of barium is precipitated and lime is formed :—

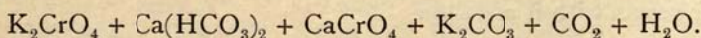


The lime itself may react on the calcic bicarbonate in the water saturating one molecule of carbonic acid and precipitating carbonate of lime :—

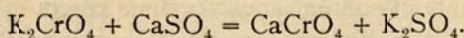


We may add that some manufacturers add a mixture of the hydrate and chloride of barium to the boiler water.

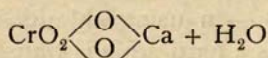
Chromates.—The use of alkaline chromates depends upon the formation of chromates of calcium and of calcic salts soluble in water. Thus with calcic bicarbonate in solution in the water we obtain :—



With calcium sulphate the following reactions occur :—



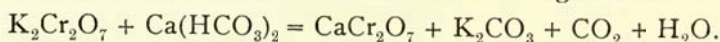
The chromate of calcium obtained :—



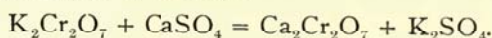
may be used in pigment manufacture.

By studying the molecular weights it is evident that it is more

advantageous to use the neutral chromates than the bichromates. With alkaline bichromates we obtain the following reaction :—



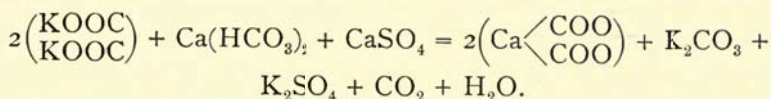
And with sulphate of calcium :—



In addition to the neutral chromates of calcium, carbonate and sulphate of potassium are formed and remain in solution.

Alkaline Oxalates.—The alkaline oxalates are bodies that form insoluble salts with the calcic constituents of the water and therefore may be used in preventing scale.

They cause the following reaction :—



According to this equation, two molecules of oxalate of potassium are expended in the production of one molecule of carbonate of potassium, which in its turn sets up the cycle of scale preventing reactions which we have noted in writing of the alkaline carbonates.

In spite of the secondary reactions, and the possibility of recovering the alkaline oxalate by special treatment of the oxalate of calcium, the high price of the oxalates has always been against their employment, although an oxalate is the classic reagent in the laboratories.

Note.—All that we have said on the subject of the salts of sodium is applicable also to the salts of potassium, and *vice versa*.

3. CALCULATION OF THE QUANTITIES OF REAGENTS NECESSARY TO PREVENT SCALE WITH A WATER OF KNOWN COMPOSITION.

There are many products on the market under a variety of names which are intended for use as scale preventatives. Usually these preparations either only act incompletely in this manner or have to be used in very large proportions. It is easy to understand from what we have already noted that the proportion of reagent to be used must be in proportion to the quantities of encrusting salts contained in the water, and that these reagents must vary according to the nature of the water. Therefore analytical knowledge of the water is necessary, and not even this is sufficient to deal thoroughly with scale. We must know in addition the composition of the scale preventative employed, and be able to use exactly the necessary quantity of it.

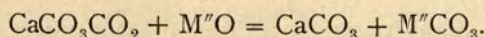
Unfortunately the scale preventatives on the market are of unknown composition, and we are consequently without sufficient data to use them in the proportions suitable to the particular water. In any case these products should not be used until after a preliminary trial has been made of them to determine the limits of their efficacy and the conditions under which they must be used. In addition to these commercial products a large number of substances may be used in dealing with scale which act principally on the two salts of calcium, the carbonate and the sulphate. From this point of view we will consider the carbonate waters first of all, next the sulphate waters, and finally the waters containing both the carbonate and the sulphate of calcium in solution.

To free a water from scale, mineral substances of well-determined composition may be used, such as the salts of the alkaline metals, the carbonates, silicates, oxalates, chromates, bichromates, and aluminates of sodium and potassium. The oxides of the metals of the alkaline earths may also be used, such as the oxide of calcium, magnesium and barium, and also the chloride, aluminate and oxalate of barium. It is therefore useful to know the quantity of each of these reagents which it is necessary to employ to free a water from scale, and this must be determined to begin with by hydrotimetric analysis.

Let us take to commence with the case of a carbonate water.

Carbonate Water.

Let us consider the typical reaction in softening a water with one of the oxides of the alkaline metals or of the alkaline earths, potassium, sodium, calcium, magnesium, and barium. Representing the alkaline metal or the alkaline earths by M we obtain the equation :—



M'' represents a diatomic body.

In this equation it will be seen that carbonate of calcium is formed and precipitated by saturation of the carbonic acid in excess by means of the alkaline oxide or oxide of the alkaline earth. The determination of the molecular weights of the various mineral reagents, whether oxides or salts, will furnish the quantity of the reagent to be employed.

With the aid of the table below the quantity of reagent to use with a carbonate water may be calculated by multiplying the corresponding number found in the table by the weight of the carbonate of calcium contained in the water.

	Carbonate.	Oxalate.	Oxide.	Silicate.	Aluminate.	Chromate.	Bichromate.
Sodium .	1.06	1.34	0.62	1.22	6.60	1.625	2.63
Potassium .	1.38	1.66	0.94	1.54	6.92	1.945	2.95
Magnesium .	—	—	0.40	—	—	—	—
Calcium .	—	—	0.56	—	—	—	—
Barium .	—	—	—	—	7.51	—	—

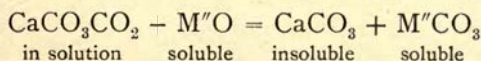
In practice, the dose of the reagent to be employed should be somewhat increased; the numbers above represent the oxides and anhydrous salts.

Sulphate Water.

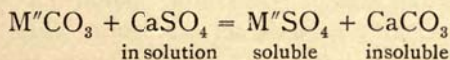
We will now suppose that the water to be softened contains not only carbonate of calcium but sulphate of calcium, and consider the steps to be taken under these conditions. Let us suppose to begin with we have used one of the substances indicated in the preceding table to deal with the carbonate of calcium. It only remains to us to free the water from the sulphate of calcium.

The two cases will have to be taken into consideration according to the particular substance we have used to deal with the carbonate of calcium.

First Case.—The carbonate, silicate, aluminate and oxides of potassium or of sodium are the reagents already employed to deal with the carbonate of calcium. Let us consider to begin with the typical reaction relative to carbonate of calcium which we have already formulated:—



We see that the precipitation of the carbonate of calcium causes the formation of a corresponding soluble carbonate with the formula $\text{M}''\text{CO}_3$, if we suppose that M is diatomic. This soluble carbonate reacts in its turn on the sulphate of calcium contained in the water and brings about the precipitation of insoluble carbonate of calcium:—



A certain relation must therefore be observed between the proportions of sulphate of calcium and of carbonate of calcium to effect completely the softening of the water.

As a matter of fact by considering these two reactions we note that for each molecule of reagent used to deal with the calcic bicarbonate, a molecule of the corresponding soluble carbonate is formed, and that this in its turn precipitates one molecule of sulphate of calcium. According to this in proportion as the soluble carbonate

is formed there will be sulphate of calcium precipitated, and this entails a limit in the process of softening, and this limit is the relation of the molecular weights of the sulphate of calcium and of the carbonate of calcium, that is to say :—

$$\frac{\text{CaSO}_4}{\text{CaCO}_3} = \frac{136}{100} = 1.36.$$

In writing previously on this subject, in the *Génie Civil* and the *Revue de Chimie Industrielle*, we have called this the “co-efficient of incrustation”. In softening a water with the reagents specified in the first case, we must establish the relation of the quantities of sulphate of calcium and of carbonate of calcium contained in the water determined by hydrotimetric analysis, and compare this with the co-efficient of incrustation 1.36.

Two cases will present themselves :—

(a) Relation of the quantities of salts contained in the water.

$$\frac{\text{CaSO}_4}{\text{CaCO}_3} < 1.36.$$

From the secondary reactions which we have examined, it is evident that in this case it is unnecessary to add fresh quantities of reagents. We simply calculate by the preceding table the quantities of reagents to be put into the water in the same way as for carbonate of calcium alone. In practice, the dose of the reagent given by this calculation is somewhat increased.

(b) Relation of the quantities of salts contained in the water.

$$\frac{\text{CaSO}_4}{\text{CaCO}_3} > 1.36.$$

In this case the sulphate of calcium is in excess. A part only of it will be precipitated by the secondary reaction, and therefore the other part which still remains to be precipitated must be ascertained, in order to determine the quantity of the reagent to be added. The carbonates of potassium, sodium or magnesium or chloride of barium may be used as a reagent. The weight of the sulphate of calcium precipitated by the carbonate of calcium formed in the secondary reaction must be calculated, and this is done by multiplying the weight of the carbonate of calcium contained in the water by 1.36.

Represent by P the total weight of carbonate of calcium contained in the water. P multiplied by 1.36 will be the total quantity of sulphate of calcium precipitated.

Therefore, if we now represent by π the total weight of sulphate of calcium contained in this water, there still remains a weight

$\pi - (P \times 1.36)$ of sulphate of calcium to be precipitated. This is effected with one of the reagents contained in the table below, and the amount is ascertained by multiplying the weight by the constant number found in this table corresponding to the reagent used.

Carbonate of sodium	0.779
„ „ potassium	1.001
„ „ magnesium	0.617
Chloride of barium	1.529

If μ represents the multiplier found in the preceding table for the reagent employed, the weight of this reagent to be introduced into the water to deal with the sulphate of calcium will be given by the formula:—

$$(\pi - 1.36 P) \mu.$$

Second Case.—The oxalate, chromate and bichromate of potassium and of sodium and the aluminate of barium are the reagents already used to deal with the carbonate of calcium. We have to soften a water containing in addition to the carbonate of calcium a considerable quantity of sulphate of calcium. When the reagents specified in this second case are used we have not to take secondary reactions into consideration. We add to the water a further quantity of the reagent previously used to deal with the carbonate of calcium, ascertaining the amount to be employed by multiplying the weight of the sulphate of calcium contained in the water by the multiplier of the reagent as indicated in the table below.

Oxalate of potassium	1.220
Oxalate of sodium	0.985
Neutral chromate of potassium	1.430
Neutral chromate of sodium	1.194
Bichromate of potassium	2.169
Bichromate of sodium	1.933
Aluminate of barium	5.521

4. ARRANGEMENT IN THE BOILER OF SPECIAL SCALE PREVENTING DEVICES, AND PRELIMINARY TREATMENT OF THE WATER WITH STEAM.

To remedy the troubles arising from deposited matter, boilers are often provided with special arrangements placed at properly chosen points which catch the matters in suspension in the water, or arising from the decomposition of the salts of the alkaline earths.

In the parts of the boiler not exposed to the direct action of the fire, the precipitated matter does not adhere.

Phenomenon of Decantation by Ebullition.

If water containing sand is boiled in a vessel, and a small capsule is lowered a few inches under the surface of the water, it will be noted that very shortly after the water is brought to the boil all the sand has passed into the capsule.

The reason of this is that the water outside the capsule is violently agitated, and the currents circulate the particles of sand, and keep them in suspension. These particles of sand are attracted by the zone of calm in the capsule and fall into it, as the liquid which it contains is not in a state of ebullition.

Several devices are based upon this phenomenon.

Schmitz Arrangement.—In the Schmitz arrangement, for in-

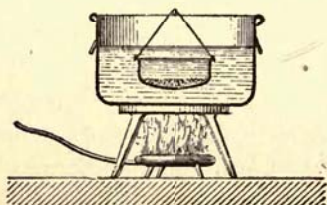


FIG. 7.—Demonstration of decantation by ebullition.

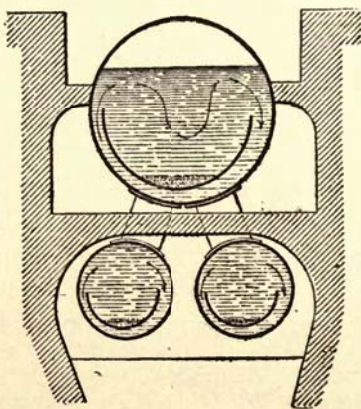


FIG. 8.—Schmitz' Apparatus.

stance, the arc of a thin cast-iron cylinder is mounted inside the boiler at a short distance from the side.

This is placed in such a way that the distances from the sides are unequal, and the passage on one side is narrower than on the other.

Dulac's Deposit Collector.—In Dulac's boiler the calcareous deposits as they are heavier than water fall into collectors suitably arranged in the interior of the boiler. This is facilitated by the ascending and descending currents in the boiling liquid. The recipients are small cast-iron vessels of thin metal, open at the top, and easy to take out for cleansing purposes. A hanging valve is fitted in the upper part of each collector in order to prevent the deposits from escaping, which might happen on prolonged boiling.

In tubular boilers the collectors are arranged in the upper cylinder. In Fig. 10 *a a* are the collectors, and *b b* the hanging valves.

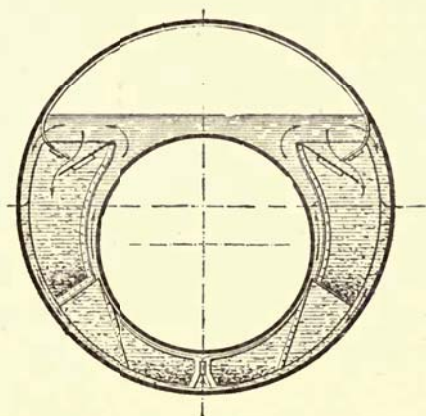


FIG. 9.—Dulac's deposit collector in a boiler with interior furnace (transverse section).

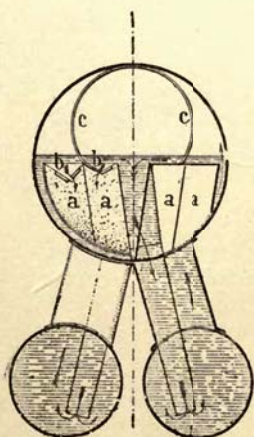


FIG. 10.—Dulac's collector in a tubular boiler (transverse section).

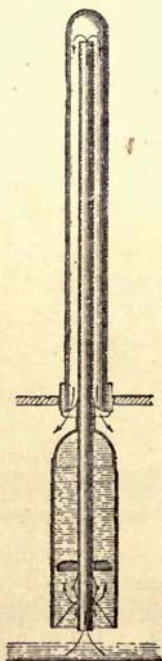


FIG. 11.—Tube in the Field boiler with Dulac's collector.

This system has been applied to the tubes in the Field boilers. It is a sort of elongated collector, open at the top, and is inserted

in the middle of the tube. An annular space therefore is formed

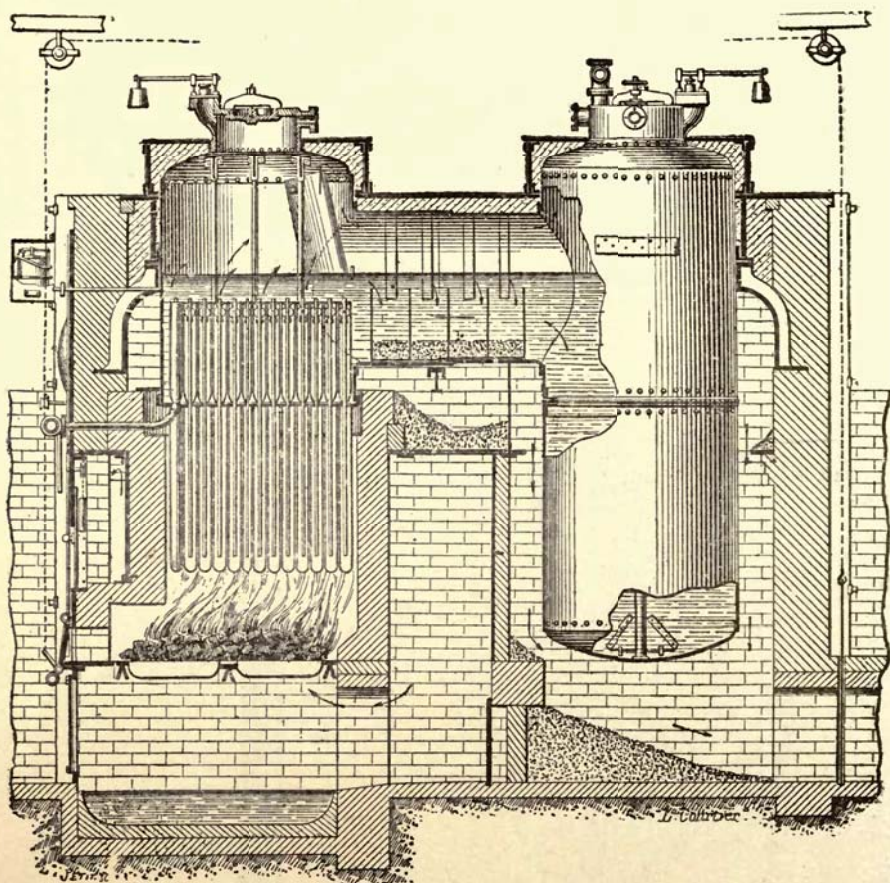


FIG. 12.—Dulac boiler.

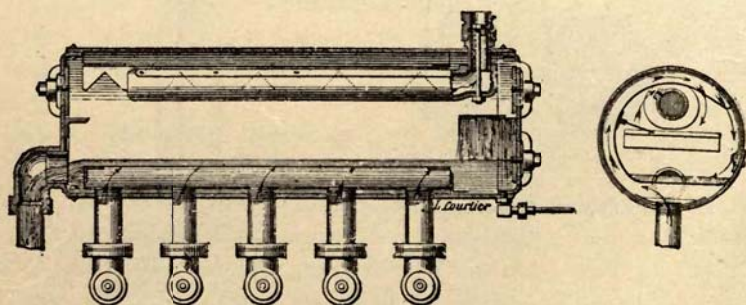


FIG. 13.—Belleville feed water purifier.

where the liquid remains calm, and this attracts and retains the deposits.

Belleville Feed Water Purifier.—The majority of boilers in our national marine service are of the Belleville type, and are provided with an injector for the purpose of purifying the feed waters. The

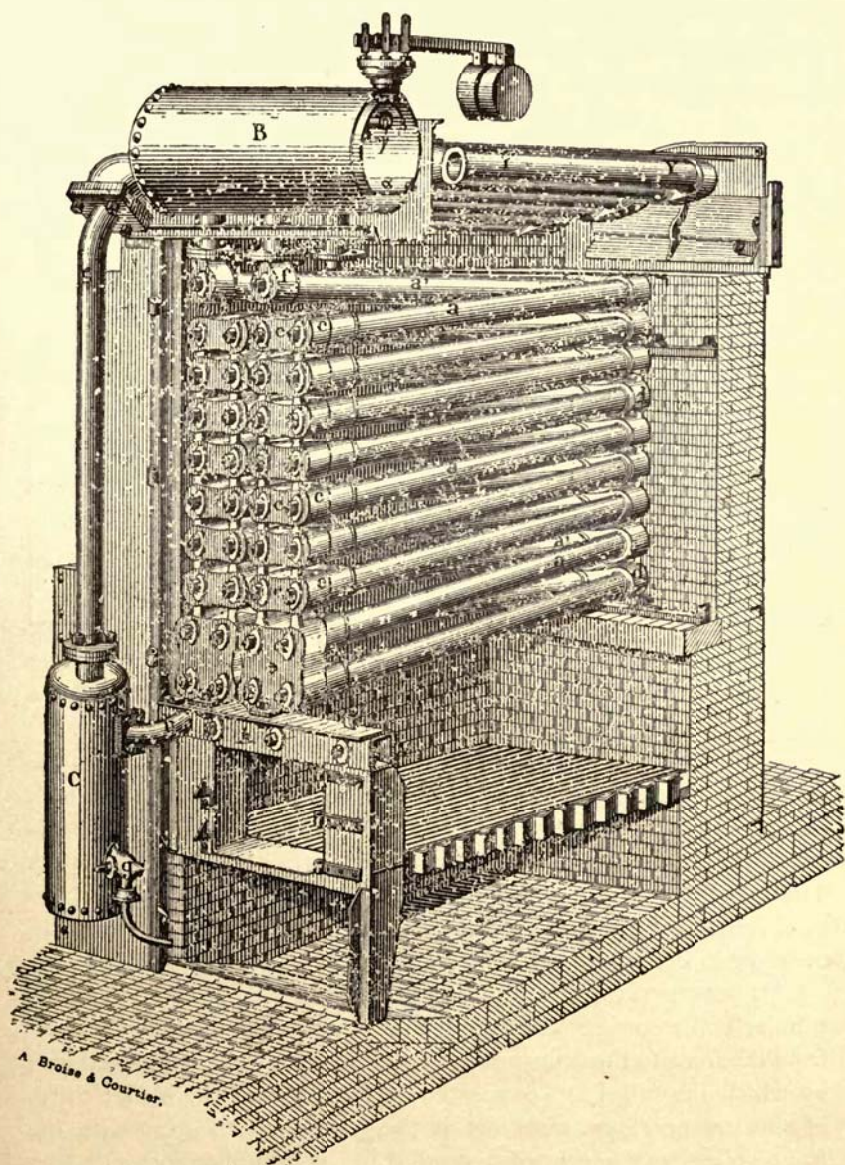


FIG. 14.—Section of Belleville purifier in perspective.

decantation from the solid matters is easily done, as where it takes place the water is not in a state of agitation. The injector atomises the water and blows it at high pressure through the steam in the

multitubular generators. The calcareous salts are then precipitated in the form of sludge, and fall into a sludge box from which they can be easily removed.

The hot water leaves the collector B B by a pipe *l*, which reaches half-way up the injector C. This injector is a single chamber in which the agitation is very little, and where consequently the deposits are collected, and can be run off by the pipe at *g*.

The Belleville boilers are not only the most advantageous because they allow the volume of water to be reduced and consequently avoid the danger of explosion, but also because of this arrangement by which the feed water is purified before it enters the boiler.

Experiments made with a Belleville injector have given the following results :—

Composition of the water per litre.	Natural water.	Water after treatment.	Precipitated salts.
	Grammes.	Grammes.	Percentage.
Carbonate of lime	0'600	0'010	83
Sulphate of lime	0'336	0'014	96
Magnesia	0'012	0'012	0
	0'948	0'036	

It will be seen by this table that the injector eliminates 96 per cent. of the sulphate of calcium, and this must be looked upon as a highly satisfactory result.

Arrangement of the Naeyer Boiler.—In the Naeyer boilers the feed water is forced directly through the current of steam which leaves the upper collecting tube C. The greater part of the salts contained in the water are thus almost immediately precipitated. The calcareous deposits are collected in the form of sludge in the mud drum D D, and the water runs into the feed tank B from an overflow in the mud drum.

Arrangement of the Montupet Boiler.—The Montupet multitubular boiler consists essentially, first, of a system of tubes inclined from the front to the back ; second, of collecting tubes of forged iron by which the tubes are connected in front and at the back ; third, of a water and steam reservoir at the top communicating with the front collectors ; fourth, of a mud drum communicating with the back collectors.

The Montupet boiler is fed from the front of the upper reservoir at the level of the water. The water is preferably fed into the steam, and in this way it reaches two large return pipes at a temperature

higher than 165° C. The encrusting salts, sulphates and carbonates of the alkaline earths, are precipitated, and then carried into circulation by the currents in the boiler, and are deposited in the mud drum at the back. In this decanting tank there is on each side a cast-iron compartment in the form of a V reversed, in which the deposits settle. Between this arrangement and the decanting tank

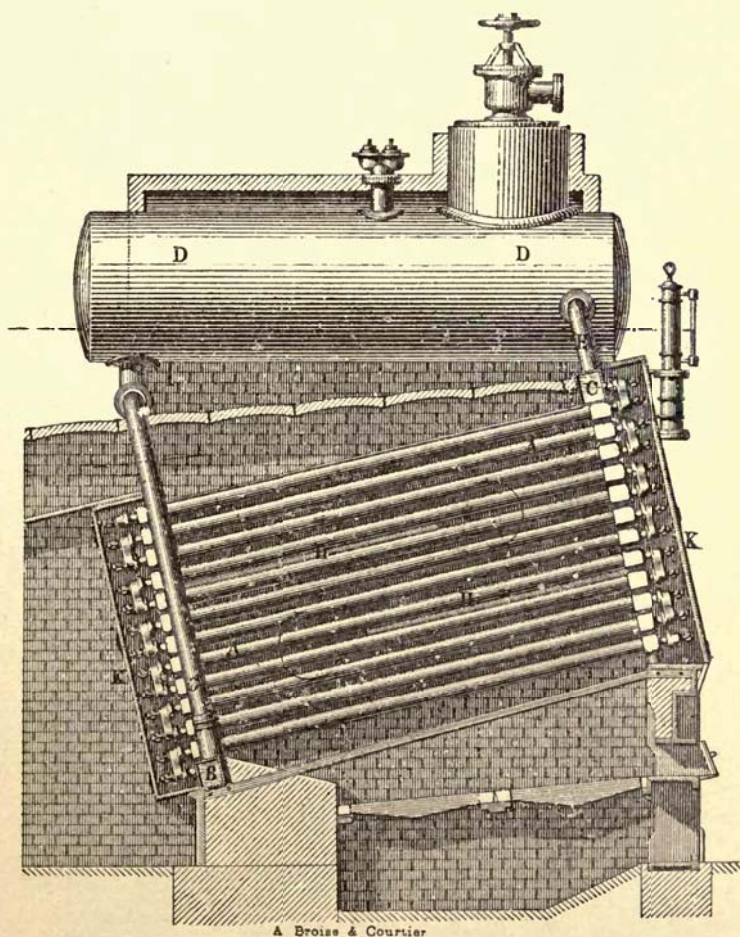


FIG. 15.—Naeyer boiler.

an empty space of twenty millimetres allows the deposits to run to the bottom of the tank. These deposits are carried towards the axis of the decanting tank, where they come in contact with a tube the length of the tank, and with an opening in the lower part. This tube has a sludge cock, by which the deposits can be evacuated.

Arrangement of the Collet Boiler.—In the Collet boiler the water also precipitates a part of its salts in passing through the steam box, where of course it is also heated. The precipitated sludge accumulates in a pocket widely opened in front, which forms the lower part of the collector where the circulation is the least active.

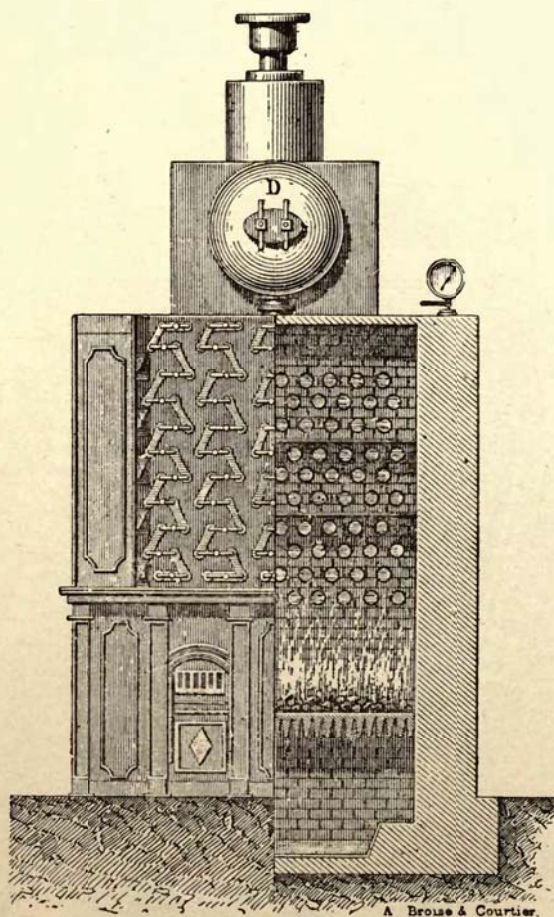


FIG. 16.—Naeyer boiler (side elevation).

Arrangements of the Serpollet Boiler.—The Serpollet boiler is formed of a flattened circular coil of copper, soft steel or brass. Steam is raised very quickly and the speed of the current is so great that the precipitated matters cannot remain in the steam coil. Nevertheless an injector is provided by means of which the current can be reversed, and the coil completely flushed.

We cannot pass on without noticing the boilers of Weyher and

Richmond of Pantin, which have special arrangements for softening the feed water, and have met with some success.

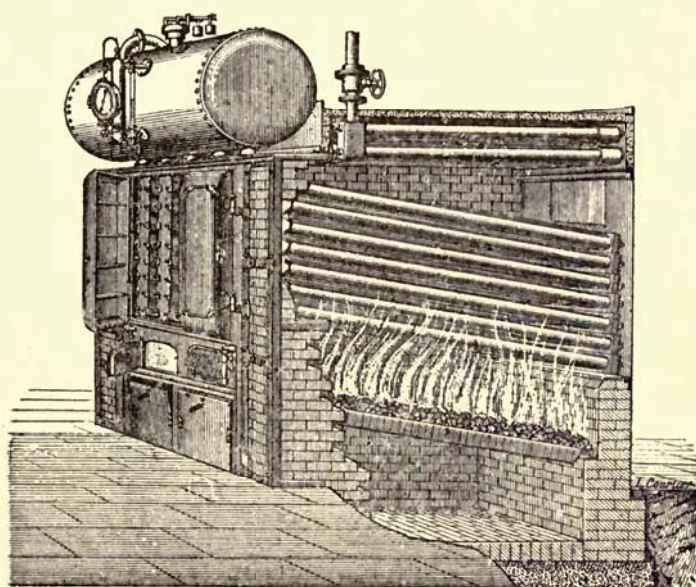


FIG. 17.—Collet boiler.

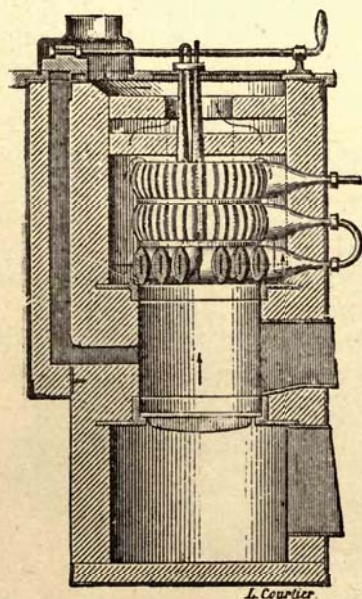


FIG. 18.—Serpollet boiler (vertical section).

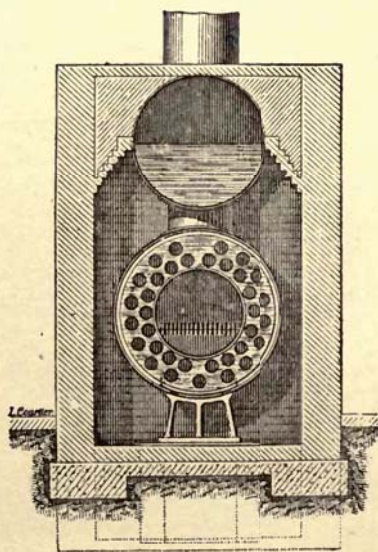


FIG. 19.—Weyher and Richmond boiler (transverse section).

Figs. 19 and 20 are longitudinal and transverse sections of this type of boiler with removable furnace.

Finally we must mention the Babcock and Wilcox boilers, which we show in figs. 21 and 22.

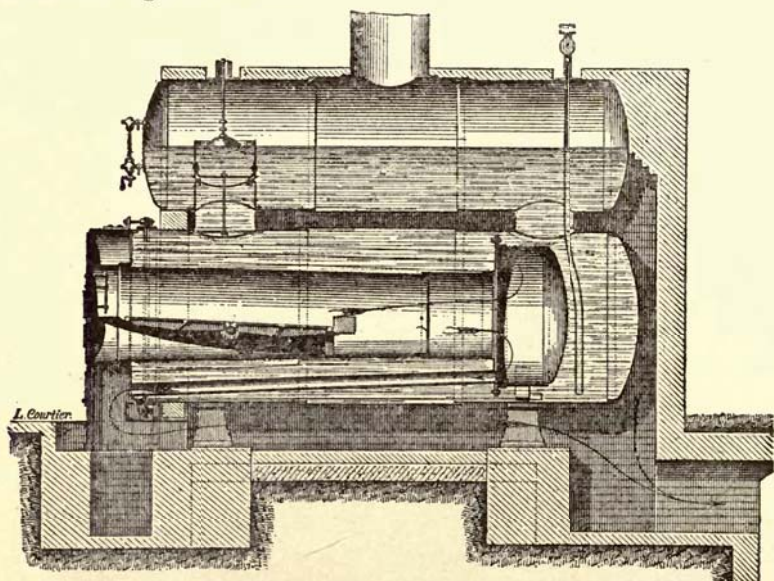


FIG. 20.—Weyher and Richmond boiler (longitudinal section).

As we are not able to afford the space to describe all the special arrangements for softening feed waters, we have noted the principal

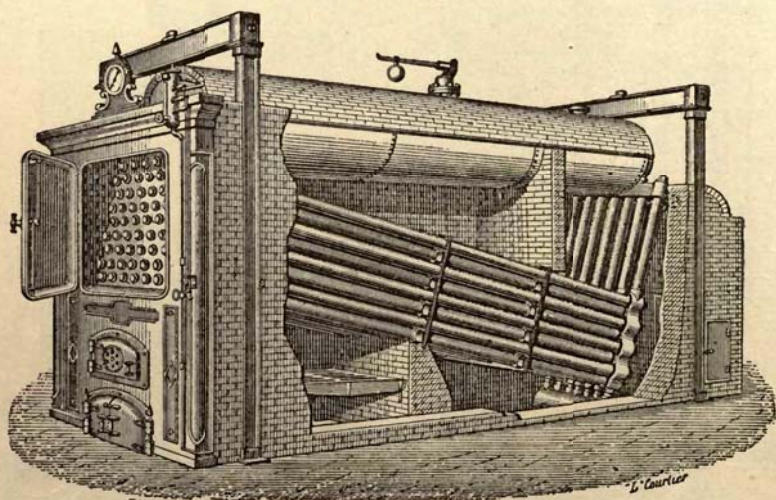


FIG. 21.—Babcock and Wilcox boiler (in perspective).

types, which appear to us to be the most interesting. We shall now proceed to describe several arrangements for the preliminary treatment of water with steam.

Buron's System of Purifying Water with Waste Steam.—

Buron's apparatus precipitates the carbonates of the alkaline earths in the water and at the same time heats it. It may therefore be used advantageously to deal with feed water for boilers. In this apparatus shown in fig. 23, the waste steam is led in by a vertical pipe A in which there is a grease trap as at F. The steam leaves its oil and condensed water in the trap and they are run off by means of a syphon communicating with the lower part of the grease trap.

Then the steam passes into a collecting pipe provided with a number of tubes K K, which penetrates slightly under the surface

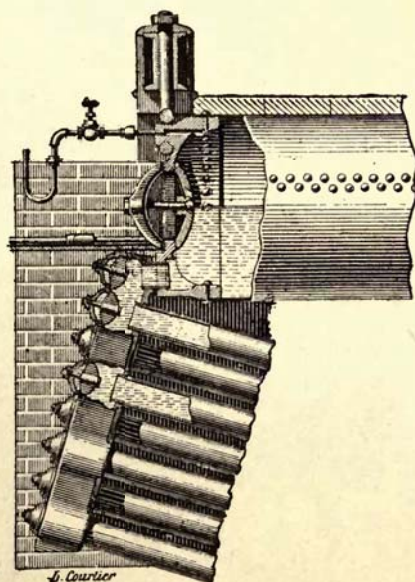


FIG. 22.—Arrangement of tubes in the Babcock and Wilcox boiler.

of the water. The water is thus heated and constantly kept in agitation by the steam. The excess steam escapes by the tube B. The cold water runs in at C into a funnel from a ball-cock regulated by the float G in the tank of water under treatment. This float follows the variations of the level of the water, and consequently the cold water is let in according to necessities.

The cold water pouring into the funnel C runs into a perforated trough, which admits it into the interior of the tank in fine jets, which run through the steam leaving the tubes K. The water is thus heated easily, and is freed from the salts of the alkaline earths, which are precipitated. The purified water ready for delivery to the boiler is heated to about the boiling-point. The sludge is

evacuated by the sludge-cock E, and moreover there is a manhole in the upper part of the apparatus allowing it to be completely cleaned out. In the case of a water containing also sulphate of calcium, a small tank L is mounted, in which the sulphate is precipitated by means of carbonate of sodium.

Chevalet's Heater and Softener.—By using this apparatus the feed water can be brought to about the boiling-point.

Calcareous water, such as that of the Seine, can be easily treated. The hydrotimetric degree, 18° , is reduced to about 5° , and if it is necessary to still further lower it, this can be done by adding a little carbonate of soda to the water.

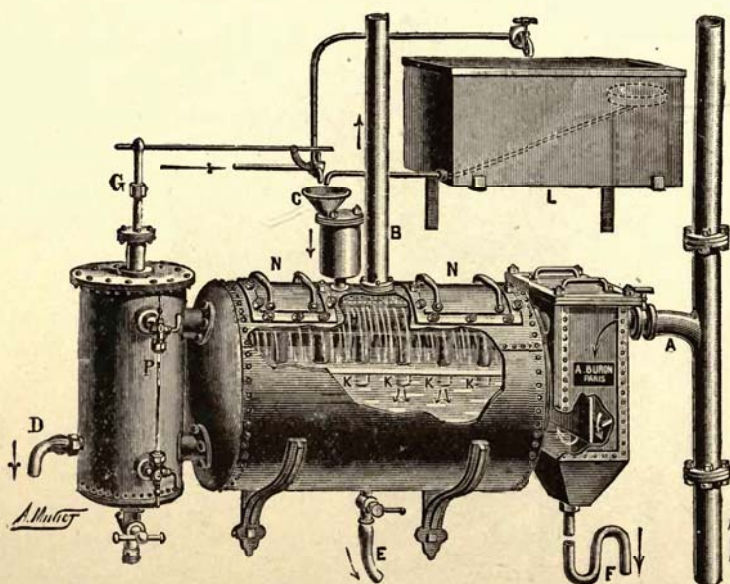


FIG. 23.—Buron's softener.

Chevalet's apparatus is a series of tanks mounted one on the top of the other, over a cold-water reservoir A, in which the deposit is collected. In work, the water runs in through a ball cock regulated by a float H, which follows the level of hot water in the reservoir A.

The water first enters the top compartment through a funnel K, at the top of the apparatus, and finds its level in the first tank B_1 .

From there it runs off by an overflow D_1 into a second tank B_2 , which it partly fills and runs off by its overflow D_2 into the third tank B_3 , and so on. On leaving the last tank the water finally runs into the hot-water reservoir A. During its downward course, the water has met an ascending current of waste steam. This

steam is let in over a grease trap C, which catches the greasy

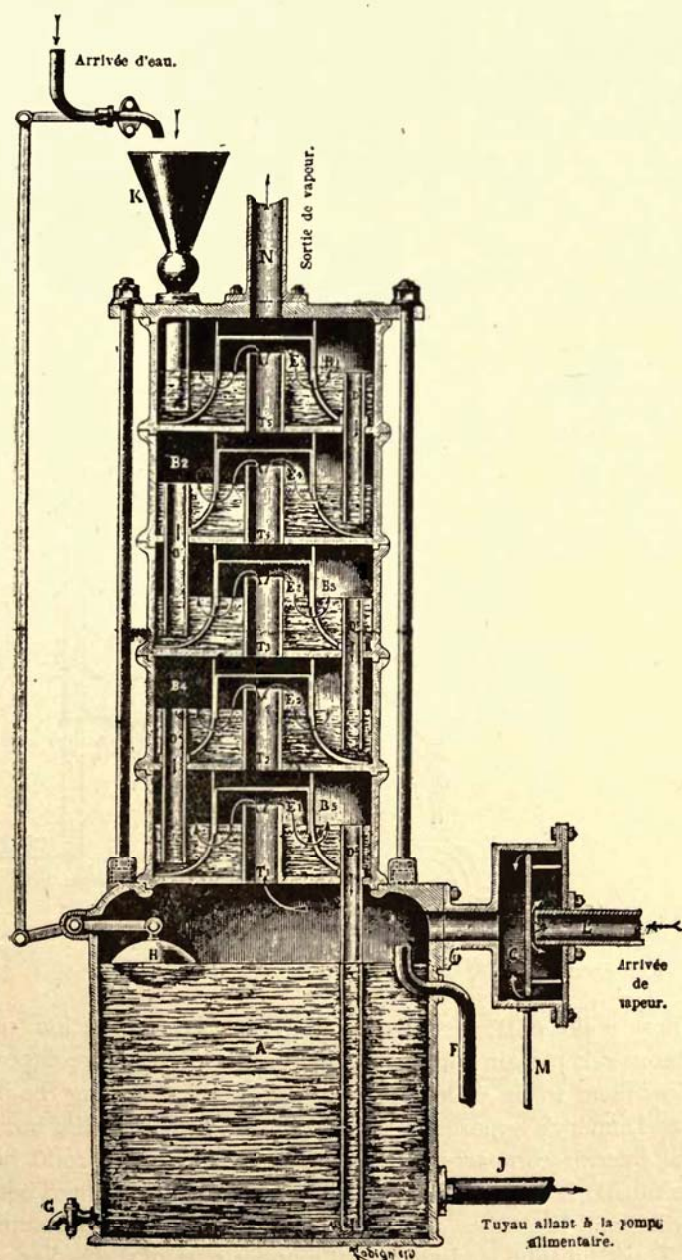


FIG. 24.—Chevalet's heater and softener.

condensed water, and then continuing its course passes by the central tube T_1 under the cap E_1 , and bubbles through the water

in the tank B_5 . From there it passes by the central tube, under the upper cap of the tank E, and so on.

Finally, the steam reaches the tank B_1 at the top, and if it is in excess, it escapes into the open air by the tube N. In its upward course the steam bubbles through the water in each of the superimposed tanks, and it condenses, bringing the water to the boil. The tanks are so mounted that the whole apparatus can easily be taken to pieces and cleaned.

Duméry's Injector.—The action of this apparatus depends upon the fact that water brought to the boil keeps the solid particles in suspension towards the upper portion of the boiling liquid.

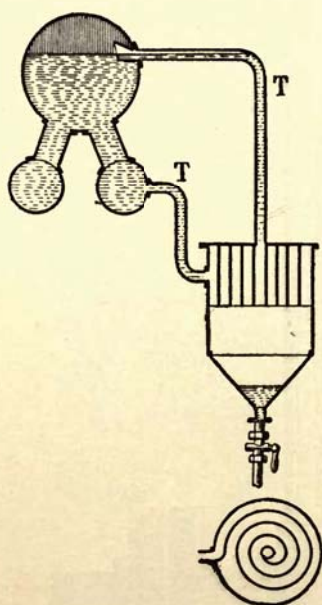


FIG. 25.—Duméry's injector.

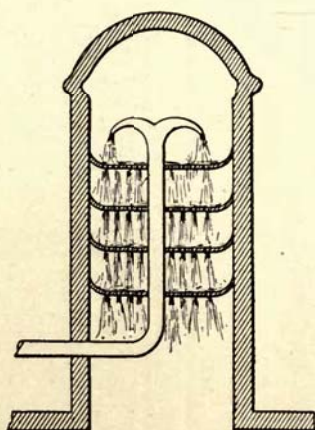


FIG. 26.—Schau's apparatus.

These solid particles arising from the decomposition of the calcareous salt remain long enough in suspension before depositing to allow them to be collected in an apparatus adjoining the boiler, such as Duméry's apparatus. This consists of a metallic box with several interior compartments arranged to retain the solid bodies. In the tubular boilers, for instance, the apparatus is mounted between the boiler and the tubes, and the top of the injector communicates as at T' with a tube leading into the upper part of the boiler, where the matters remain in suspension.

These matters are led by this tube into the apparatus, and by the prolonged circulation deposit their solids in the compartments.

The water thus softened leaves the apparatus by the pipe T, which feeds it into the boiler.

Schau's Apparatus.—This arrangement is based on the precipitation by heat of the calcareous salts contained in the water.

The water is forced into a dome, in which it falls in a fine rain on grids mounted inversely one to the other and arranged at different heights.

The apparatus communicates with the boiler, the waste steam

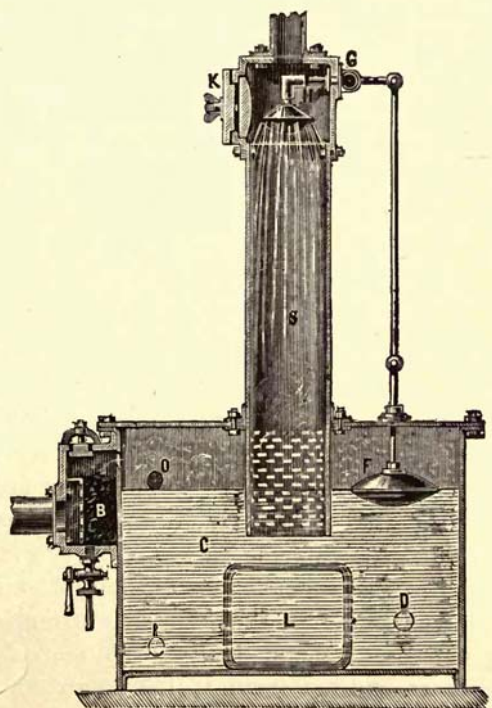


FIG. 27.—Montupet's condenser.

from which heats the water and precipitates the calcareous salts which are deposited at the bottom of the dome. The water thus treated is fed into the boiler by an overflow pipe.

Montupet's Condenser.—Montupet's condenser allows the whole or part of the steam of any engine to be condensed, in order to purify the feed water and bring it up to about boiling-point. This extremely simple and practical apparatus consists of a cast-iron hot-water reservoir G, provided with a manhole L and a bolted cover.

An escape pipe S fixed on the cover is perforated at the bottom part, and on this is mounted a small rectangular tank of cast iron.

At one side of this box the water-pipe H is let in, which terminates in a rose, and has a ball cock G, regulated by a float F, which follows the level of the hot water in the reservoir G. A grease trap of coke B mounted on the side of the reservoir C is provided with a perforated plate through which the waste steam is let in, a tap at its lower part to run off the greasy condensed water, and at the top is a plug hole for cleaning purposes.

The steam is first of all freed from its grease by the coke, and enters the top of the reservoir C, where it commences to heat the water. It escapes through the perforations in the bottom of the pipe S, and ascending in this pipe it meets the water coming down in a fine rain. By this means it is heated to the boiling-point, and the carbonate of lime is precipitated, and falls down to the bottom of the reservoir G, from which it is cleared out through the manhole L. The water thus freed from carbonate of lime runs off by the overflow O, and is fed into the boilers.

Lencauchez' Apparatus.—This apparatus consists first of a grease trap, in which the waste steam from the engines is freed from greasy matters and the condensed water which it may bring with it. After this treatment the steam flows into a metallic cylinder, in which the feed water is purified. The water to be treated is in a reservoir at a higher level, and leaving this by an overflow pipe it runs into the top of the cylinder, where it meets a series of cones which convert it into a thin stream. These cones are so arranged that the base of one faces the base of the next, and so on, so that the water is first led towards the sides of the cylinder and next towards the centre. The water is thus divided into a large number of thread-like streams, and these in their downward course meet the ascending current of steam, which has an inverse movement to that of the water, and the steam is thus condensed. The water being thus brought up to a temperature bordering on boiling-point, gives up its carbonic acid and the carbonate of lime is precipitated.

After being decanted in the lower reservoir, the water is freed from its matters in suspension by being forced upwards through a filtering bed of fine gravel. The water runs off at the top of the filter at the height of two to three metres above the feeding pumps, so that it is delivered to them under pressure.

To use live steam in the Lencauchez apparatus it must first be passed through an exhauster. In this case the salts of the alkaline earths are precipitated to a larger extent, as the temperature reaches about 120°C .

To free the water to a satisfactory extent from sulphate of lime a little carbonate of soda should be added when either waste steam

or live steam is used. To clean the filter and clear out the apparatus

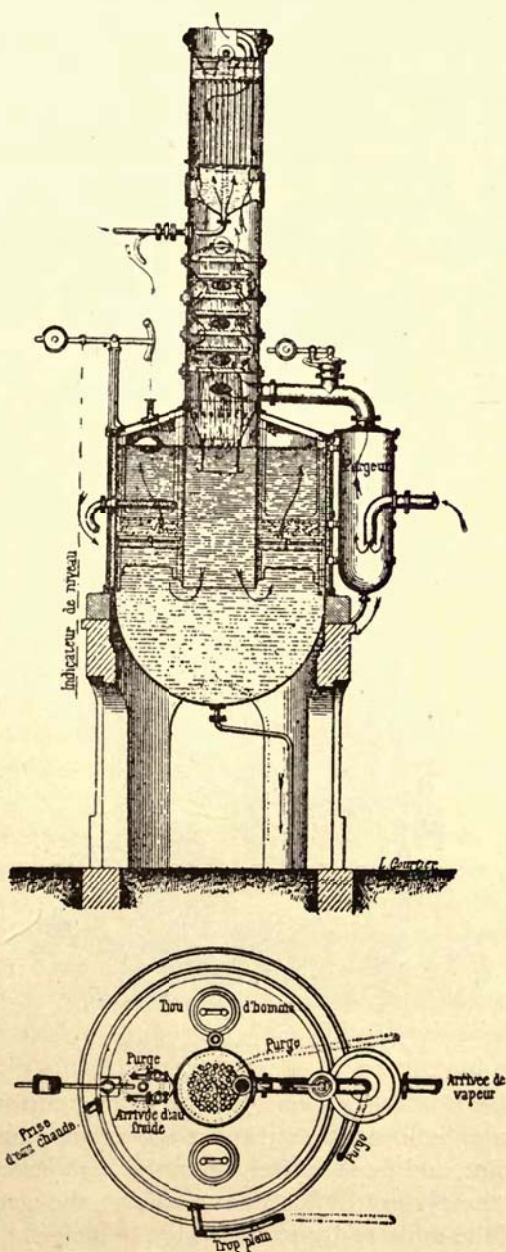


FIG. 28.—Lencauchez' apparatus (plan and section).

the tap in the lower part of the reservoir is opened, and as the water is under pressure, it is forced out, carrying the solid matters with it.

Howatson's Softener.—The aim of this apparatus is to bring about the deposit of the carbonates of the alkaline earths before passing the water into the boilers.

Howatson's apparatus is a cylindrical reservoir, with plates arranged in stages. The water runs in by a ball cock, regulated by a float, as shown in the figure.

This water fills a small tank in the upper part of the apparatus, and overflows in a fine stream over the first plate, from whence it falls on to the next and so on.

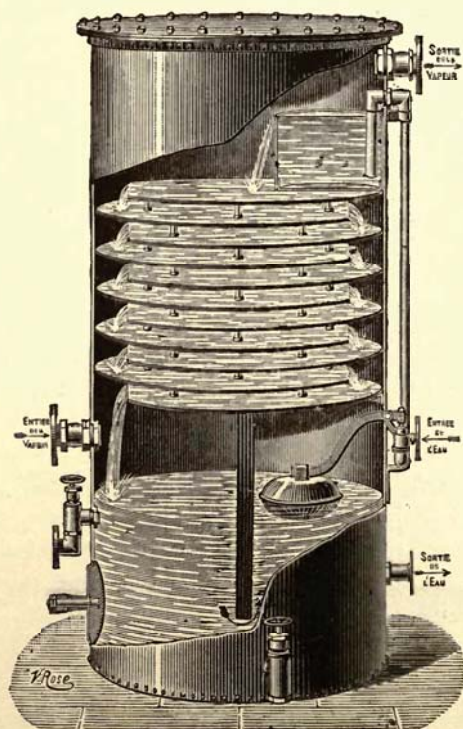


FIG. 29.—Howatson's apparatus.

In its course it is acted upon by an ascending current of steam, and as the water is in a fine stream it is brought immediately to the boiling-point, and freed entirely from the carbonates, which are deposited on the plates. After this treatment, the water falls into the bottom of the tank, ready to be fed to the boilers.

Below the opening where the steam enters is a tap by which the greasy water can be drawn off. An escape for the steam is arranged at the top of the apparatus, and a mud-hole and a sludge cock are provided to clean out the deposits.

5. SCALING BOILERS AFTER COMPLETE COOLING.

The texture, form and hardness of the scale closely depends upon the physical and chemical conditions. The observation of certain phenomena suggests methods by which the quantity of the deposits can be notably diminished and their nature improved. Experience has shown that the physical phenomena of the cooling of water in steam boilers has great influence on the deposit and the hardness of the scale.

On this subject Savreux and Schmidt have made some interesting communications to the Congrès des Ingénieurs en chef des Associations de Propriétaires d'Appareils à Vapeur, and to the Société d'Encouragement pour l'Industrie Nationale.

The process of clearing out the boilers, after cooling off, depends upon what has been noted after a complete cooling of the boiler, which takes about eight days to effect:—

1. The greater part of the sludge can be flushed out.
2. The deposits remaining adhere only slightly to the boiler-plates.

What has to be done, therefore, is to allow the water in the boiler to cool gradually, and then to rake out the sludge before it can harden.

At the Montières works, Savreux proved that this method gave excellent results, but, unfortunately, its adoption necessitates two conditions:—

1. The possibility of emptying out without pressure.
2. The possibility of doing without the boiler for a week while it cools.

The first of these conditions is absolutely necessary, and is only difficult to realise in the case of sunken boilers. As for the second condition, it of course depends upon the arrangements that can be made to dispense with the use of the boiler for the required time.

Dubois, in a note to the Amiens Linen Society, remarked that the deposits are dealt with less easily a quarter of an hour after the water is run out of the boiler. Half an hour after this has been done the deposit becomes hard and adheres to the plate. When the boilers can be emptied without pressure, and there is a boiler in reserve, it is possible to prevent the deposits from adhering, and thus to avoid scale from river and well water in any description of boiler. To do this, after complete cooling, the boiler is emptied and every part of it cleaned as soon as possible after the water is run off.

Secondary operations may be practised, such as renewing the water to hasten the cooling, washing with a spurt pipe in the case of tubular boilers, and, finally, the immediate raking of the still damp deposits.

All these operations tend to facilitate the process.

6. CORROSIVE AND INCRUSTO-CORROSIVE WATERS.

Corrosions in General Caused by Water.

As a rule natural waters are corrosive, but to a greater or less degree. The carbonic gas and the oxygen which they hold in solution are capable of very appreciable corrosive action, even when the waters do not contain salts. When the water contains salts or acids the corrosive effect of these bodies joins in the attack with the carbonic-acid gas and oxygen.

Polished iron or steel does not rust in pure water, and the presence of carbonic-acid gas or a similar body seems to be necessary to exert an oxidising effect upon it.

In the ordinary formation of rust, ferrous carbonate would seem to form to begin with, to the detriment of the iron. Then this dissolves in water and forms ferrous bicarbonate with the carbonic acid of the water. This under the influence of the air and water is transformed into magnetic oxide, and finally into the hydrate of the sesquioxide of iron.

When water attacks iron, diverse compounds of the corrosive principles with the metal itself result to the detriment of the iron.

Moreover, as a rule, the corrosive power of water shows that this water has loaded itself with minerals from the strata through which it has passed, and consequently will deposit them, when concentrated, in the boiler. These deposits are frequently of a very encrusting nature, as, for instance, sulphate of calcium, which is met with in sea water and deep well water. The deep well waters are charged with this sulphate of calcium by first taking into solution the carbonate of lime in the strata through which they have passed, and the subsequent transformation of this into sulphate, the sulphuric acid being obtained by the oxidation of pyrites in the presence of water.

Deep well water and sea water, then, may be the cause both of corrosion and of scale, and have hence been termed encrusto-corrosive in an article written by the author, and published in the *Génie Civil*. The boiler user too often forgets to take into consideration the necessity in dealing with the water of guarding against

these two sources of mischief, and to seek for a remedy which, so to speak, will kill the two birds with one stone.

As regards corrosion generally, iron seems more capable of resisting attack than steel, and in the same order of things poor quality iron does not rust as quickly as iron of better quality. The resistance to attack is greater in proportion to the amount of phosphorus the iron contains, and there is always a good deal of it in poor quality iron.

Iron alloys vary in their resistance to rust. Manganese seems to hasten it, whereas nickel, chromium and cobalt appear on the other hand to retard the attack.

In steam boilers two sorts of corrosions are noted :—

1. Exterior corrosions, produced by atmospheric agency. These are outside our subject.

2. Interior corrosions, due to feeding the boiler with more or less corrosive water, which attacks the boiler-plates under the influence of heat and pressure.

As a rule, the corrosion is localised, sometimes however it is general. The same water, used in boilers of different types, may very well corrode the one without attacking the other, or the corrosions may occur in different parts of the boilers.

If the boilers are of the same type, and worked in the same manner, with the same water, the corrosions in the one will be reproduced in the same manner and in the same places. According to the nature and quantity of the matters in solution in the water, the corrosion will be more or less intense and take a particular form.

In a boiler the attack may be made in three ways, and give rise to three sorts of corrosion.

(a) **Pittings.**—In this case, the plates are pitted in different parts. Small round cavities form, filled with a black powder mainly consisting of oxide of iron, but also containing the salts originally in the water. These cavities increase in size, and especially in depth, and are covered with a sort of cap of oxide of iron.

(b) **Corrosion over a Large Surface.**—The plates are sometimes

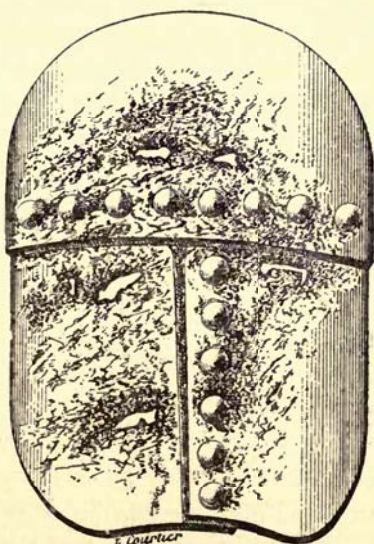


FIG. 30.—General corrosion.

attacked over a large surface, and are usually covered with a sedimentary deposit, showing no trace of acidity.

(c) **Corrosion Aided by Mechanical Action.**—By reason of different pressures on different parts of the boiler, the plates bulge and part, and as the water leaks this aids corrosion at these parts.

In addition to chemical action the corrosion is aided by certain physical influences. The parts of the boiler most subject to corrosion are the plates directly over the fire, and these usually corrode over a large surface. As for the plates in the coldest part of the boiler, they are usually pitted locally. These isolated pittings are met with in boiler-plates where the water is or has been at rest, and where ebullition is not produced. It must be noted that sometimes if the pittings are too close to each other the plates are so weakened that an explosion results.

In testing the substance which fills the pittings, in addition to oxides of iron, other salts, and in particular carbonates, will be found.

From this, arguing that the presence of carbonates proves that there is no acid action, some engineers have concluded that pittings do not owe their formation to an acid, and believe that the corrosion is due in a great measure to ferric oxide.

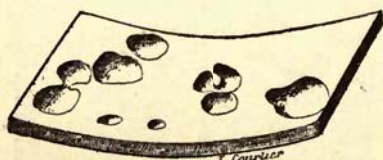


FIG. 31.—Pittings.

Ferric oxide is certainly a very corrosive body. Its hygroscopicity aids the absorption of humidity, and, moreover, it is electro-positive to iron. It must be carefully removed from the cavities when the boiler is cleaned out.

But before speaking of the effects that this ferric oxide may produce, we must examine the manner in which it is formed. We shall see as a matter of fact that the ferric oxides may be not only the direct result of the attack on the iron by the carbonic-acid gas and oxygen contained in the water, but may be the result of an attack by acid as a consequence of chemical changes brought about with the aid of physical phenomena.

In the isolated cavities the presence of carbonates is easily explained, as the bi-carbonates are instable, and precipitate their carbonates of the alkaline earths. These carbonates may certainly have a corrosive action, as carbonic acid, aided by the oxygen and the steam in the boiler, is very corrosive.

But, nevertheless, it must not be taken for granted that these pittings are not the result of an acid action. The attack on the

boiler-plates may very well be the result of the direct action of certain salts in solution in the water. The acid of these salts may combine with the iron to form corresponding salts, the reaction being aided by the steam and the particular conditions of temperature and pressure.

The examination of the substances contained in the isolated pittings does not show the presence of acidity, but nevertheless these corrosions are the result of an acid attack on the iron.

We are able to prove beyond doubt the presence of acids in some substances from the corroded parts. If, in fact, the salt produced by the corrosion is decomposed, it indicates the presence of an acid.

But in addition to this, the salts in solution in the water may by decomposition or by reacting on each other bring about acid transformations, and therefore lead to corrosions.

This acidity is then very appreciable, and can easily be proved with litmus. We may add that the substance filling up pittings often shows a weak acid action, because of the great solubility of acids and salts in water, which tends to eliminate them in a large measure from the products of corrosion which were impregnated with them.

Examples of Corrosions with Notes.

The experiences of Desgeans of the Compagnie de l'Est, recorded in the *Revue des Chemins de Fer*, which we are about to note, still further support our view.

We may note the important rôle which water plays in the corrosive action provoked by chemical reaction.

The interior corrosions in boilers of iron or steel may be classed under two headings :—

1. Corrosions arising from exclusively chemical action.
2. Corrosions and leakages, due to mechanical action, aided by chemical action.

INTERNAL CORROSIONS IN BOILERS OF CAST-IRON AND STEEL.

I. Corrosion Due Solely to Chemical Action.

Mileage of boiler : 835,212 kilometres.

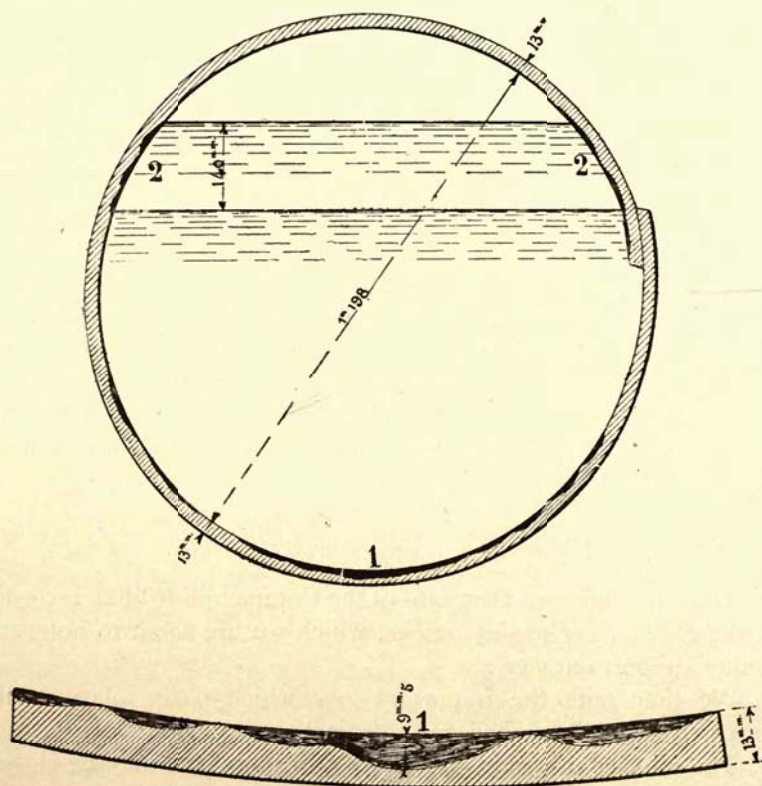


FIG. 32.

1. *Faults.*—On the underside of the cylinder, over a width of from 30 to 60 cubic metres, all over the plate. Beyond this zone, only isolated corrsions of no importance.

Causes.—Action of the water or substances contained dissolved in it.

Consequences.—Weakening of the plates, usually to an unimportant extent, but sometimes necessitating the lining or replacement of the affected parts.

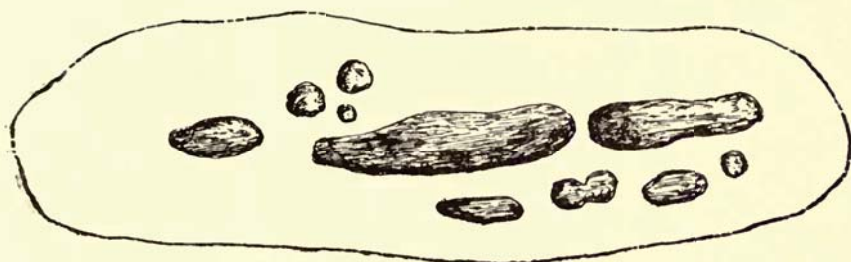


FIG. 33.

2. *Faults*.—In some rarer cases, the corrosions extend to the highest level reached by the water in the boiler. In this case, the corrosions are worse between the highest and the lowest level of the water than in the parts always immersed. In short, there is always a zone exempt, between the lower corrosions of 1 and those of 2.

Causes.—Action of the water or of substances dissolved in it.

Consequences.—Unimportant weakening of the plates.

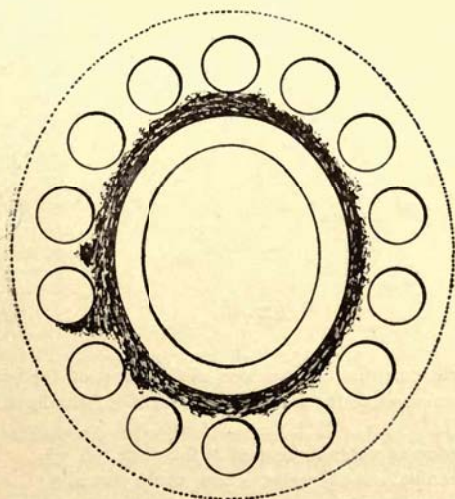


FIG. 34.

3. *Faults*.—At the blow-out holes, whether under boiler or fire-box, there are corrosions.

Causes.—Slight cracks may be produced at these points, giving vent to the air on cooling, and consequent oxidation of the metal.

The friction of tools may also cause wear at these points, which are at the lowest part of the boiler and consequently at the part most liable to corrosion.

Consequences.—Slight corrosions, weakening the metal and necessitating patches.

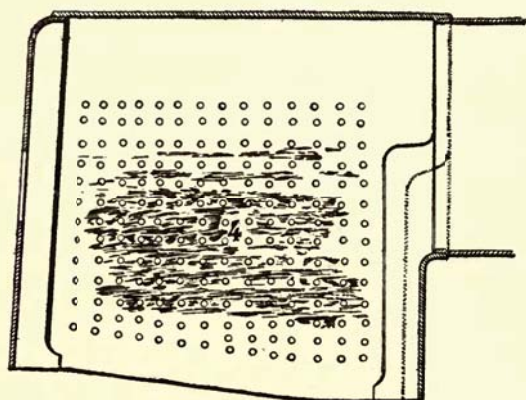


FIG. 35.

4. *Faults*.—On the sides of the fire-box, corrosion of great extent but usually shallow.

Causes.—Chemical action of the water.

Consequences.—Weakening of the sides, usually unimportant.

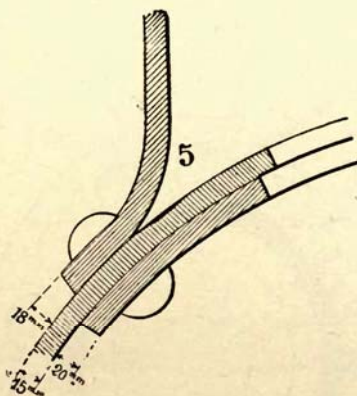


FIG. 36.

5. *Faults*.—Very slight corrosion at the base of the dome, on the barrel of the boiler. Of exceptional occurrence with the Compagnie de l'Est, who have used domes only since 1878.

Causes.—Chemical action of water condensed at the place.

Consequences.—Weakening, usually unimportant, of the plates.

II. Corrosions and Fissures Due to Mechanical Action and Accentuated by Chemical Action.

Mileage of boiler: 301,920 kilometres.

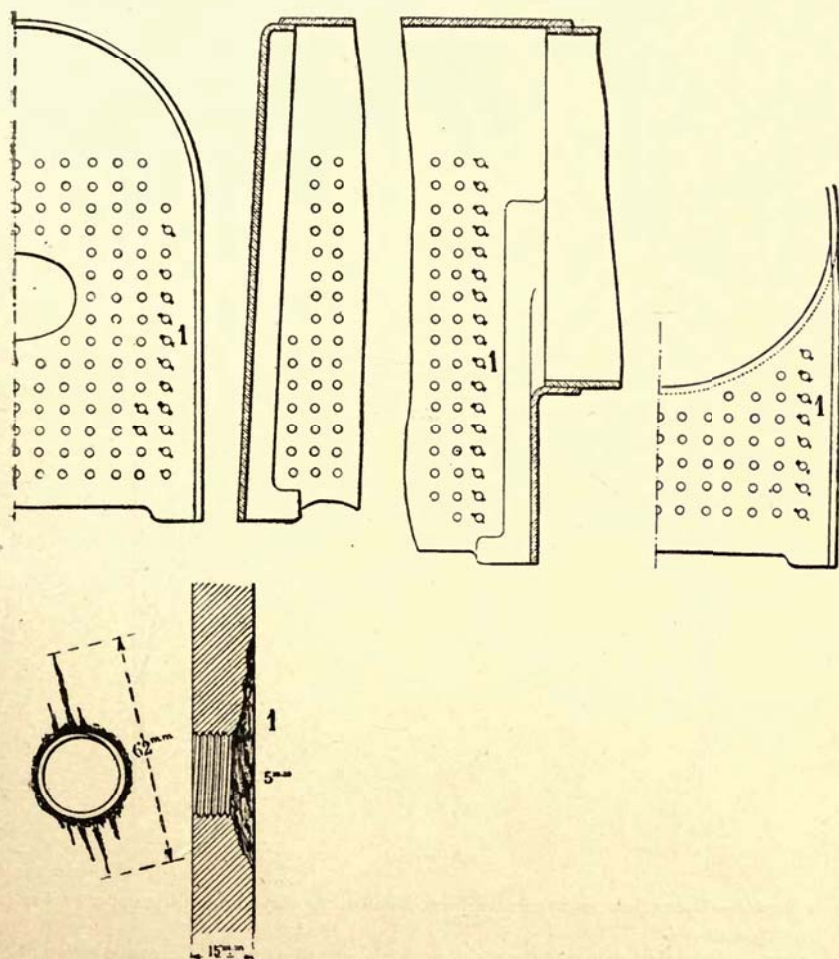


FIG. 37.

1. *Faults.*—In the stayed part of the fire-box, and generally in the last vertical rows of stay-bolts, and on the plates AV and AR¹ of the fire-box, and sometimes on the sides and the front of it.

Causes.—Mechanical action of the stays during displacement of the fire-box with relation to the grate. Corrosive action of water.

Consequences.—Production of a crack which may involve the renewal of the sides of the fire-box or the application of patches.

¹ AV in front, AR at the back.

Mileage of boiler: 411,390 kilometres.

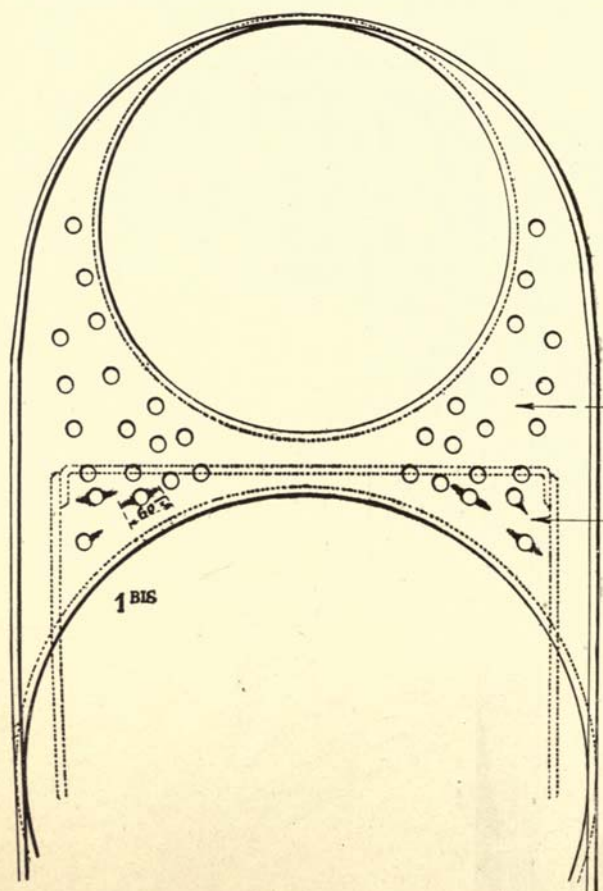


FIG. 38.

1. *Faults*.—These fissures have also been found at the stay-bolts of the upper part of the plate AV.

Causes.—Mechanical action of the stays as in the preceding case. Corrosive action of water.

Consequences.—Patching.

Mileage of boiler : 562,430 kilometres.

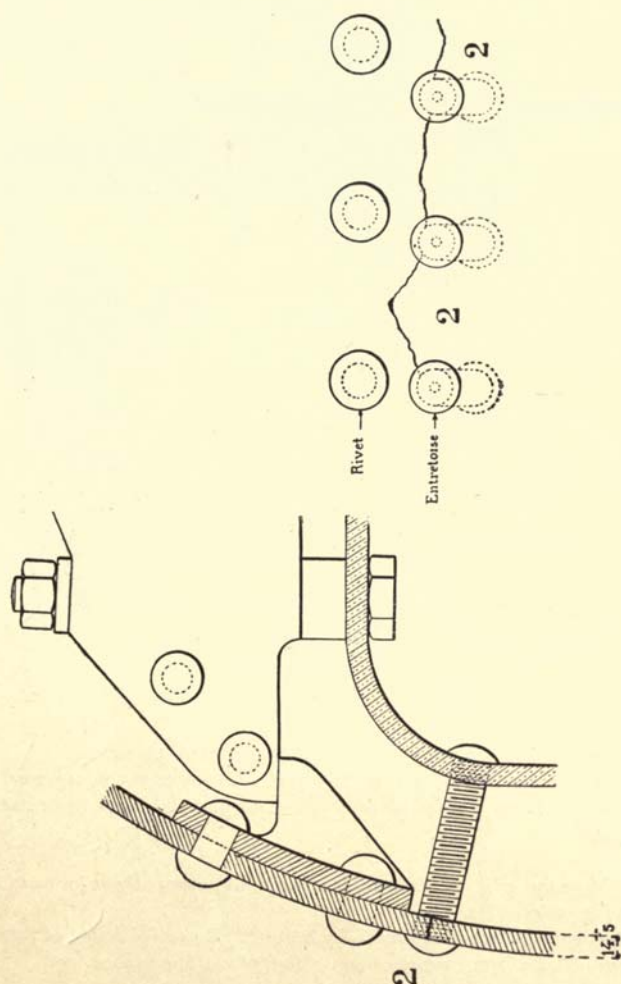


FIG. 39.

2. *Faults*.—M. Desgeans has also found fractures in plates at the upper horizontal row of the side-stays. In some very special cases the grate was provided with transverse ribs resting on brackets.

Causes.—Pressure of the ribs on the brackets, tending to make the part of the plate carrying the bracket swing round the first line of stay-bolts, themselves already under the strain of the steam pressure.

Consequences.—Formation of a crack necessitating patching or new plates altogether.

Boiler-mileage: 396,723 kilometres.

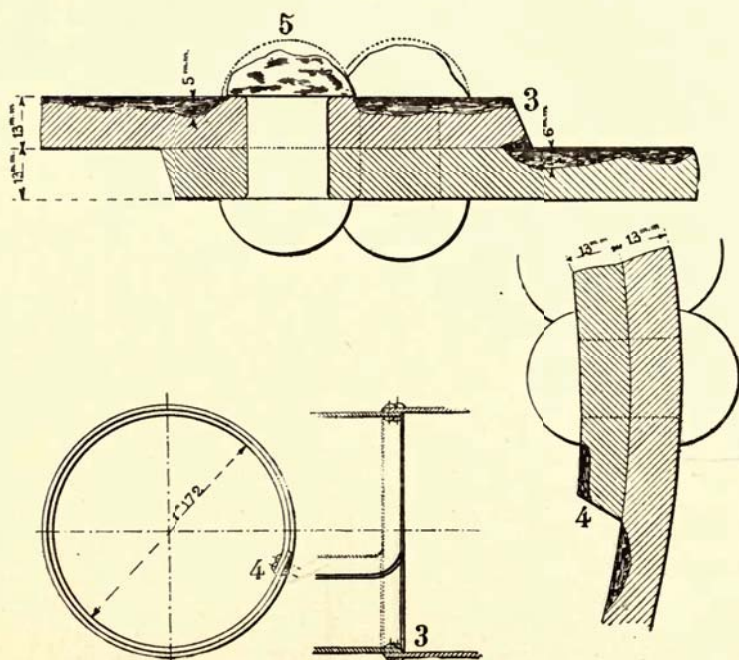


FIG. 40.

3. *Faults.*—At opposite points on the sides of the barrel of the boiler.
Causes.—Mechanical action of expansion by heat. Corrosive action of water.
Consequences.—Weakening of the places affected, so that they have to be strengthened or replaced.
4. *Faults.*—More rarely at the ends of the barrel and especially at joints in the lower part of the boiler.
Causes.—Mechanical effect of expansion by heating. Corrosive action of water.
Consequences.—These rarer corrosions are seldom of any importance.
5. *Faults.*—These corrosions not unfrequently reach the tube-ferrule rivets.
Causes.—Mechanical action of expansion by heat. Corrosive action of water.
Consequences.—Replacement of corroded rivets.

Boiler-mileage: 339,549 kilometres.

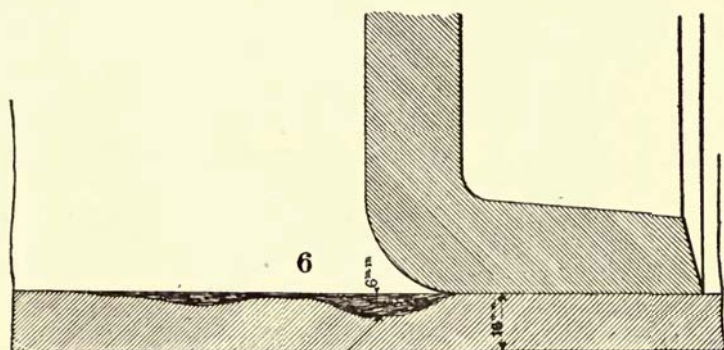


FIG. 41.

(Diameter of barrel, 150 cubic metres. Tube-plate of the smoke-box.)

6. *Faults.*—Corrosions in the lower part of the barrel near the tube-plate of the smoke-box.
Causes.—Corrosive action of water, and very probably mechanical action exerted by the tube-plate on account of the thrust of the tubes.

Consequences.—Weakness, necessitating patching or replacement of the ferrules of the smoke-box.

Boiler-mileage: 1,089,466 kilometres.

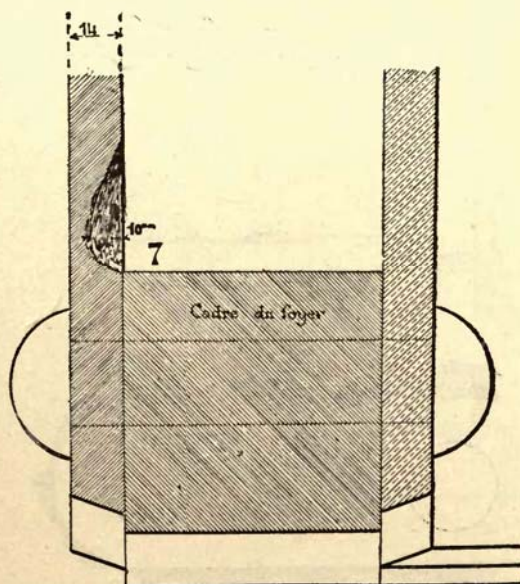


FIG. 42.

7. *Faults.*—At the upper edge of the frame of the fire-box.

Causes.—Bending, first one way then the other, all round the frame, due to heat and pressure, and also to the thrust of the grate. Chemical action of water.

Consequences.—Weakening of the walls, necessitating lining, applied to the plates to prevent the corrosion extending. In certain cases, the lower parts of the plates have to be replaced by angle-irons.

Boiler-mileage: 249,657 kilometres.

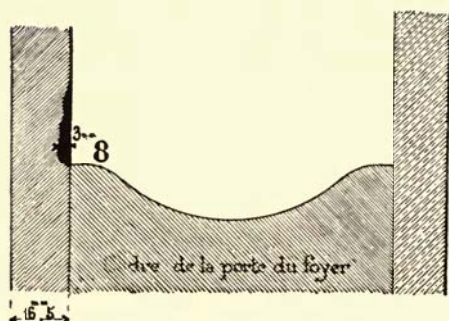


FIG. 43.

8. *Faults*.—At the edge of the frame of the fire-door. These corruptions are rare.
Causes.—Bending to and fro all round the fire-box, due to heat and pressure and the thrust of the grate. Chemical action of water.
Consequences.—Weakness of the walls, necessitating patching, or more rarely a new setting for the fire-door.

Boiler-mileage: 410,499 kilometres.

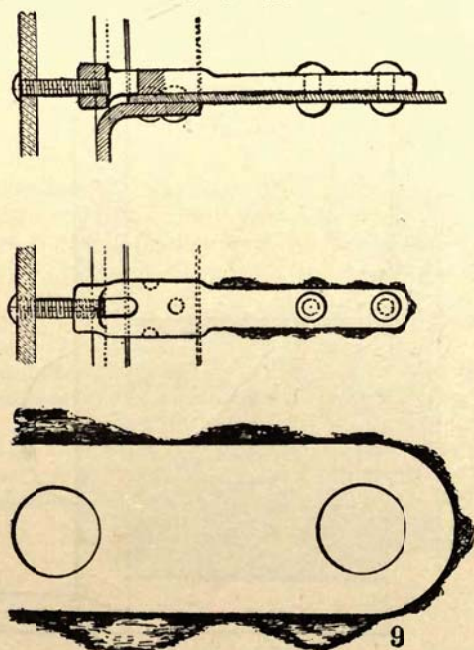


FIG. 44.

9. *Faults*.—In the middle of the plate round the stays of the tube-plate of the fire-box.
Causes.—Fatigue of the plate from the tension of the stays when the tubes expand. Chemical action of the water, chiefly at the lower part of the barrel.
Consequences.—Weakening of the plates, necessitating either their replacement or the use of special stiffening stays.

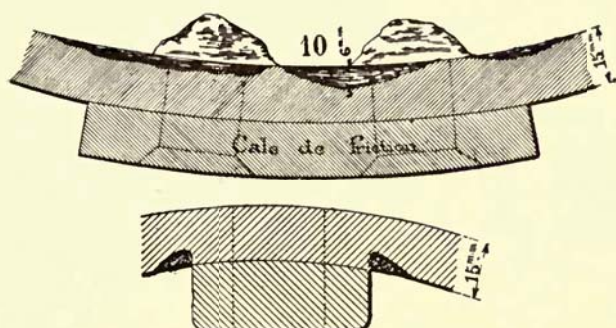


FIG. 45.

10. *Faults*.—Above the boiler-supports at the expansion block. Sometimes corrosions occur here even when the rest of the barrel is free from them, and are worse than those at other places when other parts are attacked.

Causes.—Tension due to the inertia, the friction of the boiler on its supports, and to shaking of the frame of the engine. Chemical action of water.

Consequences.—Weakening of the plates, necessitating the application of a lining.

Boiler-mileage: 339,549 kilometres.

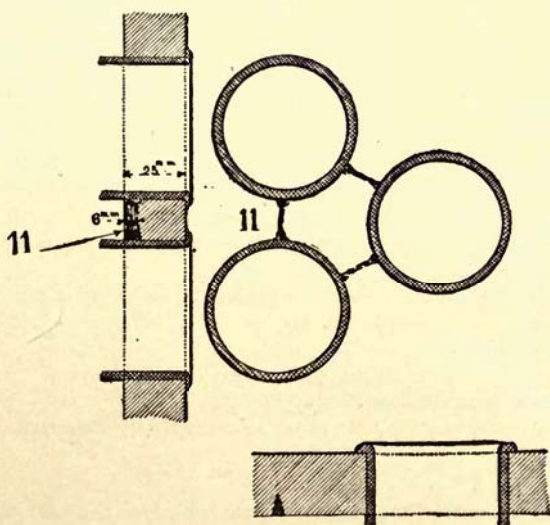


FIG. 46.

11. *Faults*.—Internal fractures in the tube-plate of the smoke-box.

Causes.—Expansion and contraction due to the thrust of the tubes. Chemical action of the water.

Consequences.—Fractures of the plates, necessitating the application of small 8-shaped pieces in the intervals, or of plugs filled with elastic rings, or even replacement of the plates.

Boiler-mileage: 593,773 kilometres.

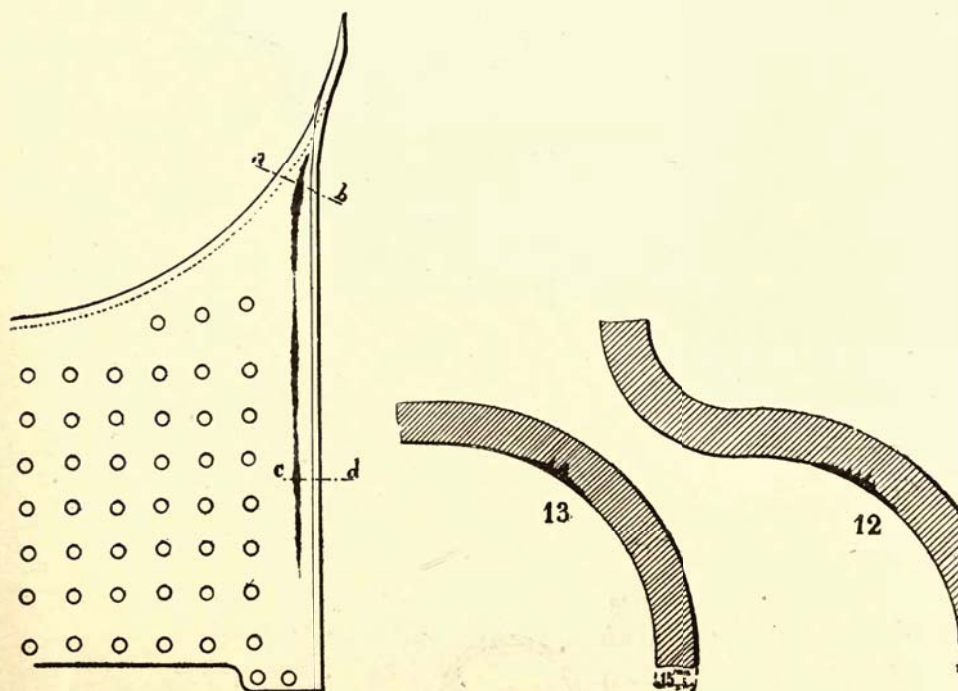


FIG. 47.

12. *Faults*.—At the upper part of the front plates of the fire-box, in the bend.

Causes.—Bendings, expansions and contractions resulting from the internal strain of expansion tendencies to deformation under the action of pressure where the curved and flat surfaces meet.

Fatigue of the plate from the difficulty the boiler has in expanding, and the thrust of the barrel against the fire-box, which is always fixed rather rigidly between its supports.

Fatigue of the plate caused by the original shaping process.

Chemical action of water.

Consequences.—Weakening of these parts, necessitating reinforcement or replacement of the plates.

13. *Faults*.—In the vertical angles of the plates, in the front and back of the fire-box.

Causes.—Mechanical action of the steam pressure and the thrust caused by expansion of the grate.

Fatigue of the plate due to the shaping of the plate.

Chemical action of water.

Consequences.—Weakening of these places, necessitating the reinforcement or replacing of the plates.

Boiler-mileage : 763,825 kilometres.

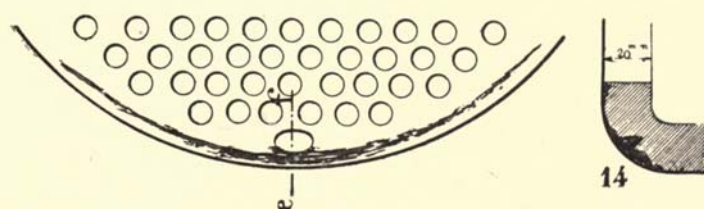


FIG. 48.

14. *Faults.*—Round the edge of the tube-plate of the smoke-box.

Causes.—Bending from the internal pressure and the thrust of the tubes.

Fatigue of the plate due to the shaping.

Chemical action of water on the lower part.

Consequences.—Fracture of the plates, and cracks communicating with the outside, necessitating the use of strengthening pieces, usually chamrel-iron or the replacement of the part of the plate that carries the tubes.

Boiler-mileage : 761,859 kilometres.

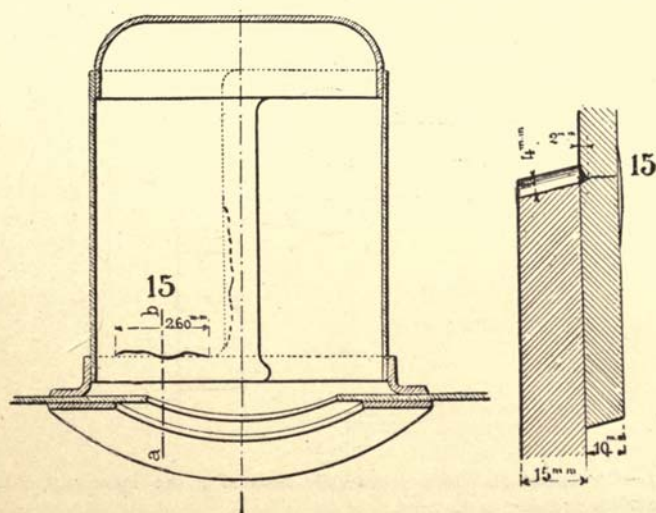


FIG. 49.

15. *Faults.*—Transverse fissures at the base of the dome.

Causes.—Exclusively mechanical, arising from caulking cracks in the riveted part too hard.

Consequences.—Replacement of the ferrule of the dome.

*A. Copper Fire-boxes.**Corrosions and fissures on the water side.*

Boiler-mileage: 471,551 kilometres.

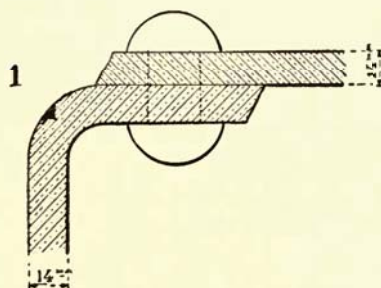


FIG. 50.

1. *Faults*.—Corrosions and fissures, usually localised in the upper part of the back plate of the box, and in the bend.

Causes.—Bending to and fro caused by alternate expansion and contraction of the plate, and by the pressure on the crown of the fire-box.

Consequences.—Weakening of the walls, necessitating the application of stiffening pieces or the replacement of the plates.

Boiler-mileage: 108,369 kilometres.

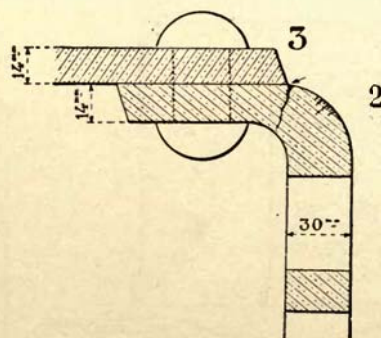


FIG. 51.

2. *Faults*.—Corrosions and fissures generally situated at the upper part of the tube-plate of the fire-box, in the bend.

Causes.—Bending to and fro under the action of expansion, the pressure on the crown of the fire-box, and the expansion of the tubes.

Consequences.—Weakening of the walls, necessitating the application of stiffening pieces with the replacement of the plates.

3. *Faults*.—Corrosions and fissures generally localised where the tube-plate of the fire-box meets the crown.

Causes.—Bending to and fro, due to expansion, the thrust of the tubes, and the pressure on the crown.

Consequences.—Weakening of the walls, necessitating the application of different pieces, or the replacement of the plates.

Boiler-mileage: 471,551 kilometres.

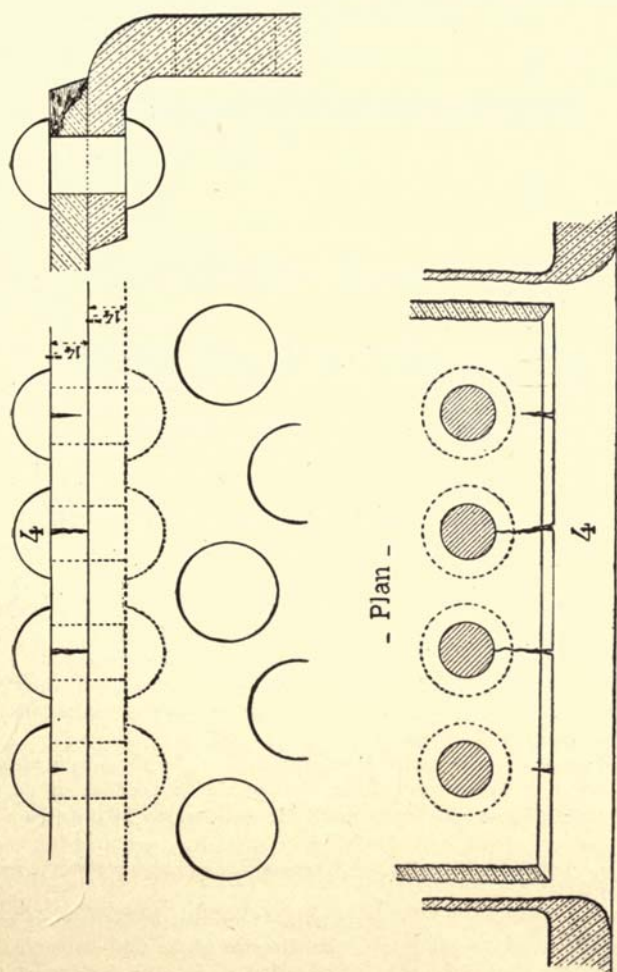


FIG. 52.

4. *Faults*.—Corrosions and fissures generally confined to the crown, and following lines connecting the rivet-rows to the edges of the plate. Especially common near the tube-plate.

Causes.—Bending to and fro under the pressure on the crown, and under the thrust of the tubes.

Consequences.—Lining the crown with a perforated plate with wide edges or applying ordinary stiffeners, or putting in a new crown.

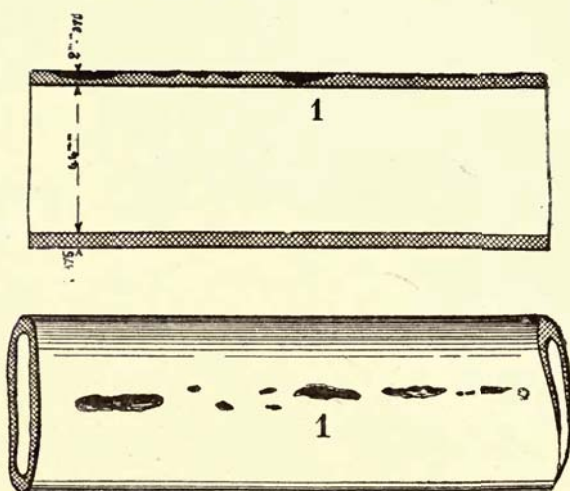
B. Tubes of Iron or Mild Steel.

FIG. 53.

1. *Faults.*—On the tubes the corruptions are often localised on the upper heating surface and sometimes on the lower, but rarely occur on the sides.

Causes.—Chemical action of water, which acts on tubes as well as on plates.

The importance of the corruptions appears to be increased when the tubes were originally not perfectly smooth inside and so presenting depressions eminently favourable to the production of corrosion.

The metal loses its nature in consequence of the abnormally high temperature to which it is subjected on account of the bad conducting power of the incrustation. Mechanical action due to bending caused by the expansion of the tubes.

Consequences.—Local cracks in the tubes, necessitating plugging with the replacement of the tube.

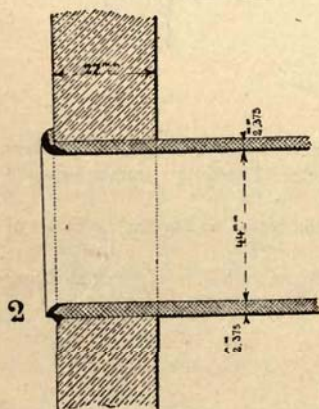


FIG. 54.

2. *Faults.*—Corrosion of the riveting of the tubes on fire side of the tube-plate. This form of corrosion occurs with both steel and brass tubes.

Causes.—Action of water coming from leaks produced in various ways, such as the thrust of the tubes, defective riveting, or the action of the hot gases and the dust they carry with them.

In these three cases there is faster wear, due to the exclusive employment of coke.

Consequences.—Weakening of the tube, necessitating replacement of the ferrule or of the whole tube.

NOTE.—The use of tubes of iron or mild steel by the Compagnie de l'Est is becoming more and more general.

We thus see how energetic is the action of the waters on the iron and steel of boilers. The red copper parts of the furnace bathed by the water are only feebly attacked.

In the case of copper, the pittings are not so deep as in the case of iron. It is rare to find corrosions in the red copper part of the furnace on the water side. In all cases they are principally of mechanical origin, and generally are simply gaps between the plates.

Corrosive Substances in Solution in the Water.

An eminently corrosive water need not necessarily show an acid reaction to begin with.

The salts in solution in the water, in addition to a direct corrosive action, which they may have on iron, are often transformed, under the influence of the temperature and pressure, into other bodies capable of attacking the metal very energetically.

The experiments of Cornut, and of Scheurer-Kestner and Meunier-Dolfus in collaboration, have shown that the corrosion of iron is due to the appropriation of the oxygen of the water by the iron, the reaction being aided by the presence of carbonic acid, and the experiments of Petit have shown that carbonate of lime in water will attack iron even in a cold solution.

As a matter of fact, if we put porphyrised iron filings into a cold solution of carbonate of lime neutral to phenol phtaleine, we note that a certain quantity of neutral carbonate of lime is soon precipitated and that the iron at the same time enters in solution, this reaction continuing as long as the iron is kept in solution.

Water containing only carbonic acid and nothing else quickly attacks iron. The iron enters into solution and hydrogen is given off. Thus carbonate of the protoxide of iron is obtained in solution, and on exposure to the air this turns turbid and deposits the hydrate of the sesquioxide of iron. The action of the iron on the bicarbonate of lime and on the dissolved carbonic acid, will explain the way in which iron tanks and pipes are attacked and also the rationale of the process by which the sugar boiler purifies his waters and syrups with iron filings.

Finally, the corrosive action of organisms in the sea water must not be forgotten. As a matter of fact sea water is capable of very energetic action, as it contains ammoniacal, nitrous and nitric ferments. These are found in the largest quantities in the water nearest the shore and especially in that contaminated with sewage.

The corrosion of metals by secretions of bacterian origin has been clearly proved in Germany by a microscopical examination of

type after use. This corrosive action could be transferred to new type, and it was found that it stopped at once on sterilisation in the stove, thus proving indisputably that the attack on the metal was made by micro-organisms.

We give the results of some interesting experiments made by F. Baucher, principal pharmacist to the navy, on the effect upon iron of different waters.

The results shown in the following table were obtained by experimenting with well-cleaned and polished blades of iron of the same composition, each weighing 18 grammes, and steeped for eight days in each of the specified liquids.

		Milligrammes,		Total.
		Peroxide of iron in suspension.	Oxide of iron in solution.	
Distilled water	19	0	19
" "	fresh boiled	10	0	10
" "	sterilised	12	0	12
" "	boiled, then saturated with oxygen	21	3	24
" "	boiled, then saturated with carbonic acid	7	9	16
Rain water	19	0	19
Town water (Divette)	17	0	17
Sea water from the basin of the Mâtire (Cherbourg)	16½	19½	36
Above water boiled	3½	0	3½
" "	" then saturated with oxygen	10	6	16
" "	with seaweed	31	6	37
Harbour water	27	2	29

The attack on the iron usually commences in a few minutes, showing greenish traces, which peroxidise later on. When once the attack has commenced, the corrosive action proceeds regularly, aided by the electro-chemical phenomena set up between the oxides formed and the iron.

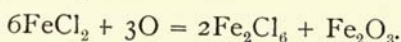
(a) Corrosions Caused by Acid Waters.

Let us now examine the action on iron of the salts most frequently met with in waters, and we will suppose, to begin with, that the feed water has been acidulated with the acids of the salts. This occurs because natural waters are frequently acid when they have been collected before the neutralising effect of the carbonates in the soil has had time to operate.

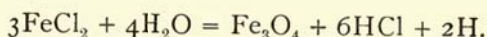
Hydrochloric Acid.—Water acidulated with hydrochloric acid attacks iron energetically, producing soluble ferrous chloride and freeing the hydrogen:—



This ferrous chloride is rapidly oxidised, and is transformed into ferric chloride depositing ferric oxide :—

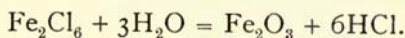


In presence of steam, and at the high temperature in the boiler, there may be still another reaction, in which hydrochloric acid is produced :—



According to these three reactions an intermediate oxide, Fe_3O_4 , and two ferric salts, Fe_2O_3 and Fe_2Cl_6 , are obtained.

The steam decomposes the ferric chloride itself into hydrochloric acid, which is regenerated :—

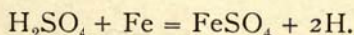


The attack on the boiler-plates thus results in the continuous production of oxides of iron, and the regeneration of the hydrochloric acid. A cycle of corrosion is thus set up, and hydrochloric acid is produced.

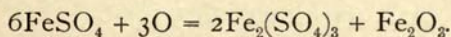
We will examine later the reaction caused by the chlorides formed.

Sulphuric Acid.—A water containing sulphuric acid in solution gives analogous reaction to that of a water acidulated with hydrochloric acid.

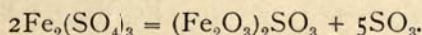
To begin with the iron is attacked, ferrous sulphate is formed, and hydrogen is given off :—



In the boilers, however, this ferrous sulphate oxidises, forming normal ferric sulphate, which remains in solution, and ferric oxide which is precipitated :—



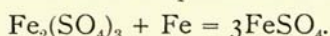
The ferric sulphate obtained is decomposed by the steam and the high temperature, basic ferric sulphate is precipitated, and sulphuric acid set free :—



This regenerated sulphuric acid attacks the iron anew, and in an oxidising medium forms ferric sulphate, and the cycle of reactions which we have just described recommences.

Another body, the precipitated basic ferric sulphate, can also be reduced in the same way as any other ferric salt. The consequence of this reduction, which is at the expense of the iron of the boiler-plates, is the formation of a corresponding ferrous salt.

In the case of normal ferric sulphate we obtain :—

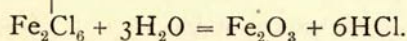
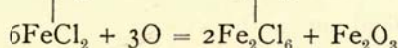
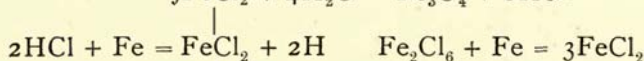
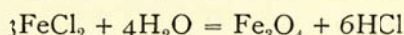


In boilers fed with water acidulated with sulphuric acid, in addition to ferrous sulphate in solution and ferric oxide, a deposit of basic ferric sulphate may be found, if this has not been completely reduced by the iron of the boiler-plates.

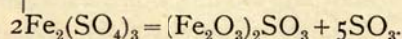
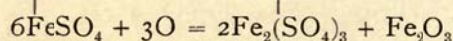
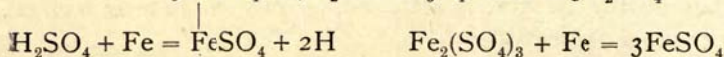
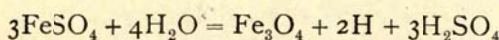
Nitric Acid.—In the case of a feed water acidulated with nitric acid, analogous reactions to those furnished by hydrochloric acid and sulphuric acid are obtained.

Formulæ of Acid Attacks on Iron.—From the foregoing we can draw up concise formulæ showing the nature of the reactions in the corrosion of iron with the acids of the salts most frequently met with in waters :—

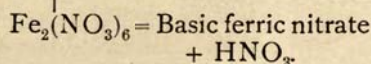
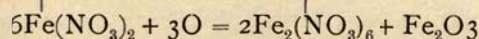
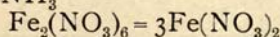
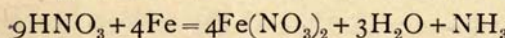
1. With water acidulated with hydrochloric acid :—



2. With water acidulated with sulphuric acid :—



3. With water acidulated with nitric acid :—



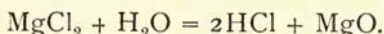
(b) Corrosions Caused by Water Containing Salts.

In considering the attack on iron by acidulated water, we showed that certain salts, such as the ferric sulphates and chlorides, were eminently corrosive. These salts, under an appearance of inertia, may attack the boiler-plates either directly or indirectly, in reaction with other salts.

We will now consider the corrosive action of the different salts, commencing with the chlorides.

Chlorides.—Ferric chloride is not the only salt which may exercise a corrosive influence on boilers. The instability of chloride of magnesium makes it also harmful in this respect. We have already noted the easy manner in which this salt is decomposed at relatively low temperatures, in writing of the solubility of salts in water.

Its decomposition takes place according to the following reaction :—



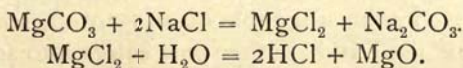
The hydrochloric acid thus freed commences the cycle of corrosive reactions which we have just previously noted. Ferrous and ferric chloride are formed, and the decomposition of the latter sets up a cyclic reaction.

Chloride of magnesium is itself very corrosive, and another salt, sulphate of magnesium, which alone may be considered as harmless to the boiler-plate, becomes extremely corrosive if the water holds chlorides in solution.

If we represent the chlorides by the formula ECl , E representing a monatomic element, we obtain the reaction :—

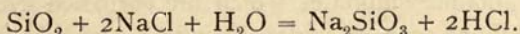


It will be seen that a corresponding sulphate is formed and that the hydrochloric acid is set at liberty, and of course the cycle of reactions which we have just noted commences. Carbonate of magnesium with the chlorides may also lead to the formation of chloride of magnesium, the corrosive effect of which is known :—



Although chloride of calcium is more stable, the steam and the high temperature may decompose it in the presence of other salts, and corrosive substances may be formed.

Chloride of sodium has an extremely corrosive action on iron in the presence of steam and silica :—



The hydrochloric acid thus formed then attacks the iron in the cycle of reactions we have already described.

In waters containing organic matters chloride of ammonium may be met with. This is an instable salt and may have a corrosive effect :—

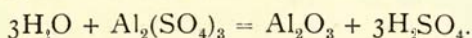


Hydrochloric acid is formed, which reacts on the iron to give

ferrous chloride, which is then subjected to the secondary reactions already studied.

Sulphates.—We have seen, in considering the action of water acidulated with sulphuric acid, that ferric sulphate is a corrosive body, and we have indicated the reactions which result from its presence.

Another salt, sulphate of aluminium, gives absolutely analogous reactions, and like sulphate of iron must be looked upon as corrosive. Under the influence of heat, oxide of aluminium is precipitated, and sulphuric acid set at liberty, and in addition a precipitate of basic sulphate of aluminium is thrown down :—



Thus the iron is corroded by the sulphuric acid.

As for sulphate of copper, which is sometimes met with in solution in the feed water, it deposits metallic copper on the boiler-plates, and the sulphuric acid set free attacks the iron :—



The ferrous sulphate thus obtained is subjected to the reactions which we have studied, and is transformed into a highly corrosive body. It is an interesting fact noted by Petit, that iron is attacked by water containing alkaline sulphate even in a cold solution.

If a solution of sulphate of potassium with water free from air and carbonic acid be made, it will be found that such a solution containing 0.091 gr. of sulphate of potassium per litre in contact for eleven days, at a temperature of 12° C., with 100 gr. of porphyrised iron, has oxidised 7½ gr. of iron.

If the water contains a notable quantity of carbonic acid a part of the iron is oxidised and another part enters into solution.

Thus 100 gr. of porphyrised iron, treated under the same conditions in a similar solution but containing carbonic acid, dissolves nearly 15 per cent. of the iron and nearly 8 per cent. is oxidised.

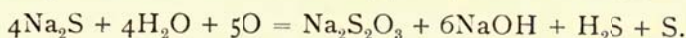
The attack on the iron is therefore considerably more severe, the solution becomes alkaline, and the residue contains sulphide of iron. The alkaline sulphates, which are corrosive even in a cold solution, are much more so under the influence of heat in the boilers. The corrosive action of the alkaline sulphate is increased in the presence of carbonic acid, but this applies to salts in general.

Sulphides.—Sulphides and sulphites are both met with in water, and the acids of these salts set up reactions in the presence of other salts and under the physical conditions in the boiler.

Ph. de Clermont and J. Frommel in collaboration have noted that the hydrates of sulphides are decomposed by heat, and that

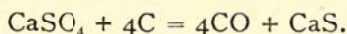
the sulphides which do not give off sulphuretted hydrogen on boiling in water are those which are not transformed into hydrates under the same conditions.

The sulphides of the alkalies and of the alkaline earths are salts which are easily split up into the oxide of the metal and sulphuretted hydrogen, and the subsequent oxidation of the sulphuretted hydrogen brings about the formation of hyposulphite of sodium :—



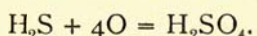
Sulphuretted hydrogen is often met with in waters which have to begin with contained sulphates in the presence of organic matters.

If water containing sulphates and organic matters is fed into the steam boiler the high temperature aids the reducing action of the organic matter on the sulphates, which are transformed into the corresponding sulphides :—



We have detected the presence of sulphides in the products of boiler corrosion.

Sulphuretted hydrogen arising from the decomposition of the sulphides may be oxidised and transformed into sulphuric acid :—



The formation of this sulphuric acid necessarily brings about the cycle of corrosive reactions already studied.

The direct attack on the iron by the sulphuretted hydrogen takes place as follows :—



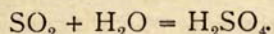
The sulphide of iron thus formed is easily decomposed. It is changed into the hydrate of sulphide which gives sulphuretted hydrogen :—



According to the experiments of Ph. de Clermont sulphide of iron in the presence of water in a vacuum gives off sulphuretted hydrogen at 50° C.

Sulphites.—We have now to examine the corrosive action of sulphurous acid.

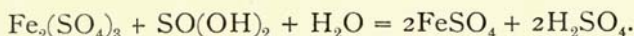
Sulphurous acid may be oxidised by the steam in the boiler :—



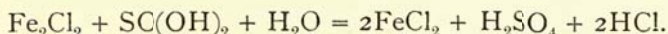
Thus sulphuric acid is formed, with the results we have already described.

We have also to take into consideration the fact that the ferric

salts, sulphates and chlorides, may be reduced by the sulphurous acid into ferrous salts, and the acid thus set at liberty :—



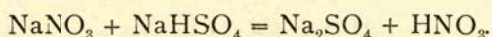
The case in the formula supposes that ferric sulphate has been reduced, with the production of sulphuric acid. With ferric chloride of course the acid produced would be hydrochloric in addition to the sulphuric acid :—



On examining these two reactions it will be seen that the corrosive effect is increased, and that the bodies formed in the second halves of the two equations are acids and ferrous salts, chlorides and sulphates, which are rapidly transformed into corrosive ferric salts.

Nitrates.—In describing the corrosive action of water acidulated with nitric acid, we remarked that ferric nitrate was a corrosive salt, and that in reaction with other bodies its nitric acid was set at liberty. The nitric acid of nitrates may be set at liberty in the presence of an acid salt, or of a water rendered acid by the decomposition of salts.

Thus with acid sulphate of sodium we obtain :—



The nitric acid thus set at liberty attacks the iron, a reaction which has already been studied, and if the water contains both chlorides and nitrates in solution the corrosive action of the two salts combined becomes particularly dangerous, as *aqua regia* is very quickly formed in the boilers.

We have had practical proof of this, and in the products arising from energetic corrosion of iron, we have been able to prove the association of chlorides and nitrates by testing with the salts of silver and sulphate of diphenylamine. The presence of nitrates in water, moreover, is by no means uncommon, and they are often forgotten in inquiring into the cause of corrosion. On the borders of streams and in all water contaminated with sewage, there is a considerable quantity of micro-organisms, ammoniacal, nitrous and nitric ferments capable of forming nitrates.

Table of the Reactions Producing Acids.—As we have already seen, by analysing a water we can foresee its corrosive effect by considering the nature of the salts which it contains, and a quantitative analysis will warn us as to the activity of this corrosive action.

The following tables show the reactions by which hydrochloric, sulphuric and nitric acids may be formed in the boilers.

a. Formation of Hydrochloric Acid.

Chloride of magnesium and steam	$\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgO} + 2\text{HCl}.$
Sulphate of magnesium and alkaline chlorides	$\text{MgSO}_4 + \text{H}_2\text{O} + 2\text{NaCl} = \text{Na}_2\text{SO}_4 + \text{MgO} + 2\text{HCl}.$
Silica and alkaline chlorides	$\text{SiO}_2 + 2\text{NaCl} + \text{H}_2\text{O} = \text{Na}_2\text{SiO}_3 + 2\text{HCl}.$
Ferric chloride	$\text{Fe}_2\text{Cl}_6 + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{HCl}.$
Ferrous chloride	$3\text{FeCl}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2 + 6\text{HCl}.$
Carbonate of magnesium and chlorides	$\text{MgCO}_3 + 2\text{NaCl} + \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + \text{MgO} + 2\text{HCl}.$
Chloride of ammonium	$\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}.$

b. Formation of Sulphuric Acid.

Normal ferric sulphate	$2\text{Fe}_2(\text{SO}_4)_3 = (\text{Fe}_2\text{O}_3)_2\text{SO}_2 + 5\text{SO}_3.$
Ferrous sulphate	$3\text{FeSO}_4 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 2\text{H}_2 + 2\text{H}_2\text{SO}_4$
Sulphurous acid, sulphite	$\text{SO}_2 + \text{H}_2\text{O} + \text{O} = \text{H}_2\text{SO}_4.$
Sulphurous acid and ferric sulphate	$\text{H}_2\text{SO}_3 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4.$
Sulphurous acid and ferric chloride	$\text{SO}_2 + \text{Fe}_2\text{Cl}_6 + 2\text{H}_2\text{O} = 2\text{FeCl}_2 + 2\text{HCl} + \text{H}_2\text{SO}_4.$
Sulphuretted hydrogen, sulphides	$\text{H}_2\text{S} + 4\text{O} = \text{H}_2\text{SO}_4.$
Sulphate of calcium and organic matters	$2\text{CaSO}_4 + \text{C} + 3\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{CO} + 2\text{H}_2\text{SO}_4.$
Sulphate of aluminium	$\text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{SO}_4.$
Sulphate of ammonium	$(\text{NH}_4)_2\text{SO}_4 = 2\text{NH}_3 + \text{H}_2\text{SO}_4.$
Sulphate of copper	$\text{CuSO}_4 + \text{Fe} = \text{FeSO}_4 + \text{Cu}.$

c. Formation of Nitric Acid.

Normal ferric nitrate	$\text{Fe}_2(\text{NO}_3)_6 = \text{Ferric nitrate} + \text{HNO}_3.$
Alkaline nitrate and acid sulphate or sulphuric acid	$\text{NaNO}_3 + \text{NaHSO}_4 = \text{Na}_2\text{SO}_4 + \text{HNO}_3.$
Nitrate of ammonium	$\text{NH}_4\text{NO}_3 = \text{NH}_3 + \text{HNO}_3.$

Treatment of Sea Water and Deep Well Water.

The analytical examination of sea water and deep well water shows us that in their constitution they have many points in common.

In sea water as in deep well water the proportion of matters in solution is very high. Without stopping to consider the composition of these waters, which we have already had occasion to examine in a preceding chapter, we must note that in deep well water and sea water there are certain salts particularly corrosive and capable of forming scale.

These are :—

Sulphate of calcium.	Chloride of sodium.
Sulphate of magnesium.	Chloride of magnesium.
	Chloride of calcium.
	Chloride of potassium.

It may be said, therefore, that the two waters are very much alike in their action. As a matter of fact the most dangerous scale-forming salt, sulphate of calcium, is met with in as large proportion in sea water as in deep well water.

The other salts in solution in the water assist it to a greater or less extent, but it is this salt which is the most dangerous from the point of view of scale. Other salts, amongst which are the chlorides, and especially chloride of magnesium, are common to both waters, and are corrosive.

Sulphate of magnesium also found in both waters is rendered corrosive by the reaction of other salts.

The salts, scale forming and corrosive, may thus be put in two groups, the sulphates and the chlorides, and the treatment of sea water and deep well water should be arranged with a view to the neutralisation of these acids.

Sea Water in the Boiler.—When sea water is evaporated there is a rapid deposit of saline matters, with which the water is of course very heavily charged. Sea salt is the principal one, and this forms large obstructive masses at the bottom of the boiler which speedily interfere with the regular production of steam.

The inconvenience of this is felt particularly in the case of multitubular boilers, as, for instance, those of torpedo boats. To begin with, there is a large waste of fuel caused by the bad conductivity of the saline mass, and the obstruction grows until the engine stops for lack of steam.

In addition to chloride of sodium, other salts are deposited in smaller and larger proportion, and these contribute to the bad effects of the salt either by precipitating or decomposing.

The sea salt is always accompanied by sulphate of calcium, the most pernicious of scale formers, and by unstable salts such as chloride of magnesium, the easy decomposition of which leads to corrosion. The remedy on board ship is very simple in theory. All that is needed is a sufficient store of soft water, that is to say water containing neither carbonate nor sulphate, and to use this alone for the boilers.

In this way the feed water will be neither corrosive nor encrusting, and to get over the difficulty of storing so great a quantity of water on board ship condensed steam is used.

Surface condensers are now found on all ships, but for all that the stock of drinking water must be resorted to at times or sea water used for the boilers.

The precautions to be taken in this latter case and the methods which have been invented to make the use of sea water practicable

are interesting. The first precaution to take is to prevent the deposition of the sea salt, and this can be done by taking into consideration its co-efficient of solubility, and ascertaining the degree of concentration of the sea water under the influence of heat in the boiler.

As soon as a degree of concentration is reached neighbouring the co-efficient of solubility at the existing temperature, the concentrated water is run off and a fresh supply of sea water is introduced. It is therefore useful to know at what degree of concentration the sea-salt deposits commence to form.

To ascertain this, a sort of hydrometer known as a saturometer is used. This differs only from the ordinary instrument in the manner in which it is marked. The 0 mark on the stem is the point to which the hydrometer will sink in distilled water, and the number 10 is that which will be level with the surface of the liquid in a solution containing 350 grammes of sea salt in 1,000 cubic centimetres of water.

It is estimated that the temperature of water from the condensation of steam is 95° C., and the graduations of the saturometer are made at this temperature and the interval between the 0 and the 10 is divided into equal parts, so that 1° read on the instrument shows an increase of 35 one-thousandths in the concentration of the sea water.

Consequently if n° is read on the hydrometer in making a test, the concentration of the water in the boiler is $n \times 0.035$.

We therefore obtain the following table of concentration.

Saturometer degree.	Concentration.	Saturometer degree.	Concentration.
1	0.035	6	0.210
2	0.070	7	0.245
3	0.105	8	0.280
4	0.140	9	0.315
5	0.175	10	0.350

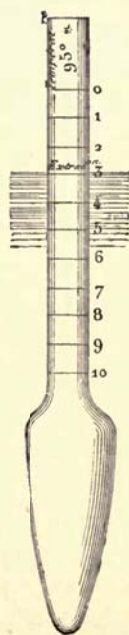


FIG. 55.—Saturometer.

In order to learn the degree of concentration of the water in the boiler at any moment, the little apparatus illustrated in fig. 56 is used. A is the boiler, and a tap B is arranged to run the water into a funnel C containing a test flask S in which the saturometer can be easily plunged and the degree read off.

Formulæ.—Supposing that we have found δ in taking the saturometer reading, this number therefore corresponds to $0.035 \times \delta$ and is given by the table.

If π is the weight of the water in the boiler and x the total weight of salts in this water, we obtain the general formula:—

$$x = 0.035 \times \delta \pi.$$

It is evident that this formula allows us to take any letter as the unknown quantity, and to make calculations according to the unknown quantity sought for. Having ascertained the degree of concentration of the water, we can tell when the saline deposits will be produced.

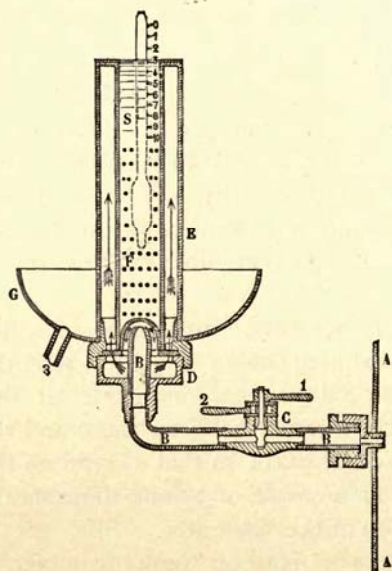


FIG. 56.—Apparatus for taking the saturometer degree of sea water.

These deposits commence when the concentration of the water in the boiler at a given temperature corresponds to the co-efficient of solubility of chloride of sodium at this temperature. In a saline solution the concentration of a liquid in relation to the salt which it contains is the ratio of the weight of the completely dissolved salts to the total weight of the solution.

Representing by σ the co-efficient of solubility of sea salt at a temperature of t in the boiler and by x' the degree of concentration of the saline solution at this temperature, we obtain:—

$$\frac{\sigma}{1000 + \sigma} = x'.$$

We learn, therefore, what will be the conditions of the formation of the deposit by this formula.

To simplify the calculation, we will take it for granted that the temperature is 95° C., and replace in the preceding equation the letters by their value, and taking the co-efficient of solubility of sea salt at 95° C. as 0.392, the equation will then become :—

$$x' = \frac{392}{1392} = 0.281$$

Application of the Formulæ.—We will now seek in the table already prepared for the saturometer degree which corresponds with this concentration number, 0.281.

We note that it corresponds with 7.8 on the stem of the saturometer. Thus, therefore, when the saturometer marks 7.8 in water at 95° C. from the boiler, deposits of sea salt will form.

The degree read on the saturometer, however, is never exact, as of course salts other than chloride of sodium are in solution in the sea water. This is taken into account in the navy, and a very wide limit is allowed. The saturometer degree is not allowed to exceed 3.

As soon as the reading of the saturometer shows this degree, the water is run off by a tap specially provided for this purpose. This is at the bottom of the boiler, and a tube penetrates into the interior to extract the water laden with salts, the expulsion of which is facilitated by the interior pressure.

Another Formula.—To change the water periodically and sufficiently frequently, the ratio to be established between the weight to extract and that of the steam generated between two runnings-off is ascertained.

Haton de la Goupillière has invented a very neat formula to effect this calculation.

We will represent by P the total weight of water in the boiler at the time when operations are commenced. Let p be the weight evaporised between two runnings-off, and π the weight extracted each time.

Finally represent by S the degree of saturation at the moment the boiler is cleared out, and σ that of the ocean.

The operation is thus conducted before removing π . To begin with, half is restored, that is to say $\frac{\pi}{2}$ of natural sea water, and the total contents of the boiler then becomes :—

$$P + \frac{\pi}{2}.$$

We then extract the weight π .

In the boiler there remains $P - \frac{\pi}{2}$, that is to say the quantity of salt equal to $\left(P - \frac{\pi}{2}\right) S$.

After this, the rest of the fresh supply of water, that is to say $\frac{\pi}{2}$, is introduced, which brings with it its degree of saturation $\frac{\pi}{2} \sigma$.

Until the next running-off steam is produced, and a weight p of distilled water is evaporated.

But this weight of evaporated water is replaced by the normal feed of a weight p of sea water which brings into the boiler a quantity of salt equal to $p\sigma$.

By what has preceded, the necessary calculation can be made.

By representing by Σ the limit of saturation which must not be passed, we obtain the total $P\Sigma$:—

$$P\Sigma = \left(P - \frac{\pi}{2}\right) S + (p + \pi)\sigma.$$

In the following extraction we add to begin with a weight $\frac{\pi}{2}$ of sea water, which brings with it a weight $\frac{\pi}{2}\sigma$ of saline matters.

If we allow for this fact in the preceding equation, we obtain :—

$$\left(P - \frac{\pi}{2}\right) S + (p + \pi)\sigma.$$

This is the weight of salt which is at this moment contained in the quantity of water P . We now deduct the value of the degree S of saturation at the moment of running-off :—

$$S = \frac{\left(P - \frac{\pi}{2}\right) S + (p + \pi)\sigma}{P + \frac{\pi}{2}}.$$

Hence :—

$$S = \frac{p + \pi}{\pi} \sigma.$$

Bringing this value of S into the equation, we obtain :—

$$P\Sigma = \left(P - \frac{\pi}{2}\right) \frac{p + \pi}{\pi} \sigma + \left(p + \frac{\pi}{2}\right) \sigma.$$

Hence :—

$$\frac{P\Sigma}{\sigma} = P \left(1 + \frac{p}{\pi}\right) + \frac{p}{2}.$$

And finally :—

$$\frac{p}{\pi} = \frac{\Sigma - \sigma}{\sigma} - \frac{1}{2} \frac{p}{P}.$$

We have thus the value that we sought for, that is to say the value that must be given to the weight π of water drawn off in terms of the degree of saturation Σ which must not be exceeded, and the contents of the boiler, represented by P , the total weight of water in the boiler.

We note, moreover, that during two consecutive runnings-off a weight p of water has been vaporised.

Suppose the feed continued; p and π annul each other, but their ratio verges towards the limit :—

$$\frac{p}{\pi} = \frac{\Sigma - \sigma}{\sigma}.$$

If we concentrate to ten times the degree of concentration of water in the sea, we obtain:—

$$\Sigma = 10\sigma,$$

and consequently :—

$$\frac{\pi}{p} = 0.11.$$

Therefore, 110 grammes of sea water should be run off per kilogramme of steam produced. It is necessary to examine also the question of the sulphate of calcium contained in the sea water.

Influence of the Substances Remaining in the Water.—To begin with, this practice must be condemned, as it leaves a harmful layer of sulphate of calcium in the marine boilers, produced in large quantities in the very attempt to avoid the deposit of sea salt.

All the troubles which we have already described arise from this, and the interference with the production of steam is sufficient to make us reject this system.

Sea water always contains sulphate of calcium, and unhappily the deposit is made quickly and unavoidably, and with the constant recharging of the boilers the water may be not particularly strong in sulphates and yet produce scale out of all proportion. The process, therefore, can only lead to a particularly harmful layer of scale being formed and the proper working of the boiler must inevitably and speedily be interfered with. The system as we have seen avoids in a great measure the deposition of sea salt, but at about 140° C. the sulphate of calcium is deposited, producing incrustations, the bulk of these growing with each fresh supply of feed water.

The mass of sulphate of calcium thus formed may lead to a stoppage of the engine, and it is important to avoid it.

As for the corrosive salt, such as chloride of magnesium, this salt is decomposed in spite of the system we have described. It

attacks the boiler-plates as we have already seen. We have had occasion to examine three samples of deposits in marine boilers, and analysis gave us the following results:—

	No. 1.	No. 2.	No. 3.
Sulphate of calcium	71.20	64.09	77.85
Magnesium salts (as MgO)	7.15	8.25	4.37
Sulphate of sodium	2.97	4.86	3.98
Chloride of sodium	0.31	0.67	0.56
Ferric oxide	17.05	18.93	10.63
Organic matters	0.93	2.89	2.11
Loss	0.39	0.31	0.50
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The second sample contained a notable proportion of organic matters which showed the presence of nitrates in the deposit. As a matter of fact, it was easy to prove that nitric acid was present by testing with sulphate of diphenylamine.

As regards the iron arising from corrosive action, we note that the second sample showed the heaviest proportion of oxide of iron, and this corresponds to the largest proportion of salts of magnesium in the three samples. In the third sample, the magnesium compounds are in the smallest proportion, and it will be seen that the product resulting from corrosive action on the boiler-plates, ferric oxide, is also in the smallest proportion.

Each of the three samples contained as will be seen a notable proportion of the sulphate of calcium, which shows the danger of this salt when marine boilers are fed with sea water and the system described is adopted.

Another method therefore of avoiding the deposit of chloride of sodium must be adopted.

Prevention of the Encrusting and Corrosive Action of Sea Water and Deep Well Water.

Two sorts of troubles have therefore to be avoided in using sea water and deep well water, encrustation and corrosion.

We have seen that these actions, although quite different, owe their origin to salts which may be classed in two groups according to the acid they contain. These two salts are chlorides and sulphates, and a remedy must be sought for the evil effects they produce.

To counteract the effects of encrusto-corrosive waters, deep well water, sea water, and almost all waters capable of a corrosive action, as at the same time they are certain to be capable of forming scale, a remedy must be applied which will not only prevent

the formation of scale, but will also neutralise the corrosive action. This must be done without introducing substances into the water which will increase one of these effects in diminishing or suppressing the other.

We shall see that very few suggested remedies fulfil these conditions.

Zinc.—Zinc is a remedy for the corrosive action of waters, but it does not completely prevent the formation of scale.

When zinc is introduced into boilers, the corrosive action of the water is directed to this metal, and thus the iron is not attacked.

This fact was noted in 1881 in some steam boilers belonging to B. Normand. It was noted that in one of the boilers which had brass stays there was no corrosion, but that the zinc in this alloy had completely disappeared, leaving the copper bare.

According to Lesueur, when two metals of opposite nature are placed in a conducting medium, an electric current is set up which flows from the most attacked metal to the least attacked, and splits up the water into its elements, the oxygen acting on the zinc and oxidising it, and the hydrogen being set at liberty from the positive pole represented by the iron. In this electro-chemical couple the iron is polarised. The hydrogen thus shields it from oxidation.

The hydrogen is said to be an obstacle in the formation of scale, but this preservative action does not last very long, and the scale forms sooner or later.

In the navy a kilogramme of zinc for large boilers and 400 grammes for those of torpedo boats are introduced per square metre of heated surface. Care must be taken to remove the layer of zinc oxide formed from time to time, as this coating protects the zinc from attack, and thus prevents the formation of the electric current. When plates of zinc are used they are suspended in the boiler by wires of a conductive metal.

Electrogenes.—Zinc globes are also used in Hannay's electro-gene. The sphere of zinc is traversed by a bar of copper, which is in communication by conductive wires with the boiler-plates, and the apparatus is suspended from the top of the boiler.

In deep well water, as in sea water, the zinc acts by forming an electric current, set up by their acidity, and this is shown by the fact that hydrochloric or sulphuric acid is set at liberty. The latter is met with in particular in boilers fed with deep well water.

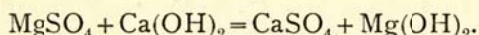
Baker's electrogene is an apparatus the object of which is to collect the electricity given off by the steam by means of properly arranged metallic points.

A hydro-electric machine is thus obtained. The metallic points

are arranged in the form of a star, and communicate with the boiler by a copper wire. The steam produces electricity, which runs from the star into the wire conductor, and by this into the boiler. The solid particles in suspension are charged with electricity as soon as they touch the boiler-plates, and are repulsed at once, so that they are not able to form scale.

Lime.—A favourite method in the navy to prevent corrosion is to make the water slightly basic with lime.

In feeding multitubular boilers, soft water is used, to which one kilogramme of lime is added per cubic metre of water. This certainly prevents or diminishes the corrosive action, but it increases the encrusting power of the water. If the lime is introduced in sufficient quantity, it will neutralise all the acid action, and also precipitate the metallic oxides and the oxide of magnesium :—



By the decomposition of chloride of magnesium, hydrochloric acid is formed, which reacting on the lime gives chloride of calcium, a much more stable body than chloride of magnesium, but still capable of corrosive action.

The sulphates contained in the sea water or deep well water give sulphate of calcium, which lends its assistance to that already in the water, thus increasing the encrusting action.

In deep well water the proportion of sulphates is often very high, and this greatly increases the encrusting capacity of the water.

To prevent scale-forming deposits in boilers fed with deep well waters, De Sénarmont adds clay in a state of fine suspension to the lime. It is evident that it is advantageous to purify the water before it is fed into the boilers. In the case of sea water, Stapfer suggests the use of lime in excess, which precipitates all the magnesia.

The excess of lime in solution in the water is then got rid of by bubbling carbonic-acid gas through the water. The gas is obtained from the furnace by means of Koerting's injector.

Chloride of sodium, and sulphate and chloride of calcium, remain in the water. The sulphate of calcium can be eliminated with carbonate of sodium.

As for filtration, it can be done quickly in a turbine with filtering cloths and abestos when carbonate of sodium is used.

Carbonate of Calcium.—The use of carbonate of calcium has been suggested by Lechatelier, professor at the School of Mines, who has shown in an exhaustive treatise the value of this inexpensive remedy in dealing with deep well waters.

By introducing carbonate of calcium into boilers fed with deep well water the sulphates of the peroxide of iron and of alumina are decomposed, and their oxides of iron and aluminium are precipitated. The sulphuric acid is then saturated, and sulphate of calcium is formed.

As for the sulphate of magnesium contained in the water, it is not decomposed as with lime.

When carbonate of calcium is used, the quantity of sulphate of calcium primitively contained in the deep well water is not diminished, but the mechanical action of the chalk seems to interfere with the crystallisation of the sulphate of calcium.

Caustic Soda and Potash.—The caustic alkalis are very efficacious preventatives of corrosion, but it must not be forgotten that they are expensive products.

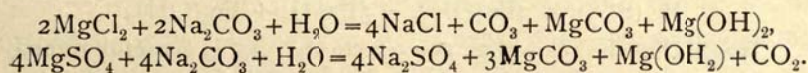
In multitubular boilers caustic soda is often used instead of lime. In the case of deep well waters, caustic soda is also used. The ferric salts are precipitated, but the sulphate of aluminium remains in solution, as it redissolves in an excess of the reagent.

Soda acts on the chloride of magnesium, precipitating the oxide of magnesium and neutralising the hydrochloric acid.

On sulphate of calcium it has hardly any action, but nevertheless if the water contains also carbonate of calcium, carbonate of sodium is formed, and this precipitates the sulphate of calcium.

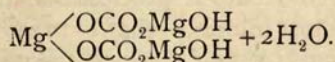
Carbonate of Sodium.—Carbonate of sodium is a first-class remedy for encrusto-corrosive waters. It acts both on the scale-forming qualities and the corrosive influence of sea water and deep well water. Certain facts have to be taken into consideration in using it, in order to make the remedy efficacious.

On the very corrosive salts of magnesium, its action is as follows :—



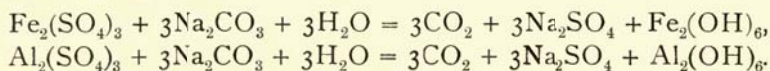
If this precipitation takes place in a cold bath, it is incomplete, even with an excess of carbonate of soda; carbonic acid is given off, and bicarbonate of magnesium is formed which remains in solution.

If, however, the bath is hot as in boilers, the precipitation is complete, as in the following formula :—



In the case of deep well waters, the corrosive principles of which are chiefly the sulphates of iron and of aluminium, the metallic

oxides are precipitated by the carbonate of soda, and sulphate of soda is formed :—

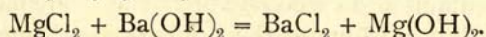


It will be noted that the corrosive actions of sea water and deep well water are avoided by the use of carbonate of soda, and as for the encrusting effect, it will be seen that this salt acts energetically by precipitating the sulphate of calcium in the state of carbonate of calcium. In marine boilers, lime, caustic soda and zinc are much employed, but carbonate of soda, which is a very efficacious and economical remedy, is neglected, and this is a mistake.

Caustic Baryta.—Caustic baryta is also an admirable remedy in the case of encrusto-corrosive waters, sea water and deep well water.

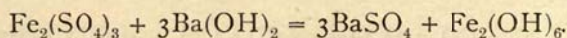
It acts not only on the encrustation but also on the corrosive action. As regards the encrustation, we have already examined its effect, and we have seen that it transforms the sulphate of calcium into sulphate of barium, which does not adhere to the boiler-plates.

On these corrosive bodies, it also acts energetically; thus in reaction with chloride of magnesium at boiling-point oxide of magnesium is rapidly precipitated :—



The chloride of barium thus obtained precipitates the sulphate of calcium in its turn.

On the sulphates of iron and of aluminium, contained in large proportions in deep well water, it reacts with the formation and precipitation of the corresponding metallic oxide, and the sulphuric acid is saturated by the caustic baryta and forms sulphate of barium :—



It will thus be seen that the caustic baryta is a useful remedy against scale and corrosive action. It is therefore a much better thing to use than lime, which instead of preventing encrustation increases it. Lime may therefore be advantageously replaced by caustic baryta in the treatment of encrusto-corrosive waters.

Carbonate of Barium.—Carbonate of barium is a by-product of sugar refinery, and may be advantageously used with deep well waters. Even in a cold bath it precipitates the metallic oxides of the salts which are most injurious, that is to say sulphate of iron and sulphate of aluminium. When, however, the water contains chloride of magnesium, carbonate of barium does not act upon it as an anti-corrosive.

Alkaline Borates and Silicates.—We have examined the influence of several salts on encrusto-corrosive waters.

By using borax, that is to say tetra-borate of sodium, $\text{Na}_2\text{Bo}_4\text{O}_7$, the salts of iron and of aluminium in deep well waters are precipitated even in the cold bath, and the calcic compounds are also thrown down as borate of calcium CaBo_4O_7 .

The acids of the salts precipitated by the borax are saturated by the alkaline metal, and form corresponding salts. As for the salts of magnesium, borax does not precipitate them in a cold solution, but under the influence of heat forms a white precipitate with them of normal borate or ortho-borate of magnesium $\text{Mg}_3(\text{BoO}_3)_2$. Unfortunately borax is a costly remedy, although the precipitates may be treated for the recovery of the boric acid.

Silicate of potassium gives good results with encrusto-corrosive waters. The salts of calcium are precipitated by its action in the form of white gelatinous bodies insoluble in water, $\text{CaO}_3\text{SiO}_2 + \text{H}_2\text{O}$.

The salts of magnesium are also precipitated in the form of a white gelatinous product $\text{MgH}_4(\text{SiO}_3)_3$ with silicate of sodium.

The salts of iron and of aluminium give precipitates of the corresponding silicates. The alkaline silicates, therefore, are good remedies in dealing with encrusto-corrosive waters.

Greasy Water.

Water Contaminated with Vegetable and Animal Grease.—Hardly was the use of surface condensers adopted on board ship when all the naval powers awoke to the fact that far from giving the results that had been expected of them, corrosions became more frequent than before they were used. Inquiries were at once set on foot to determine the reason of these corrosions. In the boilers greasy deposits containing a large quantity of iron, and adhering tenaciously to the boiler-plates, were found.

The plates, no longer being wet, overheated, and loosening of rivets and leaks occurred. Several explanations were suggested, but that which seemed the most rational was that the trouble arose from the decomposition of saponifiable oils.

The greases used in lubricating the working parts of the engine are decomposed by the high temperature.

This decomposition takes place just in the way that a fat is decomposed by soap- or candle-makers to extract the glycerine from it, and in consequence the glycerine is set at liberty and dissolves in the water, and the fatty acids are formed.

The fatty acids are led away by the steam with any part of the oil which is not completely decomposed, and on reaching the boiler attack the plates very rapidly. The parts of the boiler where the plates are most under the influence of heat and where the water is agitated least are especially attacked.

The chief engineer of the French navy, Ortolan, reports that analyses of the products of corrosion have been made at the United States arsenal at Brooklyn. They show the presence of oleate of copper and of zinc.

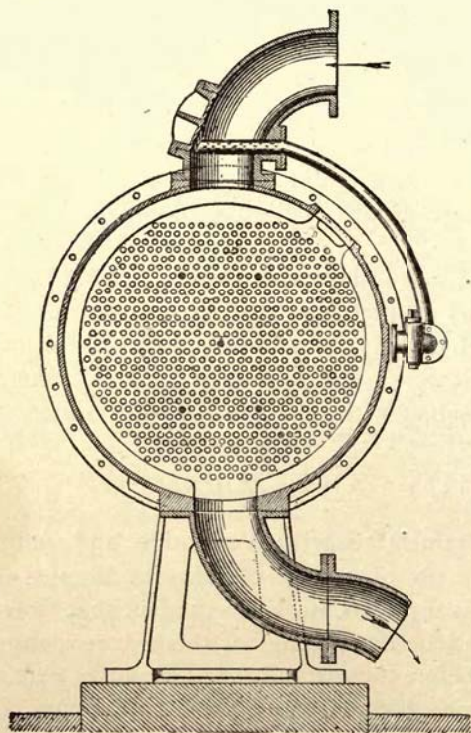


FIG. 57.—Surface condenser (transverse section).

The chief chemist at the Brooklyn arsenal concludes from this that the copper is first attacked by the fatty acids and that the oleate of copper is then decomposed by the iron of the boiler-plates.

Nevertheless it is not necessary that copper should be present, the iron may be attacked in any case, and if copper is found in analysing products of the corrosion of the iron it is noted also that it is not in proportion to the large quantity of oxide of iron formed or to the proportion of fatty acids found in the boiler.

Analyses made by Mercier of the greasy deposit in the slide box showed the following result :—

Peroxide of iron	91'55
Oleic acid	5'60
Unchanged oil	2'60
Loss	'25
	<hr/> 100'00

He exposed for a week in a steam chest working a beetling machine a bucket filled with scraps of iron impregnated with neutralised colza oil. At the end of this time he took out half a litre of a very thick brown oil, having a garlic-like odour similar to

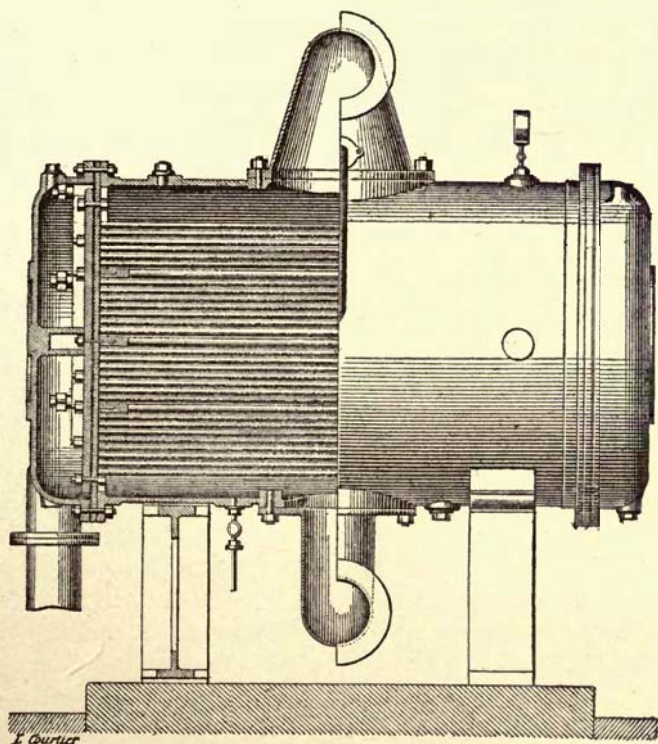


FIG. 58.—Surface condenser (longitudinal section).

that which is noted when iron is acted upon by an acid. This oil was completely soluble in ether, and contained 7 per cent. of iron. The iron had been attacked by the oleic acid produced by the decomposition of the oil, and oleate of iron had been formed.

In contact with the air, this oleate of iron was oxidised, with the formation of peroxide of iron, and the oleic acid thus freed attacked the iron anew. The energy of the attack on the iron is in proportion to the temperature and pressure in the boiler.

The wear caused by greasy deposits is very rapid, and many marine boilers have been most seriously damaged through this cause.

We may note as an instance the boilers of the *Richelieu*, which were stoked for the first time on 26th April, 1875. They had had 2,880 hours of active service when a ministerial despatch of 30th January, 1880, ordered them to be repaired. The plates were then found to be hardly more than 4 to 5 millimetres in thickness, and in one of them was found a hole covered over with rust.

According to the report of Dupont, the engineer, 2,860 kilogrammes of matter composed of a mixture of oxide of iron and salt were taken out of the boiler. On consulting the log-book, it was found that the quantities of salt extracted each year had been :—

	Kilogrammes.
1876	1,786
1877	240
1878	1,828
1879	8,808
1880	28,680

The figures in the last line of course include the amount of salt taken out of the boiler during the repairs at Toulon.

All the deposits found in the different parts of the boiler were mixed and gave on analysis :—

Sesquioxide of iron	79'000
Fatty bodies	8'000
Sulphuric acid	2'103
Lime	2'016
Potash and soda	1'600
Carbonic acid	1'584
Water	1'400
Oxide of zinc	1'934
Chlorine	0'895
Magnesia	0'610
Oxide of copper	0'532
Loss	0'326
	<hr/> 100'000

Several remedies have been proposed to avoid the absolutely disastrous effect of greasy water and Hétet suggests the employment of lime. The oleic acid combines with lime to form oleate of calcium in an excessively fine and spongy powder. This powder is easily kept in suspension by the currents in the water or floats on the surface, and deposits when the fire is drawn in the form of a non-adherent sand. Theoretically one-eighth of a part of slaked lime is needed for one part of a fatty body, but in practice this proportion is doubled.

When distilled water is to be used for drinking purposes it is first filtered through animal charcoal. When caustic soda is used

in the treatment of greasy water, soluble alkaline soaps are formed, which are worked up in the boiler ; moreover it is a costly remedy.

Apparatus is also used in purifying these waters. These depend upon the use of lime followed by filtering, and that of Selden, which has been largely used in America, will be described in a later chapter.

It may be added that the soap formed either in softening with lime or by the combination of the fatty acids with the calcic salts, is troublesome in the boiler. This lime soap is very light and is not moistened by the water, as it is surrounded by a thin envelope of unchanged oil.

Mineral Oils in the Water.—For some years mineral oils have been used in the lubrication of many machines. The heavy mineral oils in particular are constantly used as lubricants. In spite of the fact that the carbides of hydrogen, that is to say the series of mineral oils, do not undergo analogous transformations to those of the vegetable and animal oils, nevertheless when they get into the boilers they form troublesome greasy deposits.

When the boiler is emptied, the oil mixes with the oxide of iron and forms a scale on the boiler-plates preventing the proper transmission of heat and becoming an element of danger. Steam is produced with difficulty, and the bad conductivity of the scale leads to the overheating of the plates.

Although mineral oil does not produce corrosions, it must nevertheless be prevented from entering the boilers for these reasons.

Many methods have been used, and one of them, suggested by Normand, consists in using a sponge filter. This is now the universally adopted method. Before the water passes into the boiler it goes through a box containing a series of sponges. It is forced in by a pump at the top end of this filter, and admitted into the boiler at the lower end.

At certain intervals the sponges are taken out, pressed and cleaned, and put back into the filter.

To avoid these greasy deposits, another method employed is to run off the surface water in the boilers by means of a tap, properly placed on the boiler. In this way not only the oil but all the matters floating on the water can be run off when the tap is turned.

Greasy deposits are also avoided by reducing the lubrication of the engine to a minimum. When the steam is wet, the engine is not lubricated at all, or merely a few drops of oil are used.

Separation of Oil from Steam.—The oil led away by the steam may be separated out by escape pipes.

In G. Hoppenstedt's apparatus the steam is let into a funnel-

like box and passes over a helical arrangement, on the blades of which it leaves its water of condensation and greasy matter.

The steam continues its course and escapes by a pipe at the upper part of the apparatus. As for the water of condensation and

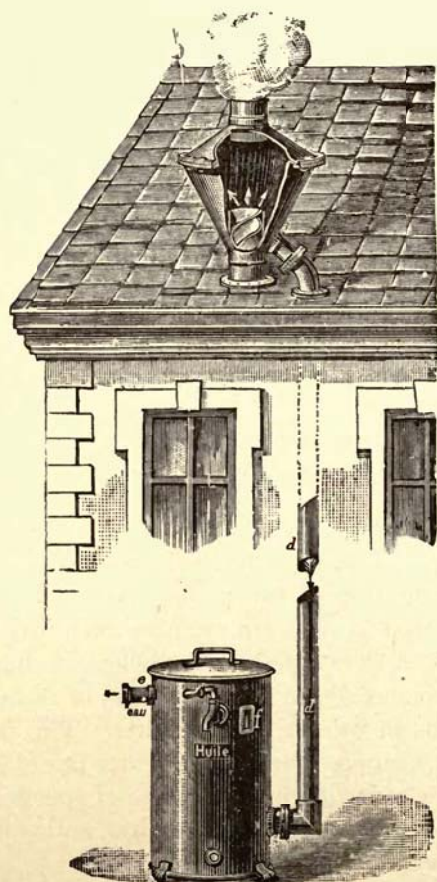


FIG. 59.—Separation of water and steam by escape pipes, and apparatus to recover greasy matter on G. Hoppenstedt's system.

the fatty matter, they run into a reservoir down a lateral tube, and in this vessel the oil is separated from the water by means of taps, and may be used anew.

L. G. Dehne & Hall also make an apparatus for the same purpose.

CHAPTER V.

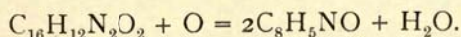
WATER IN DYE-WORKS, PRINT-WORKS AND BLEACH-WORKS.

MANY accidents in dye-works, print-works and bleach-works have their origin in the water employed. Even the temperature of the water is of great importance, and nevertheless is frequently neglected. The dyer should always use water at the same temperature, in order always to work under the same conditions.

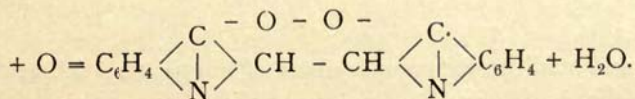
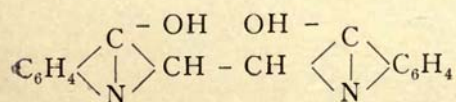
If, for instance, the water used for rinsing is cold, as in winter, the soap is dissolved with difficulty, the work is defective, and the rinsed stuffs have a clammy feel. In the winter, therefore, the rinsing water should be made lukewarm.

If, on the other hand, the water is too hot, the colours may run and bleed on to the whites, especially if the rinsing is carried on too long. On the other hand, the thickenings used in printing pastes are more easily dissolved in hot water. The water used, however, should be at a temperature of less than 30° C.

Some colouring matters are oxidised when the water employed contains air. In the case of indigo white, for instance, it is transformed into insoluble indigo blue by oxidation, as shown by the reaction :—



Or as a constitutional formula :—



Waters which contain organic matters may bring about the putrefaction of the extracts used, and prevent them from keeping. It is therefore advisable to filter water before it is used in making an extract for dyeing or printing.

A water may make a good dye-bath with one colouring matter,

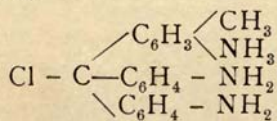
and a very bad one with another. Nevertheless, as a general rule in dye-works, as pure a water as possible should always be used. The colouring matters seem to be the more soluble in water, as they are richer in oxygen.

Indigotin, the formula of which is $C_{16}H_{10}N_2O_2$, a body poor in oxygen, is completely insoluble in water. Alizarin, $C_{14}H_8O_4$, a colouring matter richer in oxygen, is slightly soluble. Brazilin, with the formula $C_{22}H_{18}O_7$, very rich in oxygen, is very soluble in water. However, we cannot insist upon this as a hard and fast rule, as the solubility of colouring matters is not always in direct proportion to their degree of oxidation; for instance, if a colouring matter as the result of oxidation is transformed into a substance analogous to a resinoid its solubility in water is diminished. The nature of the water plays an important part in the solution of colouring matters, and calcareous waters have a special effect on the colouring matter.

Aniline colours, such as magenta, the soluble blues, methyl violet, malachite green, and safranine, dissolve badly in calcareous waters. A heavy, tar-like precipitate is formed, which leads to poor shades and uneven dyeing. These waters may nevertheless be used, either after a preliminary softening, or by the addition of acetic acid in sufficient quantity to neutralise the action of the lime, and proportional to the hardness of the water. The matters in solution in the water have a considerable influence on the colouring matter. When safranine or magenta, for instance, are not dissolved in pure water, the colouring matter rapidly changes, and loses its strength.

Dye-baths of these colouring matters should be prepared immediately before use, and with pure water. In the case of the soluble blues, solutions may be prepared in advance with boiling water. As a general rule, calcareous waters are unsuitable for the preparation of solutions of colouring matters, thus:—

1. The derivatives of triphenylmethane: Magenta or hydrochloride of rosaniline,



and acid magenta, sodium salt of the trisulphonic acids of rosaniline (the shade given by this dye-stuff is discoloured by alkalis, but the colour returns after a passage through an acid bath), xanthine, rosaniline and diphenylamine blue, azuline, Hofmann's violet, Paris violet, benzyl violet, malachite green, Victoria blue, night blue and auramine.

2. The phtaleines: Cœruleine, eosine, fluoresceine, etc.

3. The safranines : Pheno-safranine, safranine and amethyst.
4. Animal colouring matters : Cochineal and kermes.
5. Vegetable colouring matters : Cutch, valonia, galls, knoppern, gambier, kino, sumach and madder.

If calcareous waters as a rule are unsuitable in dyeing and textile printing, on the other hand when logwood or weld is dyed on a mordant of iron or aluminium, the presence of the salts of lime is indispensable. This is an exception to the rule, however. In extracting the colouring matter from the dyewoods lime in the water is very harmful. In dyeing Turkey red or cochineal scarlet, which is done in an acid bath, their presence flattens the shade produced and wastes the colouring matter.

Bismarck brown, an azo colour, gives much darker shades in calcareous waters than when a soft water is used.

Lime in the water is just as harmful in mordanting. It weakens the baths by precipitating the salts of aluminium and of iron. It decreases or neutralises the acidity of the bath, and transforms the bichromates into neutral chromate. In madder baths a change in the shade produced by the lime is very noticeable, the pure red becomes a violet. The presence of the lime causes other troubles in madder dyeing. The carbonate of lime in the water very easily precipitates on the goods. It spots the whites, and becomes a centre of attraction for colouring matter. This trouble is noticeable even in the preliminary processes of madder dyeing. The temperature is sufficient when the goods are wetted out to precipitate the carbonate of lime, which adheres firmly to the fibre.

If waters containing calcic salts are used in clearing madder shades with soap, for the sake of economy the soap should not be dissolved until after the water is corrected with soda or caustic soda, according as to whether it is a carbonate or a sulphate water.

These drugs are ladled into the water, which is then boiled, and decanted from the precipitate. The water is then ready to be made into a soap bath.

The influence of the lime in the water varies with the kind of madder used. There forms a binary lake of madder with the lime, and this is fixed on the mordanted cloths. This lake according to Schlumberger is much faster than the simple aluminium lake.

Alsace madder, which is acid, suffers no appreciable loss when calcareous waters are used, and as a matter of fact carbonate of calcium is added to the bath in order to obtain fast shades. In preparing the bath, and choosing the water, the composition of the madder has therefore to be taken into account.

Avignon madder, on the other hand, has an alkaline reaction.

It contains calcaræous salts and therefore the presence of lime in the water is harmful in dyeing with it.

Water containing no lime must therefore be used, or the bath must be corrected for lime before the colouring matter is put in.

Rosensthiel has shown that chemically pure alizarin in solution in distilled water does not completely saturate the mordants of iron and aluminium, and that to obtain this saturation a little carbonate of calcium must be added to the bath. On the other hand, when a calcareous water is used, the carbonic acid is freed, carbonate of calcium is precipitated by the heat, and the bath takes a violet colour as the result of the formation of a compound of lime and alizarin. If the bath is brought to the boil, the lime lake deposits in the form of a violet powder, and the bath is thrown out of work.

On bubbling carbonic acid through it, the lake dissolves, and the bath may again be used. We may conclude from this that to fix as completely as possible pure alizarin on a mordant of iron or aluminium, it is necessary to add lime to the bath. In this way a colour is fixed on the fibre which is a ternary compound of the dye-stuff and the oxides of lime and of iron or aluminium. The fullest shade is produced with a given quantity of dye-stuff when there is an equivalent of colouring matter and of carbonate of calcium in the bath.

Although alizarin, which when artificially prepared is derived from anthracene, cannot be dyed from a bath of distilled water, purpurin, also derived from anthracene, goes well on to mordanted cloth from a bath of pure water. Nevertheless to get the best yield from the bath, carbonate of calcium must be added in the same proportion as in alizarin dyeing. Alizarin and purpurin are the most important colouring matters in dyeing. Madder contains three colouring matters, alizarin, purpurin and pseudo-purpurin, and in dyeing with artificial alizarin as in dyeing with madder the bath should not contain lime, but the proper proportion of carbonate of lime should be added to it.

Acetate of lime has been proposed by Rosensthiel as an advantageous substitute for carbonate of calcium in alizarin and purpurin dyeing. In madder dyeing, the analysis of the madder must be co-ordinated with that of the water in order to obtain the maximum tinctorial yield.

When calcareous waters are used, wools are imperfectly freed from grease and saint; an insoluble soap forms with the fatty matter in the wool and the metals of the alkaline earths, and this is fixed on the fibres.

As a result of this the dye-liquor is irregularly absorbed. The

stuff is unevenly dyed and spotted in places, and much of the dye-stuff in the bath is wasted.

In washing woollen goods after dyeing, if calcareous waters are used they take a dull shade or a gloss which is not natural, at the same time weakening the colour.

Several dyers have sent us samples of water with which it has been impossible to dye. They contained so large a proportion of salts of the alkaline earth that a dye-bath made with them precipitated lakes of the colouring matter. This can be avoided by softening the water before using, or by neutralising the action of the salt with an acid.

In cloth bleaching the nature of the water used is of great importance, and to obtain good and regular results the works must be supplied with pure water. Calcareous waters are particularly harmful, as the compounds formed by the various lyes and the gummy matters are difficult to dissolve and adhere firmly to the fibre. Moreover, calcareous water is very wasteful of soap.

In bleaching cotton goods by Lunge's chloride of lime process, water containing an appreciable quantity of calcareous salts cannot be used. Such a water of course may be corrected by ascertaining the proportion of the salts contained in it, and neutralising them with the proper amount of acetic acid, and the process is often commenced by neutralising the carbonate of calcium in the water with either hydrochloric or sulphuric acid, after which a little of a weak organic acid, such as acetic acid, is added.

In bleaching with peroxide of hydrogen, or peroxide of sodium, a water as free as possible from the salts of lime must be used. It must specially be noted that if the waters employed contain iron salts in solution, they are altogether unsuitable for dyeing or printing with alizarin, or for any of the coal-tar colours that are fixed on a tannin mordant.

Ferric hydrate forms iron lakes with various dye-stuffs such as logwood, curcuma and cochineal, in which the iron is in the form of a protoxide.

In indigo dyeing, the iron in the water is of less consequence.

A ferruginous water cannot be used at all in bleaching, as the iron forms salts with the soda lyes and the salts of lime, and spots the cloth or yarn with yellow. If this happens the goods must be passed through a hydrochloric acid bath, in order to transform the iron into a soluble chloride. This after-treatment, however, is not always efficacious, and it is often necessary to pass the goods through a warm bath of oxalic acid in order to obtain oxalate of iron, which is very soluble in water. This process must be carried out very

carefully, and as soon as the yellow spots disappear the goods must be passed through a bath of clean water, so as to stop the action of the oxalic acid, which would weaken the fibres if prolonged unnecessarily.

The formation of the ferric hydrates must be prevented by using water free from salts of iron, or the ferric hydrate must be eliminated from the goods by the process which we have described, as it not only spots the goods but actually makes holes in them.

Ferric oxide burns the organic matters and this explains many faults in dyeing and printing. The destructive effect is caused by the ferric oxide parting with its oxygen. The oxide of iron formed by this reduction is then ready to take back oxygen from the air and to commence its work of destruction. Dull and flat shades are produced when the dye-bath is made up with water containing iron, and this is most noticeable in dyeing on a mordant.

In dye-houses and bleach-works troubles often arise and goods are spotted when condenser water is used from the waste steam.

When certain anti-scale compounds are used in the boiler, the water often contains these products which are carried off by the steam, either as they were introduced into the boiler or decomposed. Conscientious manufacturers of anti-scale specialities modify their composition when they are informed that they are to be employed in the boilers of dye-houses or bleach-works, and that the condenser water is to be used in the baths. If this is not done, all sorts of faults occur in the processes, and they are difficult to remedy, as the composition of these preparations is kept as secret as possible by the manufacturers who make them a speciality.

CHAPTER VI.

WATER IN THE TEXTILE INDUSTRIES AND IN CONDITIONING.

RAW wool as it comes from the sheep's back contains a fatty matter secreted by the animal known as suint. This fat, which adheres strongly to the fibre, can only be eliminated by a special treatment which is the preliminary process in the linen industry.

Desuinting and degreasing wool need large quantities of water, and the composition of this has a considerable influence on the success of the operation, and is capable even of changing the nature of the fibre. The quality of the water used in this first operation is often the cause of failure in the subsequent processes which the wool undergoes. Thus when wool is washed with a hard water the permeability of the fibre is diminished, and this interferes with the regular fixation of the mordants and colouring matters, and consequently an uneven shade is produced in the dye-bath. When the water is muddy, the earthy matter adheres to the fibre, and is difficult to get rid of.

Suint is composed of carbonate, chloride and acetate of potassium, all soluble salts, and of a fatty matter. In addition to these substances, some wools also contain earthy matters. Merino wools lose as much as 70 per cent. of their weight in degreasing. It might be thought that the foreign matters in the wool could be completely eliminated by a simple washing in warm water, in view of the composition of the suint and its soapy property. This is not so, however, as washing in water alone always leaves a little of the fatty matter behind.

The desuinting may be done with ordinary water.

It must be noted that the water must never be brought near the boiling-point. There is a danger of damaging the fibre if the temperature exceeds 60° C. It has been noted in practice that the desuinting of wool is done more easily in short baths. In this way, that is to say with a minimum of water, the suint acts like a soap, the fat combining with the alkaline matter, and in consequence all the grease and other matters adhering to the fibre are washed off.

The more the wool loses in desuinting, the better quality it is. Coarse wools lose much less than fine, about 36 per cent. of their total weight instead of 45 per cent.

In degreasing wool, that is to say in getting rid of the last traces of fatty matter, the nature of the water is of first importance.

This process is usually carried out with the salts of potash, and if the water used contains salts of lime there is a great waste of soap. Soap to begin with is neutralised by the salts of lime, and wastes its action on them until it has converted the whole into an insoluble soap. The calcareous insoluble soap thus formed is deposited on the fibre and adheres to it. Under these conditions, the wool cannot



FIG. 60.—Sheep washing.

be completely freed from grease, and trouble arises in every subsequent process through which it passes.

To remedy this the water must be softened before use by the addition of an alkali, soda or potash. Potash is better than soda, as although both alkalis attack wool, potash does so to a less extent than soda. Calcareous waters are also harmful in the preliminary treatment of cotton, silk, linen and hemp.

The studies of Fremy have shown us that the fibres and cells of textiles are united by a sort of vegetable cement, composed of vasculose, cutose, pectose and its derivatives, pectine, para-pectine, meta-pectine, meta-pectic acid, para-pectic acid and pectic acid.

Hemp or flax is retted in order to free the fibre from its woody covering, and to prepare it for spinning. Water is used for this purpose and in some cases an alkali is added to it. In retting the solvent action of the water depends on the transformation of the

pectose, which constitutes the major part of the vegetable cement, into pectine, a body which is soluble in water.

This transformation produces pectase under the influence of a special ferment found in the vegetable matter. Retting therefore should be carried out under the most favourable circumstances for the setting up of fermentation. Pectine is also transformed into other bodies soluble in water, the meta-pectic acids.

Three ordinary methods are used in retting hemp and flax :—

1. Retting in running water.
2. Retting in stagnant water.
3. Grass retting.

To these may be added a mixed process, in which the plant is treated both on the grass and in water. Other methods of treating hemp and flax might be cited which aim at the improvement or the suppression of the retting process.

We have to consider here, however, the method of retting in running or stagnant water. In retting as a rule a too calcareous water is avoided. Nevertheless in retting in running water it is preferable that the water should contain a little lime when fine fibres are under treatment. The lime slackens the energy of the pectic fermentation, and consequently there is less danger of damage to the fibre. For the same reason the water should be cold.

When running water is employed, the current must not be very fast, or the fibres will be destroyed, damaged, or carried away. The water of the Lys is renowned as very suitable for retting. Nevertheless if its composition is examined it will be found that it is almost normal.

The Lys water contains per litre :—

	Litres.
Dissolved air	0'026
Carbonic-acid gas	0'005
	Grammes.
Sulphate of lime	0'015
Carbonate of lime	0'070
Nitrate and chloride of magnesia	0'005
Bicarbonate of potash	Traces
Chloride of sodium	"

According to Charpentier, the justly appreciated value of the Lys water for retting depends upon the extent to which it is used for this purpose.

The constant and abundant supply of the plant keeps the water in a constantly favourable state for the setting up of fermentation and facilitates the operation.

Charpentier's views on the matter are corroborated by the fact

that retting in fresh water gives a less satisfactory result than in water that has already been used.

Retting in stagnant water is done in pits, and the flax remains in the water for twelve days or so, according to the temperature and the quality of the water. The practice of retting in stagnant water requires greater attention than in running water, on account of the large quantity of gummy matters dissolved, which remaining in the water interfere with the processes of solution, and consequently with the steady progress of the operations. The fermenting action and the production of the pectase ferment must be aided, and therefore the water in the pits is renewed as frequently as possible.

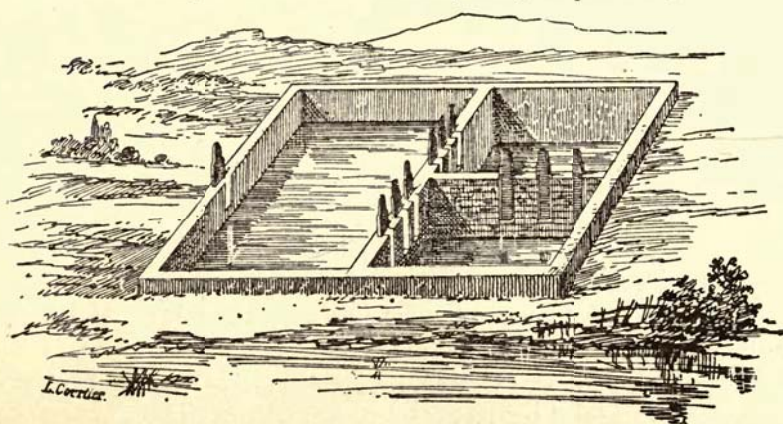


FIG. 61.—Retting pits for flax.

The results of the following analysis may be taken as representing the average composition of the water after the retting operation.

Carbon	30.69
Hydrogen	4.24
Oxygen	20.80
Nitrogen	2.24
Ash	42.03
	<hr/>
	100.00

The analysis of the ash according to Kane gives on the average :—

Potash	9.78
Soda	9.82
Lime	12.33
Magnesia	7.79
Alumina	6.08
Silica	21.35
Phosphoric acid	10.84
Chlorine	2.41
Carbonic acid	16.95
Sulphuric acid	2.65
	<hr/>
	100.00

Ferruginous water is not suitable for retting. It produces a brown coloration on the fibre, which is difficult to remove.

Elder leaves are thrown into the retting pits in order to neutralise the action of the iron in the water. The fibre obtained from flax by retting in water represents about five-sixths of the weight of the treated stem. After retting the stem is dried and then stripped.

Just as in the case of stagnant water, the residuary waters from retting in a current contain nitrogenous organic matters, which constitute a veritable source of infection. A danger to the public health arises if these waters are run off into a stream. The residuary water contains valuable fertilisers, and the farmers can use them profitably. When the retting is done in pits it is easily applicable for this purpose.

Silk is composed of fibroine or pure fibre and a gummy matter which must be completely got rid of before the silk is dyed. The calcareous waters are unsuitable in reeling the silk from the cocoon, as the salts of lime precipitate, adhere closely to the fibre, and completely spoil the subsequent processes.

Before scouring or ungumming raw silk, that is to say the first boiling of the silk to eliminate the bulk of the gummy matter it contains before it is sent to the dyer, if calcareous waters have been used the silk must be carefully washed or faults will occur in the subsequent processes. Experience shows that a raw silk which on analysis gives more than 10 per cent. of ash is in the worst possible condition for the scouring and subsequent operations.

In fact on boiling off such a silk, which is done by treating it in a hot soap bath, the silk takes a dull shade to begin with, and then insoluble lime compounds form by the action of the soluble soap on the salts in the water used for reeling, which are now fixed on the silk fibre. These lime soaps deposit on the stuff and even penetrate the fibre. As a consequence the lustre of the silk is spoilt, and uneven shades are produced in dyeing.

When therefore the raw silk has been reeled through calcareous water, the silk must be washed in a water slightly soured with hydrochloric acid. This bath dissolves all the salts which adhere to the fibre, and is followed by a passage through a weakly alkaline bath to neutralise the acidity.

The operation is finished by washing the silk in pure water, which eliminates all the salts, which have thus been made soluble, and the washing is continued until the wash waters are entirely neutral, the test being made as usual with litmus paper. In this way mishaps in the subsequent operations are avoided.

Nevertheless it is preferable, whether the fibre treated is silk, woollen or cotton, to commence by softening the water.

In the textile industries the water is frequently treated very simply with carbonate of soda in special tanks, where it is allowed to settle, to separate it from the deposited matter.

In the official establishments known as conditioning houses, lime in the water may cause serious miscalculations in the results obtained by analysis. The conditioning of textiles, pure and simple, is the determination of their hygrometric condition, in order to ascertain what amount of water has been added to them artificially, but the public conditioning houses frequently make complete analyses of the fibre. When silk is boiled off in the conditioning house, to ascertain to what extent it has been weighted, the nature of the water used has a great influence on the results obtained by the operation, which consists in two successive boilings of half an hour each in a soap bath. In testing the same silk in different conditioning houses, the figures found show very variable results, and this is the consequence of the different character of the waters used.

Thus, silk boiled off in distilled water at Lyons shows a loss of 2 per cent. more than the same silk boiled off in Rhone water, which marks hardly more than 17 hydrotimetric degrees. In boiling off silks therefore, pure water should always be used. In the same way, in quantifying any artificial additions to wool, pure water must be used, otherwise the weight of the wool is often greater after than before washing.

Very pure water is needed in washing wools, the more so that the difference between the weight before and after washing is often very slight, so that impurities in the water easily lead to mistakes.

In conditioning houses, and in all laboratories where similar tests are made, distilled water or softened water must always be used, and when the latter is employed its hydrotimetric degree must not exceed 2 to 3°.

In such establishments there should be a large enough plant to provide a constant supply of distilled water in abundance, and this should be used in preference to softened water.

CHAPTER VII.

WATER IN SOAP-WORKS.

WATERS which contain too large a quantity of the salts of calcium or of magnesium lead to a waste of the alkaline lyes used in soap-works, but when such waters alone are obtainable they can be corrected. Soda or potash lye reacts on the calcium salts, precipitating them in the form of carbonate of calcium, an insoluble body which is harmful in the subsequent processes of soap-making.

In order to avoid incorporating a certain quantity of carbonate of calcium in the soap, and in consequence aiding the formation of insoluble soaps of the metals of the alkaline earths, the salts of calcium and of magnesium should be precipitated and separated out of the water to begin with.

From the point of view of economy, it is best to use a water containing the least possible amount of salts of lime or magnesia in solution.

When the water contains a heavy proportion of chlorides and of soluble sulphates, the first operation of soap-making is badly carried out. This first process consists in boiling the oil or fat with a weak caustic lye, and the yield and quality of the soap depend upon it.

Such waters, however, may be used in making the brine which serves to salt out the soap, a process which depends upon the insolubility of soap in solutions of sea salt and in concentrated solutions of caustic soda and potash.

The soda or potash lyes must not be prepared with water charged with sea salt, sulphate of sodium, sulphate of potassium and sulphate of magnesium, as such waters introduce compounds into the water which are sources of trouble in the subsequent operations. If a pure water is not available, condenser water should be used.

If the water supply of the soap-works contains matters in suspension, such as traces of organic and earthy matters, a simple filtration through several successive layers of gravel and sand, the

layers diminishing in thickness from top to bottom of the filter, will be sufficient. In this manner, a clear water quite suitable for soap-making is obtained.

In a later chapter of this work we shall give a description of several types of apparatus giving an abundant supply which can be used advantageously in soap-making.

CHAPTER VIII.

WATER IN LAUNDRIES AND WASHHOUSES.

THE laundry industry, which has developed very considerably of late, is interested in the highest possible degree in the question of water supply. On arrival at the laundry the goods are first soaked in order to remove spots of all descriptions, and in this operation soft water is an absolute necessity.

The same may be said of the actual washing operations. Hard water is wasteful and harmful.

If however the only source of water supply of the laundry is a sulphate or carbonate water, it must be softened before use. Otherwise there will be an extravagant waste of soap resulting from the formation of insoluble scaps of lime or magnesia at the expense of the soap in the washing-machine.

This is a highly important consideration, for the loss in soap through this cause may easily exceed that which is doing useful work on the clothes. It has been said that the civilisation of a nation may be gauged by the amount of soap it uses, but if an ignorant race used hard water in the laundry the maxim would not be true. The hydrotimetric degree of the water gives a simple indication of the quantity of soap necessary to neutralise the salt it contains.

Each hydrotimetric degree corresponds to a loss of one-tenth gramme per litre of soap. Thus the water of the artesian well at Grenelle requires 11 decigrammes of soap per litre before it commences to lather, this being the point at which the soap commences to act on the linen.

The following table shows the loss of soap per cubic metre of water (220 gallons):—

	Kilos.
Distilled water	0
Snow	0·250
Rain	0·350
The Allier at Moulin	0·350
The Dordogne at Libourne	0·450
The Garonne	0·500
The Loire at Tours	0·550

	Kilos.
The Loire at Nantes	0'550
The Grenelle well	0'900
Artesian well at Passy	1'100
The Soude	1'350
The Somme-Soude	1'350
The Somme, junction with the Marne	1'400
The Rhone	1'500
The Saône	1'500
The Yonne	1'500
The Seine at the Ivry Bridge	1'500
The Vanne	1'800 to 2
The Seine at Chaillot	2'300
The Marne at Charenton	2'300
The Oise at Pontoise	2'100
The Dhuis at its source	2'400
The Escaut at Valenciennes	2'450
The Ourcq Canal	3'000
Arcueil water	2'800
Près St. Gervais water	7'200
Belleville water	12'800

These last waters are so bad that they cannot be used for industrial purposes, and are hardly fit for anything but watering the streets. Waters marking 15 to 18 hydrotimetric degrees are suitable for laundry purposes, higher than 22° they should not be employed.

Carbonate waters should be corrected by the addition of carbonate of soda in the quantity considered as normal to wash well. The salts of soda used in the laundry will vary in quantity according to the nature of the water.

In practice, the lessive where Seine water is used is made with 18 to 20 kilogrammes of 75° soda per thousand kilogrammes of goods to be washed.

With Vanne water nearly 28 kilogrammes of 75° soda are used for the same quantity of goods.

Generally speaking, a calcareous water can be softened by the addition of a soda salt. The increase of the hydrotimetric degree of the water leads to a higher expense in the soda, soap and eau de Javelle used in the laundry.

Some soft waters, as for instance those of the artesian wells at Grenelle and Passy, effect a very considerable economy in the products used in the laundry. Rain water is the most economical of all sources of supply.

It is well to remark, however, that hard water can be used in rinsing and blueing the goods.

Where an unsuitable water is used in the laundry, the goods will often be spotted with mineral or organic colouring matters in solution in the water in spite of the blueing.

CHAPTER IX.

WATER IN TANNING.

TANNERY work necessitates the employment of a huge quantity of water, both in the unhairing process and in the tan-pit.

The salts in solution in the water have a considerable influence on the results obtained. Before transforming the hides into leather, that is to say an imputrescible and supple product insoluble in water, and made very resistant by the tanning process, the hides are unhaird.

The unhairing of the soft skins consists in loosening the bulbous roots of the hairs by saponifying the greasy matter secreted by the small hair glands. This is done with such an agent as quicklime, and the water used has a considerable effect on the operation.

If the water contains a large proportion of carbonate of calcium, the excess of carbonic acid produces a precipitate of carbonate of calcium, and this deposits in the dermic tissue.

This deposit interferes with the absorption of the tannin in the cells of the hide, and retards the tanning process. The carbonate of lime is also the cause of brown stains on the leather.

In the tan-pits the carbonate of lime is transformed into tannate of lime which oxidises rapidly in the air, and according to Büchner forms secondary products of tan-oxylic and tan-omelanic acids, giving a reddish-brown coloration to leather which decreases its market value.

This trouble also occurs when the water is charged with carbonate of magnesia, as tannate of magnesia gives secondary products in the same way. After fleshing, the tanner should free the hide from lime, which if left becomes transformed into the carbonate. For this reason, attempts have been made to replace quicklime by other agents.

To free the water used in working the hides from the carbonates of lime and of magnesia in solution in it, lime is added to it in a special tank.

Instead of thus precipitating the salts of lime or magnesia, Villon proposes to correct the water directly with acids.

In the presence of an excess of acid, the carbonate of lime and the carbonate of magnesia are transformed into soluble chlorides. In this way good results are obtained, and the leather is not damaged in any way.

The proportion of acid used is 20 grammes of hydrochloric acid at 20° B. per cubic metre of water for each hydrotimetric degree.

Nitric acid may be used instead, in the proportion of 20 grammes of nitric acid of 36° B., or acetic acid which is equally as good, and can be employed in the proportion of 25 grammes of 9° B. acid per cubic metre of water and per hydrotimetric degree. We consider, however, that hydrochloric acid is the best agent to use from every point of view.

Water charged with sulphates, such as sulphate of calcium and sulphate of magnesium, is far from being harmful in tanning operations. As a matter of fact if the tanner's water does not contain sulphates he adds sulphate of calcium and sulphate of magnesium to the water, using an excess of the latter drug.

As for carbonate waters, they very easily deposit on the hides their carbonate of calcium and of magnesium.

These two bodies are harmful in tanning, and therefore in working thick hides in running water the tanner endeavours to secure a water containing plenty of carbonic acid, and he can do this by forming an artificial waterfall, and thus aerating the stream.

In the actual tanning operation, waters containing the carbonates of lime and magnesia are all the more troublesome if the unhairing has been done with lime. This remains in the crevices of the dermic tissue, in spite of all attempts to free the hide from it, and it facilitates as we have seen the precipitation of the carbonate of lime and of magnesia, which add to the quantity of lime compounds already in the tan-pit.

Waters containing grease or salts of iron cannot be used in the tannery.

In contact with the air, the ferrous salts in solution are quickly transformed into ferric salts, which combine with the tannin and give the hides a black coloration of tannate of iron.

These waters may be corrected for tannery purposes by a preliminary treatment with alum, chloride of barium, silicate of soda, or oxalic acid.

The average proportion of these bodies added per cubic metre of water and per hydrotimetric degree are 20 grammes of alum, 16 grammes of chloride of barium, or 10 grammes of silicate of

sodium. The water is corrected with one of these reagents in a special tank and allowed to settle before it is used.

As for the proportion of salts to introduce in the water, it is best to make the calculation according to the hydrotimetric degree of the water, and we shall show how this is done in a later chapter.

If it is absolutely necessary to use waters charged with iron salts, the tanner commences by aerating the water as much as possible in order to transform the ferrous into ferric salts. A small quantity of soda or potash is added in a special tank.

The oxide of iron is precipitated, the water is allowed to settle, and decanted, and thus freed from the iron primitively in solution in it, it can be used without inconvenience.

In a later chapter, touching on brewery waters, we shall describe the means of eliminating iron in water, and these processes concern the tanner also.

CHAPTER X.

WATER IN PREPARING TANNIN AND DYE-WOOD EXTRACTS.

THE manufacture of extracts has developed enormously of late years, as their use has been found so advantageous in tanning, dyeing and in the composition of colours for printing on cotton, woollen and silk.

These extracts allow the dyer or printer to work with less bulk, and they contain the active principles of tannin matters or dye-woods. In preparing them, the wood to begin with is shredded into a very finely divided state, in order to enable the water to penetrate the fibre better and dissolve the tannin and the colouring matters.

The quality of the extracts often depends upon the salts contained in the water used, and it may be said that the reputation of certain makers is due to the fact that they have taken into consideration the influence of the salts in the water on the active principles of the extracts. Dyers and calico-printers extract the astringent matters they use, such as divi-divi, galls, sumach, etc., in a cold bath.

As in the case of thickenings used by textile-printers it is difficult to keep these extracts as they are fermentable, and their keeping qualities are all the poorer if the water used in making them contains germs, or decomposed matter. The practice of making extracts varies in different print-works.

The water is used either under pressure or heated to between 60 and 70° C., or even almost cold, as in the diffusion process.

Carbonate waters are altogether unsuitable in extracting the majority of the colouring matters.

In the cold process of extracting tannin principles for use in making leather, it is necessary not only to use enormous quantities of water, but also to have gigantic apparatuses, and the extract resulting from the operation is often too poor to be serviceable.

On the other hand, the tannin matter obtained with steam or boiling water contains in addition to the active tannin principles resinoid matters and products of decomposition which are harmful

in tanning. The concentration of the tannic juice by evaporation of large masses of water leads to the precipitation of the salts primitively in solution in the water, and these are harmful in the tan-pits.

Outside the precipitation of the salts of lime and magnesia which occurs, compounds of the tannic acids are formed with the metals of the alkaline earths, and the harmful action of these compounds is all the more pronounced the higher the hydrotimetric degree of the water. The presence of these salts also make the process slower, the deposits prevent the water from penetrating in the fibres, and a poorer extract is obtained.

Iron in the water combines with the tannic acids, gallic, pyrogallic, quercitannic, morintannic, catechutannic and gallotannic acids to form ferric compounds which give dark blue, greenish-olive and green precipitates, not only wasting the tannin matters but discolouring the hides.

By forming tannic compounds, waters containing lime and magnesia lead to loss in the tan-pits, therefore in preparing these extracts a pure water should be used or the water should be corrected before employment.

CHAPTER XI.

WATER IN PAPER-MAKING.

IN choosing the site for a paper-mill, the quality of the available water should be the first consideration, as water plays a most important part in paper-making. If water had to be used just as it is, and without being corrected, some papers could not be made.

Cigarette, filter, tissues, and other fine papers cannot be made with water containing impurities, whether these are in solution or in suspension. The mechanical impurities which might charge the paper pulp with hurtful matters are happily easy to remove.

Thus by passing the water through animal charcoal, it is perfectly filtered and even some bodies in solution are retained by the filter, but this process has been almost abandoned, because of its high cost, as animal charcoal quickly loses its filtering power, and has to be revived.

One of the most simple means to clear the water from impurities is to let it settle in large lodges, but this method occasions a waste of time and moreover a large area for the lodges must be at the disposal of the paper-maker.

Filters of gravel and sand have been used advantageously to free the water from suspended matter, and these give a ready and abundant supply.

In the chapter treating of commercial filters, we shall describe several with a large output, taking up very little room and suitable in every way for a paper-mill.

The purification can also be effected by decanting from a first tank and then filtering by successive passages through layers of gravel of diminishing thickness, finally running the water over a channel of sand. The water after this treatment, which is very inexpensive, is limpid, and is freed mechanically from the substances it primitively contained.

In some paper-mills the waters are softened by adding a little alum to them, a method which has been practised in the earliest times in China.

Water charged with iron salts is unfit for paper-making. Under the influence of an alkali the iron is precipitated, and gives the paper pulp a brown colour. In this way ferruginous waters do not allow light shades or art papers to be produced. These iron salts have a still worse effect when the paper is sized.

Salts such as the carbonate and sulphate of lime, and the chlorides, which have not much influence on the paper pulp, produce very serious troubles when the paper is sized.

Formerly, the sizing was done with animal glue from which the chondrine was precipitated with alum to give the size better keeping properties, but vegetable size is almost entirely substituted for this, and with this calcareous waters are particularly harmful.

In vegetable sizing, resin is precipitated from the solution of a resinate, and is fixed on the fibres of a paper. This precipitation is effected with various sulphates, but usually with alum. When this is used, a resinate of aluminium is formed, which is precipitated on the fibres.

Calcareous waters interfere with this precipitation, as the carbonic acid holding the carbonate of lime in solution in the water acts on the soda of the resinate of sodium soap primitively formed, giving carbonate of soda and precipitating the resin, which is not fixed on the fibres but combines with the lime to give a granulous soap which spoils the sizing operation. The same thing occurs when the water has been acidulated with hydrochloric or sulphuric acid, or even contains free chlorine.

In any of these cases, the resinate of sodium is decomposed, and the soda combines with the acid or chlorine to form chloride or sulphate of sodium.

The resin soap thus decomposed is fixed badly on the fibres of the paper. Alkaline water is also harmful in sizing, as double salts are formed with the alum and the alkali in the water, and these interfere with the subsequent formation of resinate of aluminium.

It is a good thing to put in an excess of alum over the quantity of resin used in making the resinate of sodium to begin with, in order that it can form double salts or compounds with the harmful salts of lime, iron or magnesia contained in the water.

This is why in many English paper-mills rather more than a pound of alum is added to every pound of resin used.

When the water is very calcareous, or contains salts of magnesia in solution, it must be corrected before being used in paper-making, and this entails a large expense.

We shall examine certain processes in a special chapter on the

subject, but one of the simplest means consists in running the water through a filter of gravel and sand into a tank containing milk of lime in excess. The salts of lime and magnesia are thus precipitated, and the water, after settling and decanting, is usable, and moreover, the advantage has been gained of precipitating the ferric oxide from the salts of iron in solution.

CHAPTER XII.

WATER IN PHOTOGRAPHY.

PHOTOGRAPHIC failures are often due to the composition of the water used in the processes.

Photography depends upon the molecular transformations of certain bodies, such as the salts of silver, by light, and the reduction of these salts by developing agents capable of reacting chemically. It is easy to understand that matters in solution in the water are also capable of giving rise to reactions, the effect of which may be harmful in the printing and developing processes.

Preparation of the Emulsion.—In making gelatino-bromide glaze, it is evident that the preparation of the emulsion must be done with a water of a certain degree of purity.

To begin with, it must be free from all solid matter in suspension, as this would deposit on the layer of gelatine and produce spots on the proofs.

In rainy weather the water is often yellow. It holds earthy matters in solution, and these are harmful in preparing emulsions and in all photographic processes.

This difficulty can be avoided by adding a little alum to the water—about half a gramme per litre. The water thus treated is then allowed to settle, and after decantation is limpid and can be used without fear.

If the emulsion is too acid, the transformation of the pulverulent bromide of silver into granular bromide is retarded and the sensibility of the plate is diminished, and some makers prefer water charged with calcareous salts, because these salts neutralise the free nitric acid in the emulsion.

As calcareous waters, however, produce insoluble compounds which diminish the sensibility of the emulsion, a more rational method is to correct the acidity with ammonia.

The acid then combines with the alkali, producing nitrite of ammonium, a very soluble salt which the water easily eliminates. If the water in the first steps of the preparation of the emulsion

need not be absolutely pure, this is necessary in the case of the water used for washing the prints. This must be done with distilled water, with which there is no fear of harmful deposits.

It must also be remarked that waters containing chlorides, sulphides, etc., may produce bad results in preparing the emulsion. The bromide of silver is obtained by mixing two solutions, a solution of bromide of potassium and another of nitrate of silver, and at the same time that bromide of silver is precipitated chloride of silver is also thrown down if the water contains chlorides in solution :—



Thus a mixture of bromide and chloride of silver is obtained, with a resulting diminution in the sensitiveness of the film.

For this reason sea water could not be used, for instance, or the proportion of chloride of silver obtained would be enormous, seeing that there are from 30 to 35 grammes of chloride of sodium per litre in sea water.

If sulphides are present, a precipitate of sulphide of silver is obtained, and all the emulsion is wasted :—



These waters containing sulphides, or sulphuretted hydrogen, are unfortunately very plentiful. Pond water and running water, in particular, contain organic matters, with a consequent presence of sulphides.

Water even that has no sulphides in it may become charged with them in its passage through caoutchouc tubing. To prevent this, the caoutchouc should be desulphurised by steeping it for some minutes in a boiling 5 per cent. solution of potash.

This done, the tube should be washed until it shows no further traces of alkalinity, that is to say, until the wash water no longer turns red litmus paper blue.

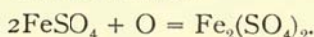
Development of the Negatives.—In developing negatives, the quality of the water is of the greatest importance, so much so, in fact, that in many cases photography has to be given up for reasons which we will examine, or at least appropriate remedies have to be adopted.

All water for photographic purposes must be carefully filtered. In this way deposits of matters in suspension on the gelatine plates, which subsequently form spots on the photograph, are avoided.

Distilled water, which ought to be always employed, is not always available, as it may not be procurable in the out-of-the-way places where the photographer is obliged to operate. According

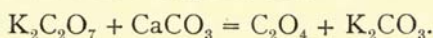
to the substances which it contains, ordinary water may lead to numerous accidents in the preparation of developing baths. The developers are intended to precipitate the metallic silver from the bromide of silver by a reducing action, and if the water contains oxidising matters, or air in solution, the reducer is oxidised to some extent, and loses its reducing power to that same extent.

Under these circumstances, developing baths of pyrogallie acid, hydroquinone, pyramidophenol, etc., are rapidly spoilt. Ferrous sulphate, for instance, rapidly becomes ferric sulphate, a salt which has no action on the nitrate of silver:—



If there is too much air in the water which has to be used, this can be easily got rid of by boiling it for some minutes. It is easy to note the action of the air, or rather of its oxygen, as the salts of iron and the pyrogallol turn rapidly brown if the bottles containing them are not carefully corked.

If the waters are calcareous when the iron developer is dissolved in oxalate of potassium, a precipitate of oxalate of calcium is formed, which is very harmful to the plate. The insoluble oxalate of calcium forms a crust on the film of gelatine, which has been softened by the different manipulations:—



The oxalate of calcium thus formed must be allowed to settle for some hours, and the solution may then be decanted off. The use of calcareous water leads to a loss of neutral oxalate of potassium, and the bath is then utilisable.

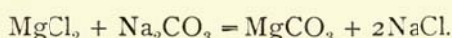
The carbonate of calcium kept in a state of solution in the water by the excess of carbonic acid should be got rid of to begin with, and to do this it is merely necessary to bring the water to the boil for a few minutes in order to precipitate the carbonate of calcium, then allow to settle and decant. The water then no longer gives a precipitate with the oxalate.

The preparation of ferrous sulphate in solution at the first glance does not seem to require a water free from calcareous salts. Nevertheless when the two solutions of ferrous sulphate and neutral oxalate of potassium are mixed with such waters, oxalate of calcium is formed.

This insoluble oxalate of calcium formed under these circumstances is all the more harmful as it is hidden by the coloration produced by the reaction of the oxalate of potassium on the salts of iron. Thus, both the solution of ferrous sulphate and of oxalate of potassium must be made with water free from calcic salts.

Organic developers, the base of which is an alkaline carbonate,

form a white precipitate of carbonate of magnesium when the water contains salts of magnesium such as the chloride, and this precipitate deposits on the sensitive film with harmful results :—



Carbonate of magnesium, which often remains in solution in the water, in the presence of an excess of carbonic acid, gives rise to troubles absolutely analogous to those caused by the calcic salts, and the remedy is exactly the same in both cases.

The organic developers made with the alkaline carbonates give a precipitate of carbonate of calcium with the sulphate of calcium in solution on the water, and this is allowed to settle and separate by filtration.

Thus treated, the water leads to no ulterior difficulties; it is simply necessary to take into consideration the amount of carbonate of lime precipitated, and add the necessary quantity of carbonate of soda, which has been used up in this reaction, in order to complete the necessary proportion of carbonate of soda in the bath.

This precipitation of the salt of lime can be effected before preparing the developing bath by means of the neutral oxalate of potassium.

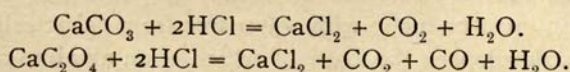
Washing the Negatives.—When the plate is developed, it is important that the first washings should be done with pure or distilled water.

On leaving the bath the sensitive coat of gelatine is impregnated with the salts of the developer, and if the washing is done with calcareous waters, these precipitate oxalate of calcium if the developer was an iron salt, or carbonate of calcium if the developer was an organic body, as in this case it would contain an alkaline carbonate.

The oxalate or carbonate of calcium formed would deposit on the gelatine coat, and produce spots on the negative, which would be communicated to the prints.

A remedy for these difficulties can be found if pure water is not available. The calcic salts can be precipitated to begin with with oxalate of potassium in the just necessary proportions or the water may be used without any preliminary correction, and the precipitate of oxalate or carbonate of calcium deposited on the plate can be redissolved.

The deposits can thus be dissolved by plunging the developed plate for a few seconds in a bath acidulated with hydrochloric, citric, or tartaric acid :—



A weak solution of hydrochloric or citric acid will act perfectly in dissolving the deposited calcic salts.

When salts of magnesia are present in the water the same troubles arise in developing the plates when organic developers are used; the result is the precipitation of carbonate of magnesia. As in the case of the calcic salts this can be prevented by precipitating it out of the water to begin with.

It is merely necessary to add carbonate of sodium to the water before preparing the developing bath. The magnesia is precipitated, it is allowed to settle, and the water may be used after filtration.

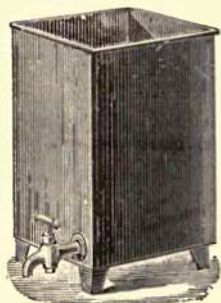


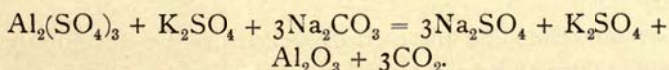
FIG. 62.—Zinc tank for washing plates.

Frequently after developing the plates the gelatine coat is hardened in a bath of a solution of alum, in order to prevent the gelatine from being dissolved. When this is done, a little hydrochloric acid is added to the alum bath to prevent the formation of the oxalate or carbonate of calcium, according to the developer employed.

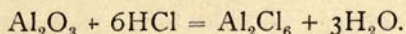
The bath may be prepared as follows:—

	Grammes.
Water	100
Alum	10
Hydrochloric acid	5

The addition of hydrochloric acid to the alum bath has another advantage as it prevents the precipitation of alumina from the alum solution. As a matter of fact if pyrogallol or other organic reducing agent has been used in developing the plate, and if the washing after the negative has been properly developed has been badly done, the plate will retain traces of alkali and give a precipitate of alumina:—



This alumina is a very flocculent white body which will adhere and form spots on the plate. This will not take place if hydrochloric acid is added to the bath, as alumina is soluble in this acid:—



Some operators, for this reason, pass the plate through the alum bath after fixing. In this way they do not risk precipitating alumina and pulverulent sulphur, which sometimes happens when alum is added to the hyposulphite bath in order to fix and harden the plate in one operation.

If the alum bath is used without adding acid, and salts of lime are deposited, it is merely necessary to dip the negative into a bath acidulated with hydrochloric acid, and then to wash it carefully.

Hyposulphite of sodium is ordinarily employed to fix the negative. The effect of this is to dissolve any bromide of silver which has not been acted upon by light and reduced by the developer. If the plate is well washed on leaving the developing bath, the fixing may be done in the sunlight; if on the other hand it has not been thoroughly washed, it should be fixed in the dark room, using a yellow or red light, otherwise the plate may turn yellow.

When the negatives are treated with pyrogallol or any other organic reagent, care must be taken to wash the plate thoroughly before fixing with hyposulphite of sodium.

Traces of alkali remaining in the sensitive film act on the hyposulphite of sodium, transforming it into the sulphide, which combines with the bromide of silver to produce a black sulphide of silver, which draws a sort of veil over the negative.

By neutralising this alkalinity in a bath of hydrochloric, citric, or tartaric acid, as we have already indicated, this is remedied. Moreover, the traces of alkali soften the gelatine and make it liable to be carried away.

Yellow or brown spots on the negatives are often produced after fixing them because the washing has not been thorough, and traces of the developer remain, such as iron, pyrogallol and particularly hydroquinone.

The alum bath facilitates the elimination of the developer employed, which may remain in the negative. A 5 per cent. solution may be used, which at the same time will harden the film of gelatine.

A 3 per cent. solution of chrome iron gives a slightly greenish tint which is not objectionable, and it produces the same effects as ordinary alum.

If at any time the plate turns yellow in the developing bath, this yellow tint can be removed by dipping it for about five minutes in a bath composed of:—

Water	Litre.
																		1
Alum	Grammes.
																		100
Hydrochloric acid	15 to 20

Of course it will be understood that the negative must be washed before fixing. When fixed, the plates should be entirely freed from hyposulphite of soda, otherwise the proofs on paper will be covered with yellowish spots.

After a little time the negative itself will be damaged by reactions caused by the hyposulphite of soda, which will attack the silver of the plate, forming sulphide of silver.

Thorough washing is therefore indispensable, and as ordinary water may be considered as not always efficacious enough, a little hypochlorite of soda should be added to it. This has energetic oxidising properties, and transforms the hyposulphite of sodium remaining into bisulphite of sodium, a very soluble salt that the water easily eliminates.

To get rid of the last traces of hyposulphite of sodium, the washing can be done with water containing from 7 to 8 cubic centimetres of eau de Javel (hypochlorite of sodium) per litre.

Instead of eau de Javel a solution of hypochlorite of zinc can be used.

To prepare this, 20 grammes of chloride of lime are ground up

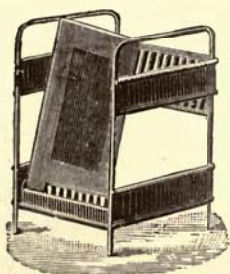


FIG. 63.—Frame for washing plates which can be put into any bath.



FIG. 64.—Wooden drainer for drying the plates.

with water to a paste in a mortar, and this is brought up to 1 litre with water, a solution of 40 grammes of sulphate of zinc is added, and the whole is allowed to settle. The negative is dipped for two minutes in a bath composed of 1 part of this product to 6 parts of water.

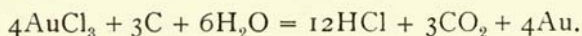
Peroxide of hydrogen and nitrate of lead may also be used.

It is well to note that the passage of the negative through the alum bath after fixing also greatly facilitates the elimination of the hyposulphite of sodium. A bath containing 3 per cent. of ordinary alum or 5 per cent. of chrome alum may be used. A bath made with equal volumes of saturated solutions of sea salt and alum also gives good results.

A thorough washing in ordinary water follows.

The Prints.—The preparation of the baths for the prints necessitates the employment of a water entirely free from organic matter.

Otherwise the chloride of gold in the baths will be reduced by the organic matter, with a consequent precipitation of metallic gold, which of course will reduce the strength of the bath:—



Water polluted with organic matter should therefore be rejected in preparing the printing bath, just as in preparing a sensitive paper with a solution of nitrate of silver, in which case the organic matter precipitates the silver in a metallic state.

Rain water in falling becomes charged with bodies such as the nitrites and ammonia. These bodies are very harmful in the printing bath, of which they reduce the strength. Even distilled water demands care in its preparation for these purposes, and this is not always taken.

In distilling the water, the still must be thoroughly cleaned in order to avoid the carrying over of any organic matter. Otherwise the organic products will be retained in the distillate and cause troubles.

Nevertheless if the photographer is obliged to use water charged with organic matter in his processes, these impurities may be eliminated by adding a solution of permanganate of potassium.

As long as organic matter is present undestroyed, the permanganate will lose its colour, but as soon as the water keeps a violet coloration the organic matter is eliminated. The operation must be carried out carefully and enough permanganate of potassium must be used without being in excess.

The water is allowed to settle, and after filtration is ready for use. After the prints are washed, they are fixed with hyposulphite of sodium, then thoroughly washed again to eliminate the last traces of hyposulphite, which is a prolific source of injury. If it remains spots will appear and the photograph will be damaged.

The permanence of the photograph depends upon this last washing, and in this case it is not necessary to use distilled water.

On the other hand, ordinary water is used as a rule, and the salts which it contains form easily eliminable compounds with a hyposulphite of sodium.

Too long a washing weakens the photograph, and destroys its brilliance, and the washing may be shortened by transforming, as in the case of the negatives, the remaining hyposulphite into bisulphite of sodium, which is very soluble in water. In order to do this, the positive is steeped for a quarter of an hour in a weak solution of eau de Javel, then washed for two hours in ordinary water, and in this way a permanent print is obtained.

CHAPTER XIII.

WATER IN SUGAR REFINING.

THE sugar industry in certain processes requires as pure a water as possible, for instance in filtering the syrups through animal charcoal, in diffusion and in osmosis.

In sugar works where animal charcoal is used in the clarification it must be washed with pure water.

If salt water or calcareous water is used, the animal charcoal quickly loses its bleaching power, because of its property of absorbing saline substances. At the end of a short time it must be revived or replaced.

Animal charcoal can be revived with water soured with hydrochloric or acetic acid, in order to transform the salts of lime and magnesia, which otherwise would be precipitated on the charcoal into soluble salts. Sometimes an alkali is added to the water, but this should not be done.

This treatment is followed by washing the charcoal with pure water, in order to carry off the salts which have been rendered soluble by the acid, and to eliminate all trace of acidity.

The organic matters absorbed are got rid of by calcining the charcoal. Phosphoric acid and the soluble phosphates have no harmful action in sugar refining, but it is not so with the other salts.

The method of extraction of the sugar from beetroot by diffusion depends upon the phenomenon of osmosis produced between the water and the juice of the beetroot, the cell-walls playing the part of dialyser. The salts contained in the water used must be taken into consideration, as by reason of the huge quantity it is necessary to employ the proportion rapidly increases in the concentrated juice, interfering with the crystallisation of the sugar, and diminishing the yield. The majority of the salts contained in the water may be looked upon as carrying some part of the sugar into the molasses, and sometimes even their action is directly harmful.

In special diffusers in which the sugar is very completely

extracted from the beetroot, the purity of the sugar produced very largely depends upon the salts in the water used.

Water charged with the sulphates of calcium and of magnesium and the alkaline chlorides is harmful, as these salts retain a notable quantity of sugar in the mother liquor. The alkaline chlorides, in particular, easily combine with the sugar, forming deliquescent compounds. A water holding a chloride in solution may retain 9.6457 of prismatic sugar per chemical unit of chlorine; chloride of sodium only retains 5.852 of sugar per unit.

Waters charged with chloride of sodium naturally give diffusion juices much more saline than those obtained with pure water, and this deteriorates the quality of the sugar. Water of about 30 hydrotimetric degrees is usually suitable for diffusion.

The deposits of carbonate of calcium, which are formed by the decomposition of the calcic bicarbonate in the water, interfere with the process of diffusion when the water is very calcareous, or what comes to the same thing, when huge quantities of weakly calcareous water are employed. These calcic deposits also damage the residuary products, and diminish their value as food for cattle. Even soft water containing matters in suspension must be rejected or must first be filtered.

For instance, if it contains sand, this is carried by the water into the diffusing apparatus and causes rapid wear of the valves, which, by-the-by, often occurs through negligence. Water containing organic matter in suspension may produce sulphuretted hydrogen, which will spoil the beetroot juice.

This production of sulphuretted hydrogen has always to be feared with water containing sulphates of the alkaline earths and organic matters. In this case the sulphates are very easily reduced to sulphides. Water contaminated with organic matter must therefore always be filtered.

Deposits of the sulphate and carbonate of lime may also take place in the serpentine steam-coils of the boiling apparatus, and the bad conductivity of the scale formed, which increases according to the thickness of the deposit, becomes very troublesome. The formation of this scale will of course depend upon the proportion of salts in the water. Pellet has proposed a rapid method of gauging the suitability of a water for use in the extraction of sugar from beetroot. From 2 to 3 litres of the water are taken for the purposes of the test. To this is added from 5 to 6 cubic centimetres of properly prepared lime water, which has been carefully decanted off the deposited lime.

This done, the diluted lime water is thoroughly carbonated by

heating it first to about 75°C ., then to 90°C ., and finally boiling it long enough. It is then filtered, and from 2 to 3 litres of the filtrate are taken to be tested. One litre of the water is then taken, evaporated to dryness, calcined, and the weight of the residue gives a sufficient indication of the amount of salts that would be deposited in practice. It is evident that the weight of the organic matter found in the residue can be calculated, and a deduction as to the quality of the water drawn from it. In purifying sugar refinery waters the point has to be considered whether the substance used may be harmful in the process of diffusion.

The precipitation of the salts of lime or of magnesia by bases ordinarily used to purify water, such as potash or soda, lead to reactions by double decomposition of the soluble salts, such as sulphate of sodium and sulphate of potassium, which remain in the water. The hydrotimetric degree of the water, which may be very high, before it is treated in this manner, may be very considerably lowered. Nevertheless, the water may give in the diffusion process a deposit almost equal to that which it would have formed before. This corrected water, therefore, is almost as bad before as after purification.

Water that needs correction, therefore, must be purified by special means, and it is preferable when the supply is too heavily charged with calcic salts to use the condensed water from the waste steam, which, moreover, is very abundant in sugar works.

The triple effect evaporator produces an enormous quantity of distilled water, and the water from the second and third cylinders is very advantageously used in washing the scum in the mechanical filters analogous to filter-presses, which have great advantages over animal charcoal filters. In this water any ammonia which might be led away with the waste steam is retained by special devices in the triple effect evaporator. It may be added that feed-waters for the boilers in sugar works should never contain chloride of magnesia.

In the chapter in which the question of feed-water for boilers is considered, we have noted that this salt is particularly dangerous, as it easily decomposes and liberates its hydrochloric acid.

In sugar works, where a huge volume of steam has to be produced, such a water must be rejected, or if corrosion and rapid deterioration of the steam pipes are to be avoided, the water must at least be softened before use. Moreover, there is a danger of this hydrochloric acid finding its way into the water of condensation used, with consequent troubles in the processes of sugar extraction.

Osmosis depends upon the same principles as the diffusion

process, with the difference that a sheet of parchment replaces the cells of the beetroot as dialysers.

By osmosis the salts which would prevent the crystallisation of the sugar are extracted from the molasses or the syrups.

Osmosis, which might be called dialysis, depends upon the principle that a diaphragm of parchment paper, when used as a filter, allows saline matters to pass through and retains matter of its own nature, *i.e.*, colloids. The parchment paper frames of the osmogene, therefore, eliminate the saline matters of the masses, leaving behind a purified mass of crystallisable sugar.

The porosity of the parchment paper is of first importance, and the nature of the water used has a considerable effect on this porosity. It must be remembered also that the quantity of water is relatively large, averaging about six times the weight of the molasses. With impure waters, therefore, the pores of the septums

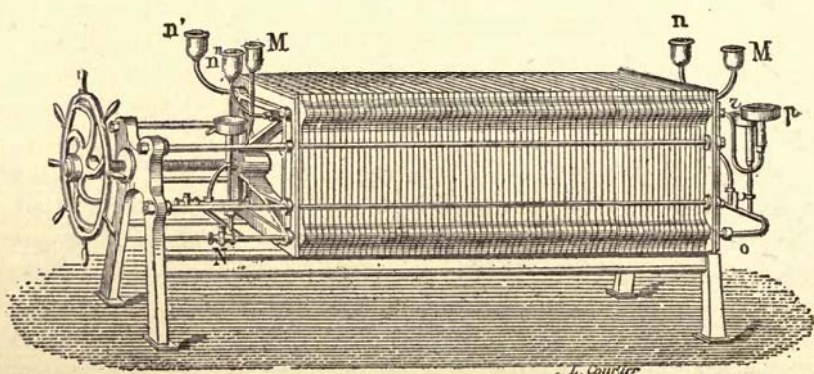


FIG. 65.—Dubrunfaut's 100-frame osmogene.

are very quickly obstructed, the osmosis proceeds badly, the yield becomes small, and either the frames of the osmogene must be cleaned or the parchment replaced.

The less salts in solution the water contains the easier it is to eliminate the saline matter from the molasses, and consequently to increase the yield of the sugar. For the same reason that the molasses is freed before osmosis from the salts of lime, which are refractory to the process, the use of calcareous waters which interfere with the separation of the saline matters should be avoided.

In several foreign countries the practice of osmosis has been successfully adopted, because the sugar works have very pure waters at their disposal. The necessity of purifying the waters used in the osmogenes adds to the difficulties of the operation, because the products employed become incorporated in the mass of liquid.

In sugar works an enormous volume of steam is produced, and it may be said that everywhere where sugar is made there must also be a production of distilled water on a commercial scale.

In osmosis, as in the diffusion process, this water is very advantageously used, and allows better results to be obtained than with natural or corrected waters. The deposits from calcareous waters and other sources, as for instance those produced by the molasses in the osmogene, necessitate a cleansing of the apparatus to eliminate the different salts. To do this the osmogene is emptied, then filled with water, and a little hydrochloric acid is gradually added until all the salts and in particular salts of lime are dissolved. A litre of hydrochloric acid is usually sufficient for one apparatus. At the end of a few minutes this acidulated water is run off and finally

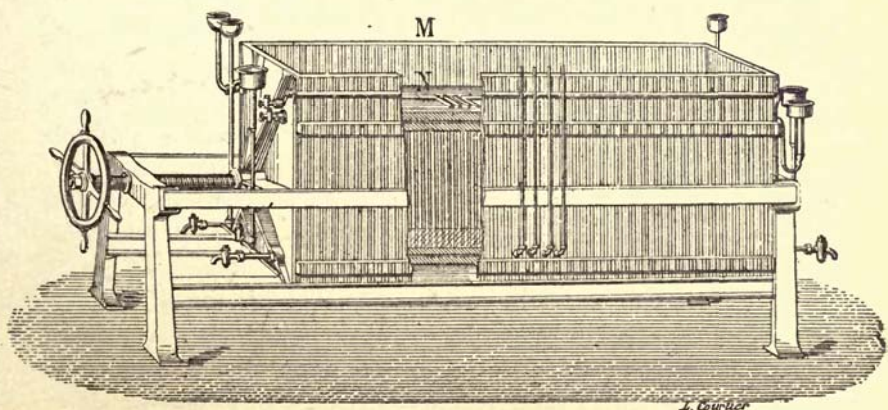


FIG. 66.—Leplay's osmogene.

the osmogene is washed with pure water, and is then ready for a fresh bath.

It must also be noted that the triple effect evaporator is quickly lined with deposits of the most complex character, formed for the most part of the various salts of lime. The triple effect evaporator, therefore, must be scoured out in order to regularise the transmission of the heat and avoid the decomposition of the sugar.

This is done by raking out the tubes and then adding a little hydrochloric acid or carbonate of sodium.

If the deposit resists this treatment it is usually silicious and a simple treatment with soda is sufficient to deal with it.

The triple effect evaporator has simply then to be emptied and flushed out with clear water to eliminate all the remaining soluble salts and all traces of acidity, and the evaporation of the sugar juice can then be continued.

CHAPTER XIV.

WATER IN MAKING ICE AND BEVERAGES.

THE quality of water used in making ice, mineral waters and beverages in general is a question of the first importance, as it concerns the public health.

The first condition that such water must fulfil is to be scrupulously potable, both from the point of view of its chemical composition and its bacteriological condition, or at least it must be purified, filtered and completely sterilised. It is indispensable, therefore, to consider the nature of the chemicals introduced to purify a water, remembering that they will be found in this water after having undergone reaction, which must be taken into account and their effects examined from the alimentary point of view.

An exhaustive report by Professor Riche on the alimentary use of ice, presented to the Conseil d'Hygiène de la Seine, shows that the congelation of water does not destroy all its microbe organisms, and that in fact ice may become a veritable vehicle of disease germs, and may contain the typhoid bacillus which is hardly affected by the low temperature.

Cold has no effect on many microbes. Certainly some of them diminish in numbers or even disappear when the water is frozen, such as for instance *bacillus prodigiosus*, but this deadly effect on the microbes is more active after several successive congelations than after a long duration of freezing. Frequently ice from natural sources, ponds, lakes or slow streams, is more harmful to the public health than artificially produced ice, as it contains all the pollutions of the water from which it has been procured. This water, which would be used in its liquid state with repugnance, is then absorbed in the form of ice.

The examination of waters in the environment of Paris, from which ice is cut, as for instance the ponds of the park of St. Cloud, and at Tourvois, and the lakes of the Bois de Boulogne and the Bois de Vincennes, has shown that these waters are very bad, and that not one of them is potable. A decree of the 30th of June,

1893, absolutely interdicted the use of the ice on the pond at La Briche.

A large part of the ice used in Paris is from the lakes of the Bois de Vincennes and the Bois de Boulogne. This natural production amounts to 38,000 tons per annum, whereas only about 23,000 tons are artificially produced. It must be added, however, that the ice famine during the summer of 1898 prompted several manufacturers to establish new factories which are largely increasing the annual production.

Like natural ice, artificial ice may be a home for microbes and contain the most dangerous bacteria if the water employed in making it has not all the qualities of a potable water. If even a pure water is converted into ice by exposure to the cold in the open air, it very quickly becomes polluted with various disease germs in the atmosphere and is dangerous to the consumer.

In manufacturing ice, therefore, it is necessary to use sterilised water. The conclusions which were adopted on the report of Professor Riche by the Conseil d'Hygiène de la Seine have also been arrived at in an analogous fashion by the Consultative Committee of Public Health of France, with Ogier as reporter. It was agreed that the ice trade should be regulated as follows:—

1. By interdicting makers, dealers or retailers from selling or exposing for sale for alimentary use any ice which on melting will not give a water found to possess the character of a good potable water on chemical or bacteriological examination.

2. By compelling makers or dealers in alimentary ice and ice for other purposes to keep these two different sorts separately, and by obliging retailers to keep the two descriptions of ice in distinct vessels or tanks with marks which could not be confused.

As the result of these decisions, a police ordinance was issued in the following terms:—

FRENCH REPUBLIC.

LIBERTÉ.—EQUALITÉ.—FRATERNITÉ.

PREFECTURE OF THE POLICE.

ORDINANCE CONCERNING THE COMMERCE IN ICE.

PARIS, 13th December, 1899.

We, the Prefect of the Police;

In view of the decrees of the Consuls of the 12 messidor, year VIII. and of the 3rd brumaire, year IX.;

The laws of the 14th of August, 1850, and of the 10th of June, 1853;

In view of the opinion arrived at by the Conseil d'Hygiène et de Salubrité de la Seine in its sitting of the 12th of May, 1893 ;

In view of the despatch of the Minister of the Interior, dated 19th of March, 1894, approving this opinion ;

Considering that the public health demands that ice containing any harmful principle should not be delivered for consumption,

We ordain as follows :—

ARTICLE 1.

It is forbidden to all merchants, makers, dealers and retailers, to sell or to expose for sale any ice which on melting does not give a potable water.

ARTICLE 2.

Makers and dealers in alimentary ice and ice for other purposes must keep these two sorts of ice in entirely separated magazines ; that in which the pure ice is stored must have the words " alimentary ice " painted on its door on a white ground ; the impure ice exclusively intended for industrial purposes must be stored in a room upon the door of which must be painted on a red ground the words " non-alimentary ice ".

ARTICLE 3.

The vehicles used for the transport of ice must bear the same inscription, according as to whether they are used for the carriage of an alimentary or non-alimentary ice.

In no case must these vehicles be used for the transport of a category of ice other than that corresponding to the inscription which they bear.

ARTICLE 4.

Retailers of ice must have two cases or water-tight reservoirs, without communication between the two, the one kept expressly for alimentary ice and the other for non-alimentary ice.

Both of these must be labelled as already ordered.

Retailers who have not two reservoirs may only sell alimentary ice.

ARTICLE 5.

The Director of the Chemical Laboratory of the Prefecture and the Commissaries of Police and the agents under their orders are charged with the execution of the present ordinance, which will be printed and posted in public places.

THE PREFECT OF POLICE,
L. LÉPINE.

For the Prefect of Police,
THE SECRETARY GENERAL,
E. LAURENT.

In manufacturing beverages, and mineral waters in particular, the tops of the syphons should not contain too much lead, as the carbonic acid energises the attack upon it and the water takes this very poisonous metal into solution. With this in view, a police order in June, 1862, limited the amount of lead used in the alloys from which the heads of syphons are made to 10 per cent.

The dangers we have already noted in the case of ice also apply to waters used in the manufacture of mineral waters, and the Consultative Committee of Public Health of France, in its sitting of the 25th of August, 1894, requested the Prefect of Police to take measures in consequence, and to prescribe all dangerous waters, notably, the water of the Ourcq Canal, and of the wells in mineral water manufacture.

In manufacturing ice and mineral waters, therefore, it is necessary to make a chemical and bacteriological examination of the water employed.

The report of Dr. Pouchet shows that the Consultative Committee of Health of France admitted at its sitting of the 10th of August, 1885, that the quality of a water could be sufficiently gauged by testing for the presence of nitrates and ascertaining:—

1. The quantity of solid residue left by the water.
2. The weight of volatile matter at red heat.
3. The hydrotimetric degree.
4. The weight of the chloride.
5. The weight of the sulphates.
6. The quantity of oxygen carried off by permanganate. This is proportional to the quantity of organic matter ascertained by weighing after combustion.

The table below gives the quality of waters according to the nature and the proportion of bodies which they contain:—

Contents per litre.	Very pure water.	Potable water.	Suspicious water.	Bad water.
Chlorine	Less than 0·015 gr.	less than 0·04 gr.	0·05 gr. 10	more than 0·1 gr.
Sulphuric acid	0·002 gr. to 0·005 gr.	0·005 gr. to 0·030 gr.	more than 0·030 gr.	more than 0·050 gr.
Organic matters (calculated in oxygen quantified in alkaline solution) {	less than 0·001 gr.	less than 0·002 gr.	0·003 gr. 10	more than 0·004 gr.
Loss of weight at red heat	less than 0·015 gr.	less than 0·040 gr.	0·040 gr. to 0·070 gr.	more than 0·100 gr.
Total hydrotimetric degree	5 to 15	15 to 30	over 30	over 200
Permanent hydrotimetric degree after boiling	2 to 5	5 to 12	12 to 18	more than 20

To ascertain precisely the quality of a water for alimentary uses, whether for mineral waters or ice, the chemical analysis must be followed by a bacteriological examination. The quality of a water varies infinitely according to the nature and number of the microbes which it contains.

According to the numbers of bacteria contained in a cubic centimetre, a water is considered as :—

Very good	0 to	50
Good	50 to	500
Mediocre	500 to	3,000
Bad	3,000 to	10,000
Very bad	10,000 to	100,000

Waters from natural sources contain from 1,000 to 1,300 bacteria.

No water is potable which contains disease germs.

The action of mineral water on the microbes varies. According to Hochstetter, the microbes such as *M. tetragenus*, the cholera bacillus, the green bacillus, *M. aurantiacus* and pink yeast, are affected less by mineral water than by distilled water, but the contrary is the case with *M. prodigiosus*, the yellow bacillus and the bacillus alpha.

Typhoid bacillus in particular lives in mineral water much longer than in distilled water. Microbes in waters used for making beverages and ice disappear completely when the water is properly sterilised, and we shall describe the methods employed in a special chapter.

CHAPTER XV.

WATER IN CIDER-MAKING.

IT is highly regrettable to note that the rigorous cleanliness in the preparation of fermented beverages insisted upon by Pasteur, although it has become the rule in almost all breweries, is not observed in many establishments where cider is made.

The apple grower himself frequently prepares cider, and neglects the most elementary rules in the selection of the water which he uses. Water plays an important part in the quality of cider, its taste and its keeping qualities. Unfortunately, the influence of the salts which may be found in solution in the water on the manufactured cider has not been studied, but it may be said that some ciders are better than others mainly because of the nature and proportion of the salts in the waters used in making them.

The cider presses cannot squeeze all the juice from the apples, and the residue of pulp contains matter which must not be wasted. In cider-making, therefore, water is used to extract the larger part of the sugary juice.

This water is of course eventually used as a beverage, and it is evident, therefore, that in cider-making an absolutely potable water should be employed. The water should therefore have this character, that is to say it must be limpid, well aerated, odourless, containing no disease germs, not turning turbid on boiling, lathering freely with soap, and suitable for the cooking of vegetables. Ignorant peasants prefer the stagnant water of ponds to a limpid and wholesome water, and some of them go so far as to assert that such water gives the cider more body.

The ponds are frequently in fields and accessible to cattle, and polluted by them in every way, yet it is pretended that such a water has no influence on the fermentation, the quality and the keeping properties of the cider! Such a water which has stagnated in the ponds and has received the excrement of animals, causes serious troubles in cider-making, as it introduces the most varied germs,

the acetic, butyric, lactic, nitric and nitrous ferments, and complex principles harmful to fermentation.

Outside the question of its quality, and its disagreeable flavour, such a cider may cause disease, as bacteria are present in such a water, which is not sterilised in the course of manufacture as it is in some other industries depending upon fermentation.

The water of ponds in the neighbourhood of stables almost always receives purin and secretions either by infiltration or by direct drainage. In addition, such a water contains greasy residues, such as butyrolein, free butyric acid, butyrates of calcium, ammoniacal salts, and the fatty matters of suint which contribute to give the cider a disagreeable odour and a rancid taste.

With well water, the salts of calcium contained in it combine with the apple juice to produce different compounds which damage the quality of the cider. By properly aerating calcareous waters, they may be freed from their carbonate of calcium by precipitation and decantation.

As in the case of the calcareous salts, the influence of ammoniacal and ferruginous bodies on the cider is manifest. The cider frequently takes a brownish or blackish tint; it is said to "draw". This can be remedied by using tartaric acid or tannin. The proportion is about 30 grammes of tartaric acid or about 10 grammes of tannin per hectolitre of cider. This addition is advantageous as outside the question of appearance the cider is flat and very disagreeable to the palate.

When water containing salts of iron is used in making cider, it takes a black tint. By adding about 20 grammes of tannin per 100 litres of cider, the salts of iron are precipitated in the form of tannate of iron.

When they have deposited the clear liquor is decanted off. As for the acetic fermentation provoked to the detriment of the alcohol in the cider, by the presence of micoderma aceti, it is avoided by preventing all contact with the air. This is done by covering the cider with a film of good olive oil, one-third of a litre per hectolitre of cider.

CHAPTER XVI.

WATER IN BREWING.

THE water used in brewing has a considerable influence on the quality of the beer, its chemical composition and its bacteriological condition both entering into the question.

Before building a brewery, the nature of the water at disposal should therefore be taken into consideration. The purity of a water is no guarantee of the quality of the beer which it will produce, and distilled water is far from being the type of a water suitable for brewing.

Nevertheless as a rule a water which has all the good qualities of a potable water is suitable for use in the brewery, as the substances which are necessary in the production of a first-class beer can be added to it. To begin with, therefore, the water used should be colourless, odourless, insipid, and free from organic matters.

In considering the mineral salts dissolved in water and their effects, we have noted that in the general run of cases they are harmful. Some of them, however, are useful in brewing, and improve the quality of the beer.

Thus the gypsiferous waters of Burton-on-Trent, which contain 111 grammes of sulphate of calcium per hectolitre, have led to the establishment of many breweries in this district, because the beer brewed with these waters has become world-renowned.

In brewing ale, the English employ sulphate waters preferably, and many brewers correct their soft waters by adding a certain proportion of sulphate of calcium. It is very necessary to understand the effects of the salts which may be found in solution in water on the different processes of the brewery.

As regards the production of beer, it is in three stages :—

1. The artificial germination of the grain.
2. The brewing process properly so called.
3. Fermentation.

The artificial germination or malting is a process of the highest

importance, as the quality of the beer obtained very largely depends upon the quality of the malt from which it is brewed.

All things must be taken into consideration in order to have the malt in the best possible condition, and the nature of the water is an important factor in the matter.

Malting is carried out in three stages :—

(a) Steeping the barley.

(b) Germination to the desired extent.

(c) Drying.

In moistening the barley, just enough water is given it to allow the embryo to develop, and to prepare it for saccharification. The barley should be soaked sufficiently to avoid having to sprinkle the layers of grain in the malting house.

When the grain is sprinkled in the malting house, as is done by many maltsters, it loses a certain amount of aroma, an abundance of carbonic-acid gas is freed, and the germs are unduly developed. The grain should be steeped at a low temperature, and the water should be frequently renewed and should be well aerated.

Water containing an insufficient amount of air asphyxiates the germ, kills it, and rot rapidly sets in. In the steeping process, oxygen is therefore very useful. It stops the rot in an efficacious fashion and obviates the necessity of using dangerous antiseptics, such as salicylic acid. The bad odours which may be given off by the steeping water in summer should be remedied, Couturier recommends lime as an antiseptic which will deal with this nuisance. When the grain is wetted with lime water instead of ordinary water, the lime destroys the ferment which would act upon the barley, and consequently prevent any later damage.

The lime does not interfere with the quality of the malt, and the germination proceeds regularly and rapidly. We will now consider the influence of the salts and other matters frequently met with in water on brewery operations.

1. INFLUENCE OF THE SUBSTANCES CONTAINED IN THE WATER.

(a) **Organic Matters.**—If the grain is steeped with water charged with organic matter, the tendency to mouldiness is favoured, the malting is done defectively, and many troubles will arise in the course of the manufacture of the beer.

In the brewing operation, the action of the yeast is often interfered with by organic matter in the water which poisons it. When

the wort is boiled, if organic matter is present the beer takes a much deeper colour than when pure water is used.

As a rule, organic matter is harmful, as it sets up fermentations in the beer other than those which the brewer desires to obtain, and these lead to bad results. Even in washing the casks and brewery utensils, it is necessary to use water free from organic matter, otherwise the organic matter and bacteria may adhere to the casks or utensils and help to damage the beer.

When water polluted with organic matter is heated, the matter is decomposed, and the decomposition products spoil the keeping qualities of the beer and completely change its taste. Sometimes even the smell of rotten eggs due to the formation of sulphuretted hydrogen may be noted in a water containing decomposed organic matter. This may generally be remedied by thoroughly aerating the water.

Unfortunately the water of streams and canals is invariably polluted by the organic substances carried down by the current or from the residuary waters they receive. It is difficult to find a water entirely free from them, but, for brewing, water containing merely a small quantity of organic matter may be used. A water which contains more than 50 milligrammes of organic matter per litre must be looked upon as impure.

If the only source of supply is a water which contains much organic matter it must undergo a preliminary treatment by boiling or purifying it with permanganate of potassium and filtering. Permanganate of lime in the proportion of 1 gramme per hectolitre also gives good results. The organic matter is oxidised and lime and oxide of manganese are formed.

Another method recommended by Traute consists in treating the water with chloride of lime and eliminating the excess of this reagent with an alkaline sulphite.

Another method of proceeding is to retain the organic matter and the greater part of the germs in a simple filter consisting of a layer of sand about 1 metre thick.

At Munich, where excellent beer is brewed, the water used is not completely freed from organic matter, and it contains about 4 milligrammes per litre. The same may be said of other brewing centres. The organic matters in the water can be transformed into compounds of nitrogen with hydrogen and oxygen, such as the ammoniacal salts, the nitrites and nitrates, and produce disastrous effects on the beer.

(b) **Ammonia, Nitrites and Nitrates.**—Ammoniacal compounds are formed by the decomposition of the organic matter in water.

Nitrites and nitrates result from the oxidation more or less complete of this organic matter. These salts favour the development of the Renard ferment, which is a disease of the beer, spoiling its keeping qualities.

The water supply of a brewery must be completely free from ammoniacal salts, and their presence is detected by Nessler's reagent. It is difficult to eliminate these ammoniacal salts in practice, and it is therefore advisable to reject all water containing them, and the same applies to that containing nitrites in solution.

The nitrites are easily oxidisable bodies, and this oxidation is capable of causing trouble in the actual process of brewing. The decomposition of the nitrites may take place as the consequence of reactions either during the malting or during the boiling of the wort.

The easy oxidation of the nitrites, however, makes it a simple matter to eliminate them, or rather to transform them into other bodies, and from this it is evident that a water containing nitrites is aerated and generally contains organic matter.

By forcing the water through the air or making an artificial waterfall or by bubbling air through the mass, the nitrites are quickly transformed into nitrates. This transformation, however, only substitutes one product for another, and the nitrates obtained are frequently just as harmful bodies. Almost all water contains nitrates, and their action is in proportion to the quantity the water holds in solution.

They have an effect on the yeast, interfering with the process of fermentation. The wort in their presence takes an intense reddish colour, and the beer acquires an acrid taste. The nitrates also cause a decreased yield of extract. They may be tolerated to the extent of 15 milligrammes of nitric acid per litre of water.

The nitrates are particularly harmful when the water contains at the same time small quantities of ammoniacal salts, nitrites or organic matters, as they are then in the best condition to produce dangerous reactions.

A water containing 2 per cent. of nitrate of soda or potash does not diminish the germinative power of the barley grain. This is A. Bruttini's opinion, and Mills and Pettigrew say even that it assists it.

(c) **Chlorides.**—When a water contains small quantities of chloride of sodium, it may be used, but if the proportion is relatively large, it must be rejected, as the germination of the grain will be interfered with.

Water containing about 2 per cent. of chloride of sodium, when used in malting, stops the development of the radicles and aids the germ of the plant to expand. Chloride of magnesium in the water has the same effect, and as a matter of fact the chlorides in general. Water charged with sea salt dissolves a much greater proportion of organic matter than distilled water, or a hard water, as the salt has a solvent action on albumen.

A good water to be absolutely potable should not contain more than 0.05 gr. of chlorine per litre, but in brewing a larger quantity is not detrimental. According to the proportion of sea salt in solution in the water the beer acquires a taste which is sometimes sweet and sometimes bitter; the sweet taste is produced by very minute quantities. The action of the yeast is weakened by sea salt.

The yield of the yeast is diminished when the water is charged with chloride of calcium. It becomes fat, and there is a difficulty in pressing it.

According to P. Petit waters containing chloride of calcium increase the malto-dextrines or combinations of maltose, and may be used in breweries to produce beers rich in dextrine. According to the experience of J. Stauffer, when a brewery water contains chlorides no zinc apparatus should be used.

Chlorine easily combines with the zinc, and during the principal fermentation converts the maltose into mannite. The beer in this case has a very disagreeable taste, and fines very slowly. To avoid this, zinc should be replaced by tin plates.

For the same reason the zinc must be replaced in all parts of the boiler, as the steam very easily carries away with it the compounds of chlorine, such as hydrochloric acid arising from the decomposition of the chloride of magnesium, and these will affect the zinc. This steam in condensing may find its way into the wort, taking with it chloride of zinc, which is a harmful compound.

(d) **Salts of Iron.**—Iron, which is found everywhere, is contained in waters in variable proportions.

When a water contains a small quantity only, it may be used in brewing, but it is very preferable that it should contain no iron at all, as the oxide of iron forms an insoluble compound with the diastase which interferes with the manufacture of the beer.

In malting, the barley is coloured brown by iron salts.

Beer brewed with ferruginous waters usually takes a greenish colour, which is the result of the formation of a black tannate of iron, the colour of which combines with that of the beer itself. Moreover, ferruginous waters may give the beer a bad odour and

taste. The iron may be eliminated by aerating the water thoroughly. This can be done by causing it to fall in a cascade of some yards in height, and filtering it through sand, to retain the precipitated ferric compounds.

By precipitating the soluble salts of iron as hydrated oxide of iron and separating mechanically the precipitate obtained, the iron may be eliminated, and apparatus has been constructed for this purpose.

At the Institute of Fermentation of Berlin, Cesterr's process is used. This consists in bubbling air through the water and filtering through gravel. The water to be purified is forced in a fine spray

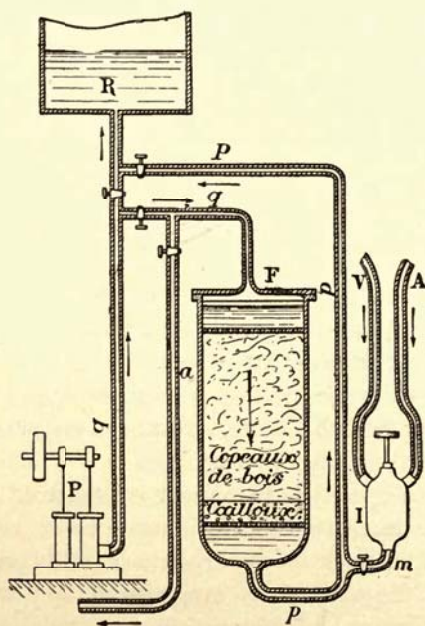


FIG. 67.—Von der Linde and Hess' apparatus.

by two pumps, and the iron it contains is thus oxidised. It then goes through layers of gravel 30 centimetres in thickness arranged on brass sieves. On leaving the filter the purified water is run into a special reservoir. The system of H. von der Linde and Hess of complete separation of the iron from the water has given excellent results in the brewery of Schultheisz and Dessaux, as shown in 1890 in the *Zeitschrift für Spiritus Industrie*.

In this process the iron is oxidised not by atmospheric influences, as the water to be purified does not come into any contact with the exterior air, but by oxide of tin spread over large surfaces of shavings of wood. The apparatus is composed of an iron filter, F, 2½ metres

high and $1\frac{1}{4}$ broad. At the base of this is a layer of small pebbles on a sheet of copper supported by an iron grid. This layer of pebbles is about 10 centimetres deep, and the rest of the filter contains wood shavings over which the oxide of tin is spread. The wood shavings are kept in place by an iron grid and a sheet of copper in the higher part of the filter.

The water to be purified is forced into the upper part of the filter by a pump P, following the direction *q*, and the oxidation is produced by the oxide of tin. The water traverses the layer of wood shavings and abandons its precipitated iron in passing through the pebbles.

The water freed from iron and filtered mounts by the tube *p* into the pure water reservoir R. The shavings can be cleaned very easily by running the pure water into the filter by the pipe *p*. All sedimentary matters are then flushed out at *f* and are evacuated by the tube at *a*. The filter may also be cleaned by forcing in air and steam by the injector I.

The air and steam are injected at the same time and the operation is repeated, then pure water is run through the filter for a few minutes.

In this way the filter is cleansed very rapidly and thoroughly.

(*e*) **Lead.**—Water containing lead must on no account be used.

The presence of lead in water may result from the action of salts and gases on leaden pipes, in which the water has remained too long. A little sulphuretted hydrogen is sufficient to detect the presence of lead by precipitating black sulphide of lead.

This precipitate is transformed into white sulphate of lead by adding peroxide of hydrogen.

(*f*) **Carbonate of Calcium and Carbonate of Magnesium.**—In brewing, the preliminary examination of water from the point of view of its hardness is of capital importance. By the hardness of a water we understand a greater or less proportion of the salts of lime and of magnesia which it contains.

It is better for brewery purposes that the water should have a certain amount of hardness. A water of from 10 to 25 hydrotimetric degrees, that is to say containing 0.10 to 0.25 of salts of the alkaline earths per litre, is excellent. In malting, if the water is too soft, it dissolves too much of the useful substances, and if it is too hard, the operation is retarded.

Waters containing carbonate of calcium in excess give the wort an intense red colour, acting on the malt and especially on the hops, and preventing a regular fermentation.

Carbonate of magnesium reduces the activity of the diastase,

diminishes the proportion of maltose and of extract, and on the other hand increases the proportion of the nitrogenous bodies and the hop resin. The beer in this case takes a dark colour and an acrid taste. It is very difficult to keep beer when it has been brewed with water too rich in carbonates. As a matter of fact beer owes its keeping properties to its acidity, which in this case is neutralised by the carbonates.

The peptones and amides, bodies which are assimilable by the yeast, and result from the nitrogenous matters of the malt, are poorly produced if the wort has not an acid reaction. In this case the albuminoid bodies which remain in the wort are harmful to the keeping qualities of the beer.

Phosphoric acid, which is an important food for the yeast, is neutralised by the carbonate of lime in the water, and precipitates in the form of insoluble phosphate of lime. In the same way with ammonia, which arises during the fermentation, it forms the double phosphate of ammonia and magnesia.

The harder the water, the smaller are the proportions of phosphoric acid and nitrogen. Very hard waters give the beer a bitter and disagreeable taste.

The water can be freed before use from its soluble carbonate of calcium by boiling, as we have shown in the chapter relating to the treatment of waters by steam, and the apparatus there described may be advantageously used in the brewery.

The carbonate of calcium may also be got rid of by precipitating it with milk of lime and decanting or filtering it.

As we have remarked, a small quantity of carbonate of calcium is far from being harmful. On the other hand, we have seen that waters that contain it to a moderate extent are advantageous. They have a less solvent action than soft water. They regulate the fermentation, facilitate clarification, and give good keeping qualities to the beer.

In some breweries sugar is used in brewing to purify the wort and to clarify the beer, but where the water contains a notable proportion of carbonate of calcium the use of sugar is unnecessary. Thus at Canterbury and in some other English towns no sugar is used with the calcareous water employed.

When the carbonic acid which keeps the carbonate of calcium in solution is freed by heat, the precipitated carbonate carries away with it the albumen of the wort, and renders useless any addition of sugar.

(g) **Sulphate of Calcium and Sulphate of Magnesium.**—The waters containing a notable quantity of sulphate of magnesium

diminish the extract of malt without lowering the proportion of phosphates and nitrogenous matters. Plenty of amyloin forms and the beer acquires an acrid taste.

Compared to soft waters, waters containing sulphate of calcium are much to be preferred. The sulphate waters have a great advantage over those containing carbonate of calcium in solution because the sulphate does not precipitate so easily as the carbonate.

When the water contains a small proportion of sulphate, it neutralises in an insensible manner the acidity of the wort and of the beer, and the formation of the amides and peptones is facilitated during the brewing.

If the wort is boiled with such water, the albuminoid bodies easily coagulate, and the beer keeps well. As for the precipitation of the phosphoric acid of the wort, it is almost the same as with distilled water.

Morritz and Morris made some experiments with three samples of water:—

1. Distilled water.
2. Water containing 0·712 gr. sulphate of calcium per litre.
3. Water containing 1·427 gr. sulphate of calcium per litre.

The quantities of phosphoric acid which remain in 100 gr. of wort were 0·129 gr., 0·104 gr. and 0·089 gr. These figures show that the yeast is well fed when a sulphate water is used. Beers made with sulphate waters have incontestable advantages over the others. They taste and keep much better. The proportion of hop resin dissolved is less and the colour of the beer is paler.

With these waters the cell formation of the yeast is much more vigorous than with soft water. For all these reasons the English breweries have acquired a world-wide reputation for their beer made with the natural sulphate waters of certain districts.

The breweries which have no natural sulphate water at their disposal add gypsum to their supply, in a larger or smaller proportion according to the nature of the beer which they wish to produce. Although in making ale a sulphate water is preferable, for porter or stout soft waters are the best.

Sulphate waters should be used in preference in preparing pale ales, and soft water in brewing dark coloured beers.

2. SOME EXPERIMENTS AND RESULTS.

Stauffer has shown that the waters qualified as hard contain more than 18 parts of lime and magnesia salts in 100,000 parts of

water, that is to say 18° of hardness, and that the water of various breweries which are very soft give excellent beers of certain descriptions.

The following table shows the number of parts of the salts of lime and of magnesia in 100,000 parts of water :—

Pilsen Brewery (limited company)	9.60
Pilsen (old brewery)	10.40
Pilsen (new brewery)	11.70
Ansbach water IV.	12.92
Tuttlingen water	13.11
Dusseldorf water	13.72
Ansbach water II.	14.32
Augsburg water	15.42
Cologne water	15.68
Ansbach water III.	18.35
Göggingen Brewery	19.81
Mayence water	19.81
Munich water (Lion Brewery) II.	20.44
„ (Royal Brewery) I.	23.38
„ (Lion Brewery) I.	28.67
„ (Royal Brewery) II.	28.85
Kaltenhausen water	38.53
Klein Schwechat (Vienna) water	38.53
Munich (Spaten Brewery) water	38.73
Ansbach water I.	94.69

According to this, a good water for malting may have from 10° to 25° of hardness, without having any harmful effect on the quality of the malt, if the nature of the water is taken into account and the conditions of steeping the grain are varied accordingly.

The steeping takes a longer time with hard water than with distilled water. Higher temperatures than 19° C. make the operation too rapid, and with lower temperatures the contrary effect is produced.

According to Ullik's experiments soft waters extract more mineral and organic substances from the grain during steeping than hard waters.

As regards the albuminoid matters, the proportion extracted by hard waters is larger than by soft waters; with regard to the hydrates of carbon soft waters extract the most.

Dr. Hannamann has made several experiments on waters of various compositions with the object of determining the action of the salts in solution in the steeping water on the germinative power of the grain, with the following results :—

Steeping water and substances added to it.	Duration of steeping in hours.	Percentage of grains.			Disaggregation and quality of the fresh malt.
		Thorough germination.	Weak germination.	Failure.	
Distilled water	48	72	22	6	Very good
Well water	96	75	21	4	"
Solution of chloride of sodium 0·5 per cent.	100	58	27	15	Unequal
Solution of chloride of calcium 0·5 per cent.	96	80	18	2	Equal
Solution of sulphate of calcium 0·5 per cent.	83	70	26	4	Good
Solution of Chili saltpetre 0·5 per cent.	100	60	22	18	Unequal
Solution of phosphate of potash 0·5 per cent.	79	66	21	13	Unequal
Water containing organic matter	74	80	15	5	Very good

G. B. Readman has collected some valuable notes on the action exercised on beer by saline solutions. He has contributed these to the *Journal of the Society of Chemical Industry* (30th April, 1894).

These notes refer to 13 solutions :—

1. Distilled water.
2. Distilled water with the addition of 71·35 gr. per hectolitre carbonate of calcium.
3. " " " " " " chloride of calcium.
4. " " " " " " sulphate of calcium.
5. " " " " " " carbonate of magnesium.
6. " " " " " " chloride of magnesium.
7. " " " " " " sulphate of magnesium.
8. " " " " " " chloride of sodium.
9. " " " " " " carbonate of sodium.
10. " " " " " " nitrate of potassium.
11. Water of the composition of Burton water.
12. Edinburgh water.
13. Distilled water containing 71·35 gr. per hectolitre of sulphate of potassium.

Solution No. 11, of the same composition as Burton water, contained the following salts per imperial gallon :—

	Grains.
Sulphate of calcium	70·99
Carbonate of calcium	9·04
Carbonate of magnesium	5·88
Sulphate of potassium	0·96
Sulphate of sodium	13·30
Chloride of sodium	9·12
Ferric oxide	1·12

The grains equal 0·0647 gr. and the imperial gallon is 4·543 litres. The analysis of beers obtained with these saline solutions, which we will indicate by their corresponding number, gave the following results.

Analysis of the Beer.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.	No. 11.	No. 12.	No. 13.
	Percentage.												
Alcohol	4.57	3.96	4.02	4.88	4.14	4.64	4.33	3.84	3.73	3.26	4.70	3.78	3.73
Actual extract	5.15	4.25	6.10	5.00	7.44	5.12	6.07	6.15	5.72	0.29	5.49	5.67	7.055
Nitrogen	0.098	0.084	0.101	0.112	—	0.095	0.101	0.100	0.067	0.090	0.112	0.084	0.087
Ash	0.265	0.019	0.247	0.283	0.273	0.28	0.296	0.34	0.285	0.282	0.359	0.228	0.310
Lime	0.007	0.013	0.021	0.018	—	—	—	—	—	—	—	—	—
Magnesia	—	—	—	—	0.025	0.052	0.052	—	—	—	0.046	—	—
Phosphoric acid	0.122	0.089	0.104	0.107	0.0101	0.104	0.113	0.590	0.093	0.118	0.092	0.094	0.097
Lactic acid	0.18	0.144	0.162	0.162	0.054	0.144	0.123	0.144	0.072	0.144	0.133	0.144	0.144
Silica	—	0.008	—	0.007	0.012	0.005	0.004	—	0.009	0.005	0.007	0.003	0.004
Specific gravity at 60° F.	1012.8°	1009.5°	1009.5°	1011.9°	—	1012.7°	1017.5°	1018.4°	—	1019.7°	1015.7°	1015.9°	1021.1°
Fermented extract	45.5	42.5	41	47	44	46	42	38	39	33	44	39	35

With all these solutions saccharification was completely terminated in an hour, with the exception of the experiments made with the carbonates of sodium and of magnesium. In the case of the carbonate of magnesium solution prepared with distilled water saccharification took two hours; with carbonate of sodium it was not finished at the end of this time. Worts prepared with waters containing carbonate of sodium always have a reddish tint.

The experiments of Windisch show that a trace of carbonate or of sulphate of sodium in solution in the presence of carbonate of lime is sufficient to give a much more noticeable coloration than with carbonate of sodium alone, about 15 grammes per hectolitre of which are required to produce an apparent coloration. All the saline solutions prepared by Readman give clear worts, with the exception of those made with the carbonates of magnesium and of sodium.

The order of the coloration of the beers obtained may be arranged as follows, according to their corresponding numbers:—

1 13 7 4 6 12 11 10 3 8 2 5 9

From the point of view of odour, flavour and keeping qualities, the beers have the following characters:—

- No. 1.—The odour of the beer is agreeable, but the flavour lacks character.
- No. 2.—The taste is very bitter and piquant, with a rough after-taste; the odour is rather strong.
- No. 3.—The odour is soft and agreeable, and the flavour perfect.
- No. 4.—A pure tasting beer.
- No. 5.—Not tasted.
- No. 6.—Peculiar flavour, strong and rather unpleasant.
- No. 7.—Medicinal flavour but an agreeable odour.
- No. 8.—Disagreeable odour and taste, and very unclear beer.
- No. 9.—As the beer has fermented imperfectly, it has a weak unpleasant taste.
- No. 10.—Disagreeable odour and unpleasant taste.
- No. 11.—Agreeable aroma, pure tasting beer.
- No. 12.—A rather unpleasant flavour.
- No. 13.—Good, but rather lacking in taste.

As regards the diminution of density, the beers may be arranged as follows:—

Nos.	Substances.		Loss of weight.
4	Sulphate of calcium	48° F. 72° F. 1'059 1'012	47'0
6	Chloride of magnesium	48° F. 71° F. 1'058 1'012	46'0
1	Distilled water	48° F. 73° F. 1'057 1'012	45'5
5	Carbonate of magnesium	48° F. 70° F. 1'065 1'021	44'0
11	Burton water	48° F. 70° F. 1'060 1'016	44'0
2	Carbonate of calcium	48° F. 72° F. 1'051 1'009	42'5
7	Sulphate of magnesium	48° F. 71° F. 1'058 1'016	42'0
3	Chloride of calcium	48° F. 72° F. 1'057 1'016	41'0
9	Carbonate of sodium	48° F. 73° F. 1'054 1'015	39'0
12	Edinburgh water	48° F. 72° F. 1'054 1'015	39'0
8	Chloride of sodium	52° F. 74° F. 1'056 1'018	38'0
13	Sulphate of potassium	50° F. 73° F. 1'055 1'020	35'0
10	Nitrate of potassium	48° F. 70° F. 1'052 1'019	33'0

Ranging them in order, the numbered beers gave the results shown in the following table :—

No.	Substances.	Specific gravity.	Alcohol. Per cent.
4	Sulphate of calcium	1'0119	4'88
11	Burton water	1'0127	4'70
6	Chloride of magnesium	1'0127	4'64
1	Distilled water	1'0128	4'57
7	Sulphate of magnesium	1'0175	4'33
5	Carbonate of magnesium	Not determined	4'19
3	Chloride of calcium	1'0165	4'02
2	Carbonate of calcium	1'0095	3'96
8	Chloride of sodium	1'0184	3'84
12	Edinburgh water	1'0159	3'78
9	Carbonate of sodium	Not determined	3'73
13	Sulphate of potassium	1'0211	3'73
10	Nitrate of potassium	1'0197	3'26

Not only the mineral and organic matters may be harmful in the manufacture of beer, but also micro-organisms contained in the water may lead to bad results. In their presence the beer acquires a disagreeable taste, and undergoes changes which deteriorate its keeping properties. The first precaution to take in the brewery is to use absolutely clean and limpid water, and to scour most thoroughly all vats, pumps, casks, and the different utensils used.

All waters contain bacteria in a larger or smaller proportion, but if no more than 150 microbes to the cubic centimetre are



found in them they may be used in brewing if no other water is available.

The water containing the least possible number of bacteria should be sought for, and any clear water that on being allowed to settle for a few days turns turbid should be rejected, as it proves that it is polluted with micro-organisms in a good medium for culture, and that a constant reproduction is going on. Not all bacteria occasion accidents in the manufacture of beer; the acetic ferment, *mycoderma aceti*, may live in the wort without harming it.

Lactic acid, produced by the lactic ferment, usually diminishes the activity of the yeast. A strict control should be exercised on the purity of the yeast, as the sure and regular process of the brewing depends upon the regularity of its development and the absence of ferments harmful to the yeast, which are frequently contributed by the water. In particular water containing a superior order of bacteria, *renothrix kulmiana*, which resembles seaweed, must be avoided. This bacteria is met with in stagnant waters polluted with organic matters.

The progress of the science of bacteriology allows us to make an attentive examination of the way in which the bacteria behave in the wort and in the beer, and consequently to know whether they develop in the wort or solely in the beer, or in both.

The development, rapidity of reproduction, and nature of the bacteria should be studied, and they should be counted in a given volume of liquor. After this, the effects of their presence should be noted, that is to say the action they exercise on the wort and beer and their influence on its taste, odour, brightness, and keeping qualities.

It is in the wort that the bacteria find their best breeding ground, and multiply most rapidly, but according to Hansen the major part of the bacteria found in water cease to develop when the yeast is added to the wort.

Impure waters and ices made from them often contain a bacteria which is very dangerous in brewing, *sarcine* often known as *Pedio-coccus cerevisiæ*. This microbe is extremely small, of much inferior dimensions to those of the yeast, and shows itself in isolated points, *coccus*, or in double points, *diplococcus*. These turn the beer turbid, give it an acrid taste, and make it acid.

It must be remembered that not only the water, but the air is polluted with micro-organisms, especially when breweries are in the neighbourhood of farms where manure heaps are exposed. The sarcine develops most in the beers which have lost most weight. According to H. Vogel, it may be remedied by adding two or

three litres of new barm to every ten hectolitres of beer, and this addition should be made just before bunging the casks.

In bitter beers, the development of the sarcine can be remedied within a certain limit by adding 30 grammes or so of hops per hectolitre, the hop acting as an antiseptic as regards sarcine. Waters containing the fungoid growth known as *Beggiatoa alba* usually give off the characteristic odour of sulphuretted hydrogen. They are then unfit for brewery purposes. It is indispensable, therefore, to have a water free not only from organic matter but from micro-organisms, and this must be done by a thorough preliminary filtering, or better still by complete sterilisation.

CHAPTER XVII.

WATER IN DISTILLING.

WATER plays an important part in the distillery. The working of the malt may be completely spoilt by the nature of the water. This happens when the water is polluted with organic matters, which provoke a putrid fermentation of the grains, and make them unfit for malting.

The sulphuretted hydrogen has an altogether harmful action, and sometimes, without its presence in the water being revealed before steeping, it shows itself afterwards, in consequence of the reduction of the sulphates, sulphate of calcium in particular, by the organic matters under the influences of temperature and pressure. The salts of iron have also a harmful effect, inasmuch as they retard germination.

In the previous chapter the effects produced by the water in malting, according to its nature and composition, or in other words, according to the bodies it contains, have been examined, and the remarks made thereupon apply equally to the preparation of the malt in the distillery.

It must be noted that the malt for distilling, contrary to that for brewing, must be very rich in diastase and, consequently, the germ has to be developed to a greater extent. As a rule, it is allowed to grow to the length of the grain. According to Kusserow, when this is done the malt gives a wort, rich in soluble phosphate, which is excellent food for the yeast, and greatly increases its vigour.

It is evident from this that the effects produced in malting for brewing are amplified in the distillery, and therefore the composition of the water should be very attentively examined. Oxide of iron lessens the activity of the diastase of the malt by forming an insoluble compound with it, and carbonate of magnesium is also harmful to the amylase.

The varied germs, lactic, butyric and other ferments, introduced by the malt, interfere considerably with fermentation, to the detriment of the yield in alcohol and of the rapidity of the work. The

reproduction of the yeast-cells becomes slower in the presence of acetic and lactic acids, this latter considerably slackens the activity of the yeast in its alcoholic action.

In the acid process, although hydrochloric acid acts as an antiseptic with regard to certain harmful ferments, water containing them should not be used.

The reproduction of the yeast-cells is slackened by the presence of chloride of calcium in the water, and sea salt acts in the same way. When they are in sufficient proportion the salts of copper prevent the reproduction of the yeast. Sometimes even the presence of copper in the wort is detected, although the water used does not contain it. This arises from the attack of the acid on the copper basins, in which case the metallic salt enters into solution. To prevent this some makers line the stills with tin. Very vigorous yeast is obtained with sulphate waters.

In the aseptic process with *Amylomyces Rouxii*, which we owe to the researches of Dr. Calmette, Director of the Pasteur Institute at Lille, followed up by the work of Collette, Boidin and Mousain, the operation is carried out in as neutral a medium as possible, so that the diastase of the *amylomyces* can exercise its sacchariferous influence to the greatest possible extent. This process opens out a new era, and is an example of the application of a scientific discovery to practical purposes.

A very advantageous modification of the process which we owe to Mousain and Boidin, substitutes *Koji*, *mucor beta*, for the *Amylomyces Rouxii*, and with this the acidity varies, as a rule, between 0.3 gr. and 0.4 gr. per litre of wort when the vat is closed; and according as the water contains a greater or less proportion of the salts of lime or magnesia the dose of hydrochloric and sulphuric acids to be added has to be increased.

For a vat holding 1,112 hectolitres, charged with 19,200 kilogrammes of grains, forming a volume of about 1,000 hectolitres of wort, 5 litres of sulphuric acid and 15 kilogrammes of hydrochloric acid are used with normal water, and after passing with the water to the steriliser are all introduced into the vat.

Some streams receive very alkaline residuary waters from factories, as, for instance, the effluents of paper mills, and in neutralising this alkalinity a large quantity of corresponding soluble salts is formed, which may interfere with the action of *Koji* in the vat. It must be noted that *Koji* is slackened in its multiplication if the water contains salts of iron. In this case the saccharification of the starch by its diastase, analogous to the amylase of the malt, proceeds more slowly. The iron vessels are attacked by the first

portions of acidified wort, with the consequent production of ferric salts, and this must be avoided as far as possible. Both in the preliminary work in the laboratory and in the application of the process on a commercial scale, the wort employed must be thoroughly sterilised.

In the *Amylomyces* process an addition of 2 to 3 per cent. of malt is added to the vat, in order to solubilise a part of the starch, and facilitate the work of the *Koji*, which under these conditions gives a 5 per cent. higher yield of alcohol than in the acid process.

The preparation of malt in the *Amylomyces* process necessitates the same precautions, and consequently the same troubles may arise as in any other malting in the daily work in the distillery. The action of waters charged with calcic salt is very noticeable in the boiling of the grain which it hinders by forming combinations of the salts of the alkaline earths. When the vats are refrigerated with water charged with the salts of lime or magnesia, a deposit is formed on the side, which greatly retards the cooling of the vats. This should be watched and the encrustation removed with hard brushes and, if necessary, it should be cleared away with a brush dipped into water slightly soured with hydrochloric acid.

In distillation and rectification the water should contain a minimum of the salts of lime and magnesia, as in depositing they interfere with the regularity of the cooling process, and may occasion an irregular and unnatural product.

As regards the boilers, the deposits therein, their effects and the possible remedies, this question has been gone into in the chapter relating to boilers. As water containing the salts of the alkaline earths gives a precipitate which makes alcohol turbid, the distillers frequently sell distilled water with their alcohol for the purposes of dilution. The distilled water sold by some distillers is unsuitable for the purpose.

Water obtained from the condensed steam from the working parts of engines must especially be guarded against, as the steam often carries off decomposed fatty matter, which gives a disagreeable flavour to alcohol diluted with this water.

This question of distilled water is of importance, but nevertheless it is often neglected by the dealer, who frequently waters his spirits with water sold under the name of distilled water, but containing various bodies arising from the transformation of substances originally contained in the water.

For instance, distilled water containing hydrochloric acid, ammonia or even chloride of ammonium, may be met with. The water produced by the special still of Egrot, which we will describe later in writing of the purity of water in analysis, may be used for watering down spirits.

PART III.

PRELIMINARY TREATMENT AND APPARATUS.

ALL chemical substances capable of preventing the harmful effects of salts in solution in water by eliminating them or transforming them into other bodies are suitable for purifying waters on condition that they do not introduce into the water directly or indirectly other matters which may cause harmful action.

Very frequently in obviating the effect of certain salts a chemical substance is added to the water which certainly acts in this manner but leads to the production of other bodies even more harmful from the industrial point of view. It is therefore of the highest importance in the preliminary treatment of a water, to take into account not only the immediate action of the body added but all secondary reactions.

The introduction into the water of a single salt has often no harmful influence in a particular industry, but the use of several salts may lead to reactions which may cause trouble in the processes of the industry. It is these reactions which as a rule are unperceived and neglected which must be foreseen and the correct deductions must be drawn from them. The composition of a water may cause much trouble in its industrial use, and an attentive examination of the water forewarns the manufacturer and provides him with a means of preventing accidents. This examination, however, must be thorough, as otherwise the chemical substances employed as remedies may have no real efficacy.

In describing the chemical purification of feed waters in boilers we have examined the use of many reagents, the oxides of the alkalis, and of the alkaline earths, such as soda, potash and baryta, the carbonates of sodium and of potassium, chloride of barium, and aluminate of barium. These salts may also be employed in the preliminary chemical purification of waters for industrial uses, and a large portion of what we have already said applies to this subject also.

Nevertheless we will describe the employment of these salts,

paying the most attention to those which, rightly or wrongly, have been specially recommended for this purpose.

We will take to begin with the oxides of the metals of the alkaline earths, that is to say, lime, magnesia and baryta, and then proceed to the alkaline carbonates and the oxides of the alkalies.

Next we will treat of the question of the precipitation of bodies in suspension in water. The importance of preliminary chemical purification has roused the inventive faculties of machine makers and many special apparatuses have been put on the market to solve the problem of the purification of water. Consequently we will examine the working of the principal types of these machines in a special chapter.

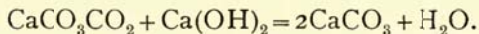
Finally we shall examine the filtration of water and the methods of freeing it from the precipitates obtained in purification by studying the most important types of apparatuses for the purpose.

CHAPTER XVIII.

SUBSTANCES USED FOR PRELIMINARY CHEMICAL PURIFICATION.

(a) **Purification by Lime.**—Carbonic acid in excess holds carbonate of calcium in solution in the water, and on saturating this carbonic acid with lime the precipitation of the neutral carbonate of calcium is brought about. Clark's method depends upon this principle.

The principle is still applied, and some really advantageous modifications have been grafted on it. The action of lime on carbonate of calcium in solution in water is shown in the following reaction:—



In the case of a simple carbonate water, that is to say holding carbonate of calcium in solution alone, the carbonate of lime is precipitated. In this case then it is sufficient to purify the water in a reservoir or special apparatus. The precipitation of the neutral carbonate of lime takes a long time if merely enough lime for the purpose is added.

To obtain a rapid separation of the precipitate enough lime is added to three-quarters of the water to precipitate the carbonate in the whole of it, then after a thorough stirring the rest of the water is added. In this way the precipitation is thorough, and takes only about eight hours.

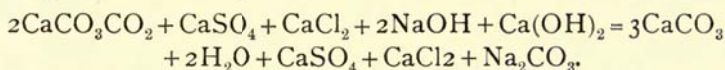
This method of procedure has the advantage that considerable and unnecessary quantities of lime are not introduced into the water. An excess of lime is often more troublesome than the carbonate of lime from which it has freed the water. Some manufacturers use lime water and to facilitate the precipitation employ special apparatuses and devices which we shall have occasion to describe in another chapter. In these apparatuses a series of reservoirs serve for the addition of the reagent and to decant the purified liquid, which is passed finally through filtering matters.

This method, however, only eliminates the carbonates of the

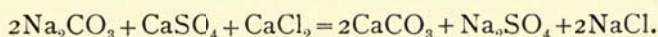
alkaline earths of calcium and of magnesium. As for the other soluble salts which are frequently found in waters, and which are the source of trouble in the industries, such as the sulphates of calcium and of magnesium, and the chloride of calcium, they are not eliminated by lime. Therefore other bodies are employed with the lime in order to eliminate the sulphates of the alkaline earths.

For this purpose the alkaline carbonates, caustic soda and potash, baryta, and the salts of barium, are employed, and these precipitate the sulphate of calcium in the water. The reagents ordinarily used along with lime are caustic soda and potash, carbonate of soda or of potash, and chloride of barium.

(b) **Purification with Caustic Soda or Potash and Lime.**—We have seen that lime eliminates the carbonates of the alkaline earth by precipitation. By adding caustic soda or potash to the milk of lime, or lime water, the sulphates of the alkaline earths, of calcium or of magnesium, and the chloride of calcium, are eliminated according to the following reactions :—



Soluble carbonate of soda is produced, which reacts in its turn on the sulphates of calcium or of magnesium and on the chloride of calcium :—



Finally, chloride of sodium and sulphate of sodium remain in solution in the water, and these are not ordinarily harmful in industrial waters.

The purification of water with lime and caustic soda combined is therefore one of the best methods, as not only does it eliminate the harmful salts but this is done without the introduction of chemical substances which lead to reactions productive of other substances harmful to industrial processes.

Several makers of special apparatus such as Bérenger and Stingl, Gaillet and Huet, Desrumaux and Dervaux, have therefore adopted this process, and highly recommend it. It must be noted that the caustic soda and potash must be carefully quantified and that the purified water must have no trace of alkalinity as otherwise its employment will lead to accidents.

For instance, if there is an excess of lime, caustic soda or potash, any metal with which the water comes in contact will be corroded, or if there is merely an excess of lime the water will lead to a waste of soap, and of the chemical products employed in certain special industries.

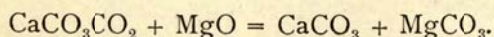
(c) **Purification by the Alkaline Carbonates and Lime.**—Caustic soda, instead of carbonate of soda, is sometimes added to the lime in purifying waters, as it is a less expensive salt.

Sometimes a manufacturer mixes together slaked lime and carbonate of sodium, taking care to have an excess of the former. In this case the lime is carbonated by the carbonate of soda, but a more rational method of obtaining the results of each of these reagents, without subjecting them to inter-reaction before they are brought into use, is to purify the water to begin with with the lime and to precipitate the sulphates of the alkaline earths with the carbonate of soda afterwards in another reservoir.

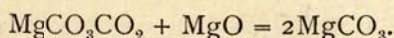
We may add that in mixing carbonate of soda and lime the carbonate of lime is precipitated and caustic soda formed; the liquor may then be decanted, and caustic soda and lime obtained only in solution, which may be used in purifying the water as in the preceding case. Instead of caustic soda or carbonate of soda, chloride of barium may be used. In this case the sulphates of calcium and of magnesium are eliminated by the chloride of barium and the carbonates are precipitated with the lime.

(d) **Purification with Magnesia.**—For some years magnesia, suggested by Bohlig, Heyne and de Derschau, has been much employed. This method depends upon the precipitation of the bicarbonates of the alkaline earths by the magnesia, which transforms them into neutral carbonate with the production of carbonate of magnesia.

Thus in the case of calcic bicarbonate we obtain:—

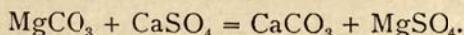


In the case of bicarbonate of magnesia the neutral carbonate of magnesium alone is formed:—



This precipitation requires heat and takes place at about 45° C.

The neutral carbonate of magnesia thus formed reacts in its turn on the sulphate of calcium in solution in the water, and precipitates it in the state of neutral carbonate of calcium:—



It will be seen that in the purification with magnesia the sulphate of lime is precipitated by the formation of carbonate of magnesium, and that the sulphate of magnesium remains in solution in the water.

We see, therefore, that the precipitation of the sulphate of calcium is subordinated to the formation of carbonate of mag-

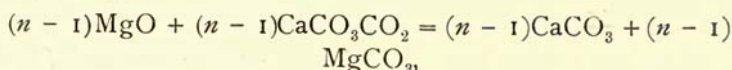
nesium, and consequently there is a limit to this precipitation which it is necessary to determine. The conditions under which this neutral carbonate of magnesium is formed must therefore be examined. Several cases present themselves according to the composition of the water.

1. The water contains bicarbonate of lime and sulphate of lime.

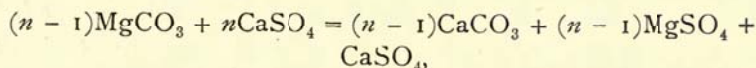
2. The water contains bicarbonate of lime, bicarbonate of magnesia, and sulphate of lime.

1. In this first case the sulphate of lime is not completely precipitated unless it is in excess over the bicarbonate of calcium.

According to the reaction :—



and the secondary reaction :—



it will be seen that the precipitation is complete as regards the $n - 1$ molecules of calcic bicarbonate, but that the molecules of sulphate of calcium are completely precipitated, and that a free molecule of sulphate of calcium still remains in the water.

Not magnesia but carbonate of magnesium must be added to precipitate this remaining sulphate of calcium :—

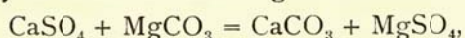


We will now calculate between what limits the proportion of sulphate of calcium should be in the water with relation to the bicarbonate of calcium, when magnesia alone is used to purify the water, without the necessity of using any other substance such as carbonate of magnesium to precipitate the remaining sulphate of calcium. As we have noted, a molecule of magnesia precipitates exactly one molecule of neutral carbonate of magnesium, which in its turn precipitates a molecule of sulphate of calcium.

As it is a question of equal molecules, we may calculate the molecular weight of sulphate of calcium and of carbonate of calcium ($\text{CaSO}_4 = 136$, $\text{CaCO}_3 = 100$).

From the preceding reactions, it is evident that water can be purified in a complete fashion with magnesia alone only when the proportion of the quantity of sulphate of calcium to that of carbonate of calcium contained in the water, given by the hydrotimetric analysis of the water, is smaller than the relation of their molecular weight, $\frac{136}{100} = 1.36$.

If, on the other hand, the relation of the quantity of sulphate of calcium to that of carbonate of calcium in the water is greater than the relation of the molecular weight, 1.36, it is necessary to add another substance, such as carbonate of magnesium, in a quantity which it is easy to calculate according to the reaction :—



that is to say, for one molecule of sulphate of calcium to be precipitated it is necessary to add a molecule of carbonate of magnesium.

To calculate the quantity of carbonate of magnesium to be added, it is necessary to note to begin with the quantity of sulphate of calcium which is capable of precipitating the carbonate formed.

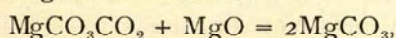
If P be the weight of carbonate of calcium contained in the water, $P \times 1.36$ will be the weight of precipitated sulphate of calcium contained in the water. If the total weight of sulphate of calcium is represented by Q there will remain still to be precipitated a weight $Q - P \times 1.36$ of sulphate of calcium.

To precipitate this weight $Q - P \times 1.36$ of sulphate of calcium the number 0.617 is the multiplier of carbonate of calcium, and the letters may be replaced by their numerical value in the following formula :—

$$(Q - 1.36)0.617.$$

This indicates the quantity of carbonate of magnesium to be added to obtain a complete purification.

2. In the second case, where the water contains carbonate of magnesium according to the reaction :—



the precipitation of a molecule of neutral carbonate of magnesium in solution in the water leads to the formation of two molecules of neutral carbonate of magnesium, which precipitate two molecules of sulphate of calcium.

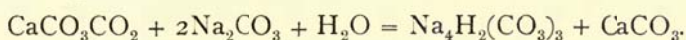
Huge quantities of magnesia are used in the iron foundries to dephosphorise iron, and hence magnesia is on the market at reasonable prices. Closson suggests that it should be extracted from dolomite. Nevertheless purification with magnesia requires great care, on account of the secondary reactions that arise. These are not sufficiently taken into account and have frequently led to industrial troubles.

We shall see later on that under its appearance of inertia sulphate of magnesium is a dangerous body in steam boilers. As the result of complex reactions it may lead to corrosion, and it must

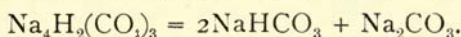
be remembered that in purifying water containing a sulphate with magnesia there is a constant production of sulphate of magnesium.

It must not be forgotten, moreover, that in addition to chloride of magnesium, which will be produced in combination with the chlorides contained in the water and is an extremely instable and very harmful body, certain reactions with very corrosive effect on the boiler may happen in the conversion of the magnesia into its hydrate. Moreover, in industries where soap is used magnesia cannot be employed, as it forms wasteful insoluble compounds with the soap.

(e) **Purification with Carbonate of Soda.**—When carbonate of soda is used, bicarbonate of lime is obtained to begin with, and the neutral carbonate of lime is precipitated with the formation of the soluble sesqui-carbonate of soda :—

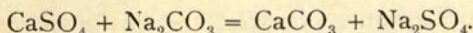


This sesqui-carbonate of sodium is decomposed in its turn into bicarbonate of sodium and neutral carbonate of sodium :—

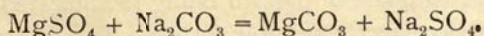


It will be seen according to this reaction that two molecules of bicarbonate of sodium are obtained, which have no influence on the subsequent reactions. It is advantageous to transform the bicarbonate into neutral carbonate of sodium and this is simply effected by heating the water to about 70°C . It then gives up one molecule of carbonic acid.

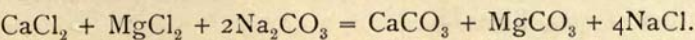
From this the introduction of two molecules of carbonate of sodium result, and these in a water which does not contain carbonate of calcium in solution give again after the precipitation of the carbonate of calcium the two molecules of neutral carbonate of sodium. This carbonate of sodium formed reacts in its turn on the sulphate of calcium, and precipitates it as neutral carbonate of calcium :—



Sulphate of sodium remains in solution, and this is not usually harmful. It may be added that the carbonate of sodium acts also on sulphate of magnesium, precipitating the magnesia as carbonate of magnesium :—



The same thing happens with the chlorides of calcium and of magnesium :—



Thus chloride of sodium is left in solution.

If the water contains only carbonate of calcium it is very easily precipitated by the carbonate of sodium even without heat.

If the water contains also sulphate of calcium, to purify it economically the sulphate of calcium must not be in excess of the carbonate of calcium contained in the water. In this case it is necessary to calculate the quantity of carbonate of sodium required to precipitate the carbonate of calcium.

In making this calculation if the relation of the quantities $\frac{\text{CaSO}_4}{\text{CaCO}_3}$ given by analysis are less than 1.36, there is no necessity to add carbonate of sodium.

If the relation $\frac{\text{CaSO}_4}{\text{CaCO}_3}$ is more than 1.36 carbonate of sodium must be added.

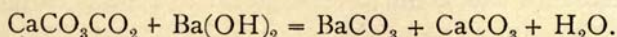
If 0.779 is the multiplier of carbonate of sodium, P the weight of carbonate of calcium contained in the water, as ascertained by hydrotimetric analysis, and Q the total weight of sulphate of calcium, the quantity of carbonate of sodium to be added to the primitive quantity to precipitate all the sulphate of calcium contained in the water will be given by the formula :—

$$(Q - 1.36 P) 0.779.$$

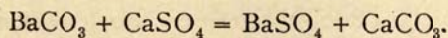
In practice, rather more than the theoretical amount is added.

In some industries there is no danger in introducing an excess of carbonate of sodium, as for instance in correcting waters for soap manufacture, but in others the amount to be added must be carefully calculated, otherwise the carbonate of sodium in excess may attack metals, and in particular the boiler-plates.

(f) **Purification with Baryta and the Salts of Barium.**—In the case of caustic baryta, both the carbonate and the sulphate of calcium in solution in the water are precipitated:—

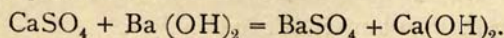


Carbonate of barium is obtained and this in its turn acts on the sulphate of calcium in the water :—



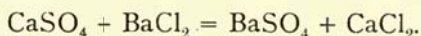
If these two reactions alone are produced the carbonate of calcium and the sulphate of barium being precipitated and eliminated, the water is perfectly suitable for use.

Another reaction may take place. The caustic baryta may act directly on the sulphate of calcium, and in this case there is a formation of quicklime :—



This quicklime or caustic lime being soluble, remains principally in solution and may lead to trouble. It will corrode the metal of the boilers and lead to the formation of insoluble calcareous soaps if it is used in an industry where soap is used.

To avoid this, the sulphate of calcium is precipitated with chloride of barium. In this case sulphate of barium is precipitated and chloride of calcium remains in solution :—



This chloride of calcium is also harmful in boilers, and in the industries in which soap is used, as it leads to a great waste of soap by forming insoluble compounds of lime. It may be added that carbonate of barium is also used to purify water, and sometimes oxalate of barium or aluminate of barium are employed.

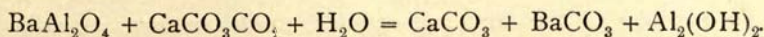
(g) **Purification with the Alkaline Oxalates.**—Carbonate and sulphate of calcium are precipitated with the alkaline oxalates.

The advantage of this process is that carbonate of sodium is obtained, which reacts in its turn on the salts of calcium, as we have already shown. On the other hand, the oxalate of calcium which is precipitated can be easily regenerated by introducing it into a solution of carbonate of sodium brought to the boil.

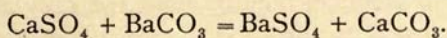
If the oxalate is properly regenerated, taking into account the saving caused by the formation of the carbonate of sodium and calculating exactly the amount of alkaline oxalate to bring about complete precipitation, this process is commercially practicable and economical. As for the use of oxalate of barium, it has the same advantages as the alkaline oxalate.

(h) **Purification with Aluminate of Barium.**—With aluminate of barium both the carbonate and sulphate of calcium can be precipitated at once.

When the calcic bicarbonate is in solution in the water, the reaction is :—



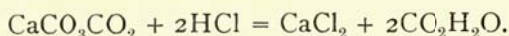
Although a secondary chemical reaction does not occur, as in the case of aluminate of sodium, which gives carbonate of soda, the carbonate of barium nevertheless acts on the sulphate of calcium and precipitates it in the form of sulphate of barium :—



To precipitate the sulphate of calcium remaining in the water aluminate of barium is added which precipitates it as sulphate of barium. When the solution is not acid, aluminate of calcium is also formed.

(2) **Purification with the Acids.**—With the acids and in particular hydrochloric acid, the carbonates of the alkaline earths are transformed into soluble chlorides without energetic action on the sulphate of calcium.

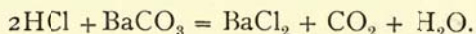
With the bicarbonate we obtain :—



That is to say, chlorides of the alkaline earths are produced which are not absolutely harmless.

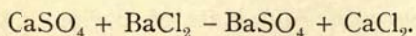
For instance, in boilers they may be decomposed and this will lead to corrosion. Moreover, in the industries using soap water purified in this way will lead to trouble, as the carbonates are simply transformed into chlorides, and the metal of the alkaline earth still remains, ready to form insoluble soaps.

Although an exact calculation is made to know the quantity of hydrochloric acid to introduce into a water, in practice it is difficult not to have any excess of it, and to remedy this it is usual to pass the water acidulated with hydrochloric acid over carbonate of barium. In this passage the free hydrochloric acid is saturated with barium, and chloride of barium is formed which remains in solution :—



This reaction is produced slowly, and it is advantageous to heat the water a little to hasten it.

The chloride of barium thus formed reacts in its turn on the sulphate of calcium, and the result is sulphate of barium, which precipitates :—



Chloride of calcium, however, still remains in solution.

COMMERCIAL ANTI-INCRUSTORS AND THEIR USE.

In addition to the numerous bodies which we have described used as purifiers of water, whether for steam boilers or for industrial use in general, certain specialities are put on the market which are mixtures of these bodies or others having analogous reactions on the salts contained in water.

Some of these products may be used not only as additions to the feed water to act as anti-incrustators and disin crustators, but they may also be used in the preliminary treatment of water before industrial use, and can be employed with the special apparatus for the purpose. Among these may be mentioned Volant-Eckhout's "Calcophobe". This is a mixture of neutral alkaline oxalates, of

the salts of barium and of a vegetable extract; this mixture varies in nature and proportions according to the composition of the water and whether it is to be used in a cold or hot solution.

We have already studied the various efficacious reactions which the neutral alkaline oxalates and the salts of barium give with the salts contained in water. In the products of Asselin and Daudé use is made of aluminate of barium.

It is satisfactory to note that these products are not sent out for use until the maker has ascertained the composition of the water with which they are to be used and has obtained other necessary information. These products cannot be used efficaciously and with economy unless they are specially mixed according to the nature of the water, and unless the proportion to be used with such and such a water is accurately calculated. This necessity was formerly neglected, but it has been taken into consideration by several makers of these products, and tends more and more to become the general rule.

We may note, for instance, Neulat's "Anti-Tartre," the Société le Sélénifuge's "Sélénifuge," and Egrot's "Hydrhyaline".

For instance the following information is required by the Neulat firm :—

1. Hydrotimetric degree of the water, or one litre of it for analysis.

2. Type of the boiler, tubular, semitubular or multitubular.

3. Horse-power or quantity of fuel burnt per day.

4. Number of working hours per day.

5. Number of working days per month.

6. Is there any crust in the boiler?

The "Sélénifuge" makers ask the following questions :—

1. A litre of the feed water for analysis.

2. Type of the boiler, full particulars.

3. Quantity of fuel burnt per day.

4. Quantity of water evaporated per day.

5. Number of working hours per day.

6. Number of working days per month.

7. Usual interval between complete stoppages for boiler cleaning and examination.

Among other well-known products we may mention Rodriguez Castroman's "Lithophage," Couchemann and L. Gilis's "Solvéine," L. Jémart's "Calsoline," Constant's "Tartriphage," Carton et Cie.'s "Anti-Calcaire," Boileau's "Désincrustant," Compère and Faucher's "Végétaline," Hamelle's "Anti-Calcaire," Bretel's "Anti-Tartre," Néron's "Anti-Incrustateur," Lavoix's "Désincrustant," Lachery's

"Expurgine," Drevdal's "Neutraline," Cambray's "Anti-Calcaire," Saurel's "Désincrustant," Meyher's "Tartrol," Fleury Legrand's "Briquette," Frémier's "Colorado," Sayer's "Désincrustant," V. Acker's "Désincrustant Indien," L. Normand's "Anti-Tartre," Lhéritier et Cie.'s "Anti-Tartre Chatillon," Trotoux's "Désincrustant," Roux's "Nihil-Tartre," Périmbert's "Désincrustant," Magnet's "Paratartre," Taillandier's "Désincrustant," Main's "Anti-Tartre," Nivet's "Tartrifuge," Weiss's "Lithoréactif," Raby and Willain's "Capnomore," Gissler's "Parasel," Pistre's "Désincrustateur," etc.

These various products may be used by introducing the proper proportion of the speciality preferred into the boiler once a month,

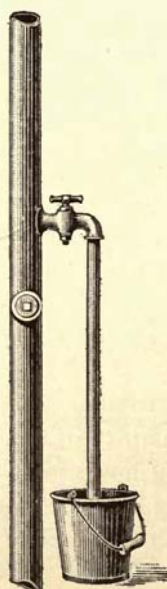


FIG. 68.—Device for introducing disincrustants into the boiler.

but it is preferable to use them daily, taking strict account of the volume of water employed. The products are mixed either by using the feed cistern, the pump or the injectors.

If there is no feed cistern the product may be introduced very simply by the arrangement shown in fig. 68. Here a tap is fixed in the suction pipe of the boiler, and connected by means of an indiarubber tube with a bucket containing the disincrustant in solution. In order to introduce the disincrustant into the boiler all that has to be done is to turn on the tap connected with the bucket by the indiarubber tube and to turn off the principal tap shown in the middle of the suction pipe. A method recommended by Volant-Eckhout consists in fixing a small reservoir similar to a

lubricator on the suction tube. This has an upper and lower tap as shown in fig. 69.

The reservoir is filled with disincrustant by opening the upper tap, then after having shut this the lower one is turned on, and the disincrustant is distributed.

Deloffre's apparatus for use with either liquid or solid disincrustants is composed of a reservoir D provided with a screw cover C, and a clearing out tap B in the lower part.

This apparatus is fixed as shown at E on the tube of the feed

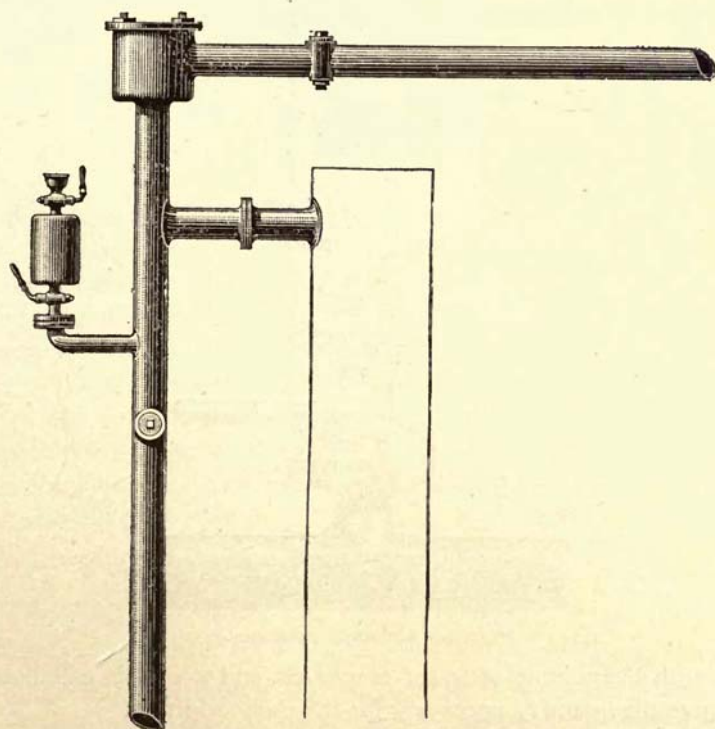


FIG. 69.—Arrangement to introduce disincrustants into boilers.

pump as near as possible at the safety valve. In working, the tap is shut and the water is run off by the tap at B. This having been done, the cover C is screwed off, the tap B is closed, and the disincrustant is put into the reservoir D.

After having screwed down the cover C tightly, the tap letting the disincrustant into the pump is gradually opened, and the disincrustant is forced into the boiler.

Some disincrustants have not well-determined chemical action on the salts contained in the water, but for all that give favourable results. In using them, it is just as necessary as in the case of the

products with well-determined chemical action to gauge the proportion needed according to the nature and volume of the water. In order to do this, a series of experiments are made with the disincrustants, diminishing the proportion used until the minimum dose consistent with efficacy is discovered.

This minimum will be the proportion of the disincrustant to be

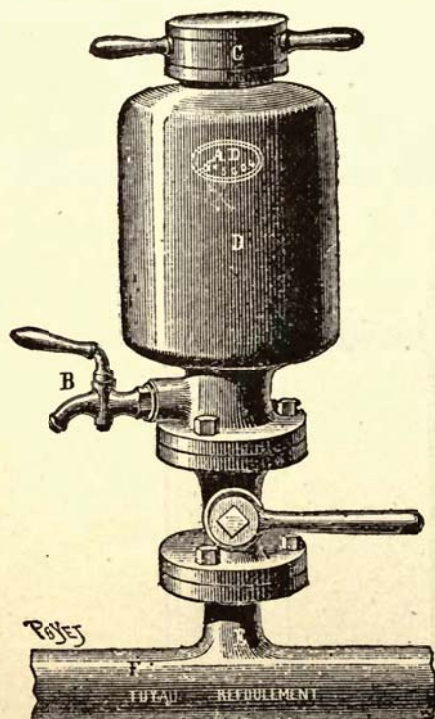


FIG. 70.—Deloffre's apparatus.

used with the volume of water employed, and a simple calculation will give the quantity necessary for the daily addition.

In the case of dye-works, finishing-works, bleach-works and paper-mills, where these various products are used, we recommend that their makers should be told exactly the nature of the business carried on, and in this case the makers should modify their specialities to suit the particular industry.

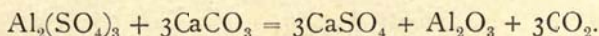
CHAPTER XIX.

PRECIPITATION OF MATTERS IN SUSPENSION IN WATER.

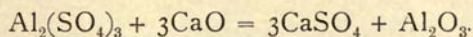
FOR ages past the Chinese and Indians have cleared waters rendered turbid by matters in suspension by using alum. This method is still applied, and can be employed not only to precipitate the matters in suspension in the water, but also in the case of very finely suspended precipitates produced by various reagents used to soften water.

In purifying water the precipitates produced ought to aggregate quickly and deposit, otherwise a long and troublesome filtration is required and the very finely suspended particles are sure to clog the pores of the filter. The use of sulphate of alumina depends upon the formation of a precipitate of alumina, which quickly carries down with it all matters in suspension in the form of lakes.

The alumina is precipitated from its sulphate in the presence of the alkaline carbonate:—



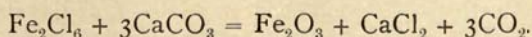
Or of lime:—



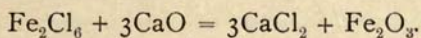
According to this, it will be seen that in purifying water with lime some sulphate of alumina should be added in order to carry down the precipitate and to obtain a rapid filtration.

The proportion to be used is about 10 grammes per cubic metre of water. The salts of iron may also be employed instead of the alum, but of course in this case the precipitate obtained is the hydrate of ferric oxide, which plays the same part as the alumina.

With perchloride of iron and the alkaline carbonates, the following reaction is obtained:—



With lime, it is as follows:—



The perchloride of iron is reacted upon by the lime or carbonate of lime, and in addition to the ferric oxide formed soluble chloride of calcium is obtained. In many cases this chloride of calcium may be troublesome if the reagents added to purify the water do not transform it into another salt, for instance into an alkaline chloride which is perfectly harmless.

CHAPTER XX.

APPARATUS FOR THE PRELIMINARY CHEMICAL PURIFICATION OF WATER.

P. Gaillet's settlers.—The vertical settler is formed of a rectangular tank, containing 15 shelves at an angle of 45° , and fixed alternately on opposite sides of the tank. They form as it were a series of buckets, each of which can be drained by a tap. The purified water to be cleared enters the apparatus at the bottom, and, arriving at the first shelf, follows the ascent of the slope, and thence passes to the shelf next above, which it descends, and then goes up the next shelf, and so on to the last, by which time it is entirely freed from solid particles.

On account of the slope of the shelves, the suspended matter which becomes deposited on them goes down to the angles at the side of the tank, where the pressure of water makes its removal easy on opening the tap. In this way clarification is facilitated, for the circulation of the water takes place where there is least deposit.

Figs. 71 and 72 represent a vertical purifier with reservoirs for reagents. In this arrangement the supply of reagents and water is assured by constant level regulators, depending on the action of floats on an inlet valve. The outflow is regulated with precision by taps, or valves worked by a rack and pinion.

By means of an indiarubber pipe, with floats in the reagent-reservoirs, the purest part of the liquid is drawn off, which passing into the settler, acts on the water to be purified, and precipitates the salts of the alkaline earths from the water.

Like the vertical settler, the horizontal one has inside a series of shelves, slanted so as conveniently to collect to one point the solid matter. The metal tank which receives the water to be purified is of rectangular form, with a triangular part at the bottom which has faces with the same slope as the shelves. By this arrangement the solid particles slide easily over the shelves and collect at the lower part, which is provided with a tap for getting rid of them.

To prevent the current in its ascending movement hindering the

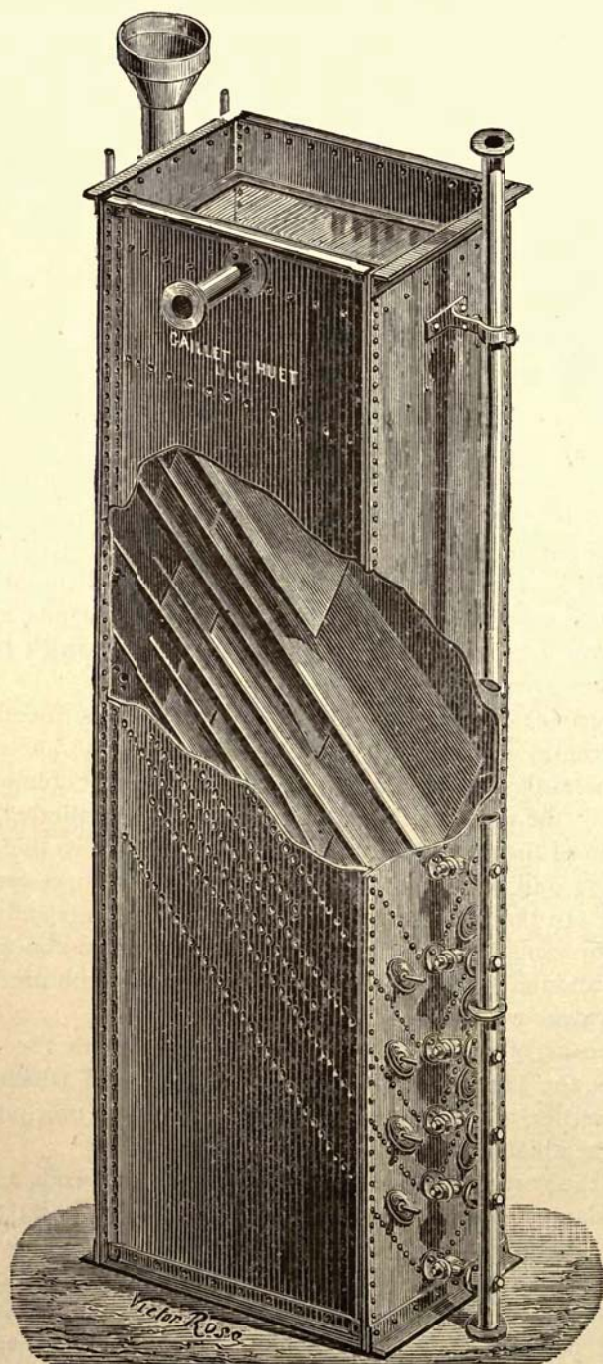


FIG. 71.—Gaillet's vertical settler.

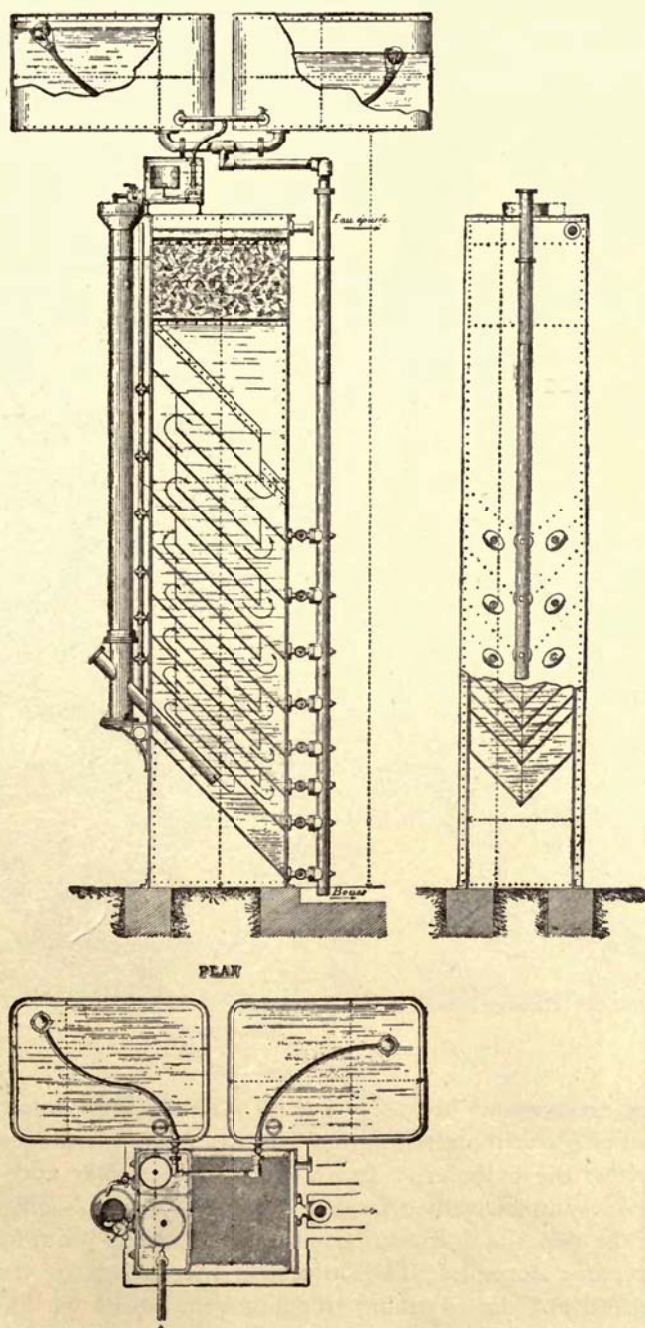


FIG. 72.—Gaillet's vertical settler in section.

settlement of the precipitate, the shelves are prolonged into the deposit-receiving vessel, into which, therefore, the solid particles slide straight off the shelves.

The liquid passes through holes in the shelves, and the edges of the holes are turned up to prevent the solids meeting in their descent. Let us add that a filter is attached to the settler and completes the clarification.

P. Gaillet's Cylindrical Purifier.—This is composed of a cylindrical

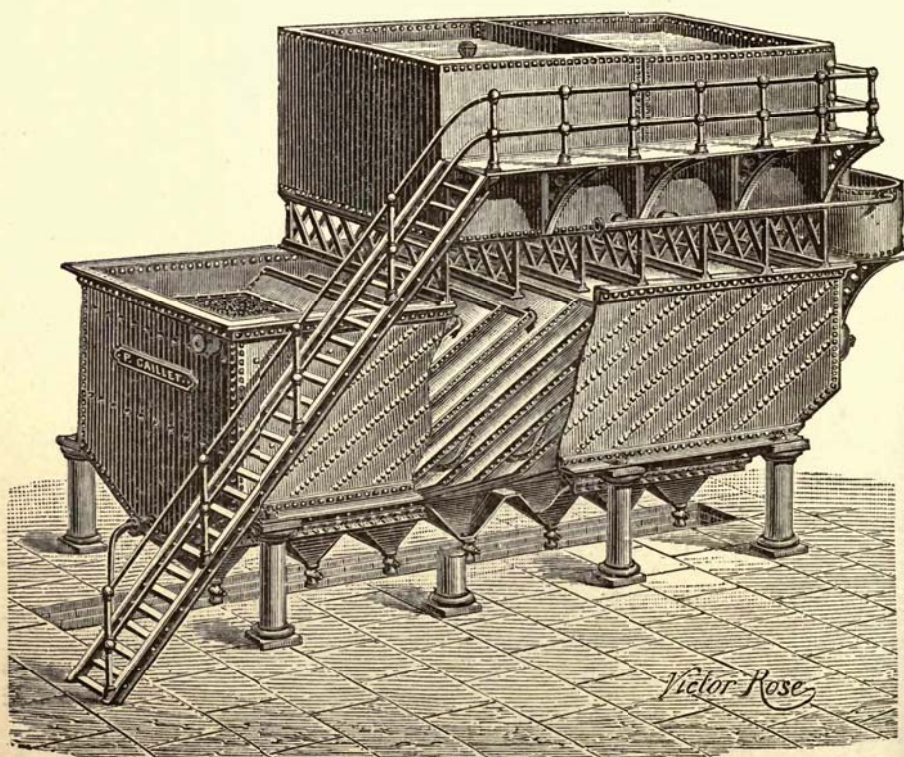


FIG. 73.—Gaillet's horizontal settler.

receiver, terminating below in a cone with an emptying tap. A series of pieces of metal, fitting one into another is arranged along the axis of the cylinder. These pieces are circular and pierced with holes symmetrically arranged and covered with a jacket which directs the deposits downwards, and prevents them from following the ascending currents. The surfaces of the shelves are triangular with turned-up edges forming trenches from the centre to the circumference, in which the water to be clarified rises over their whole extent.

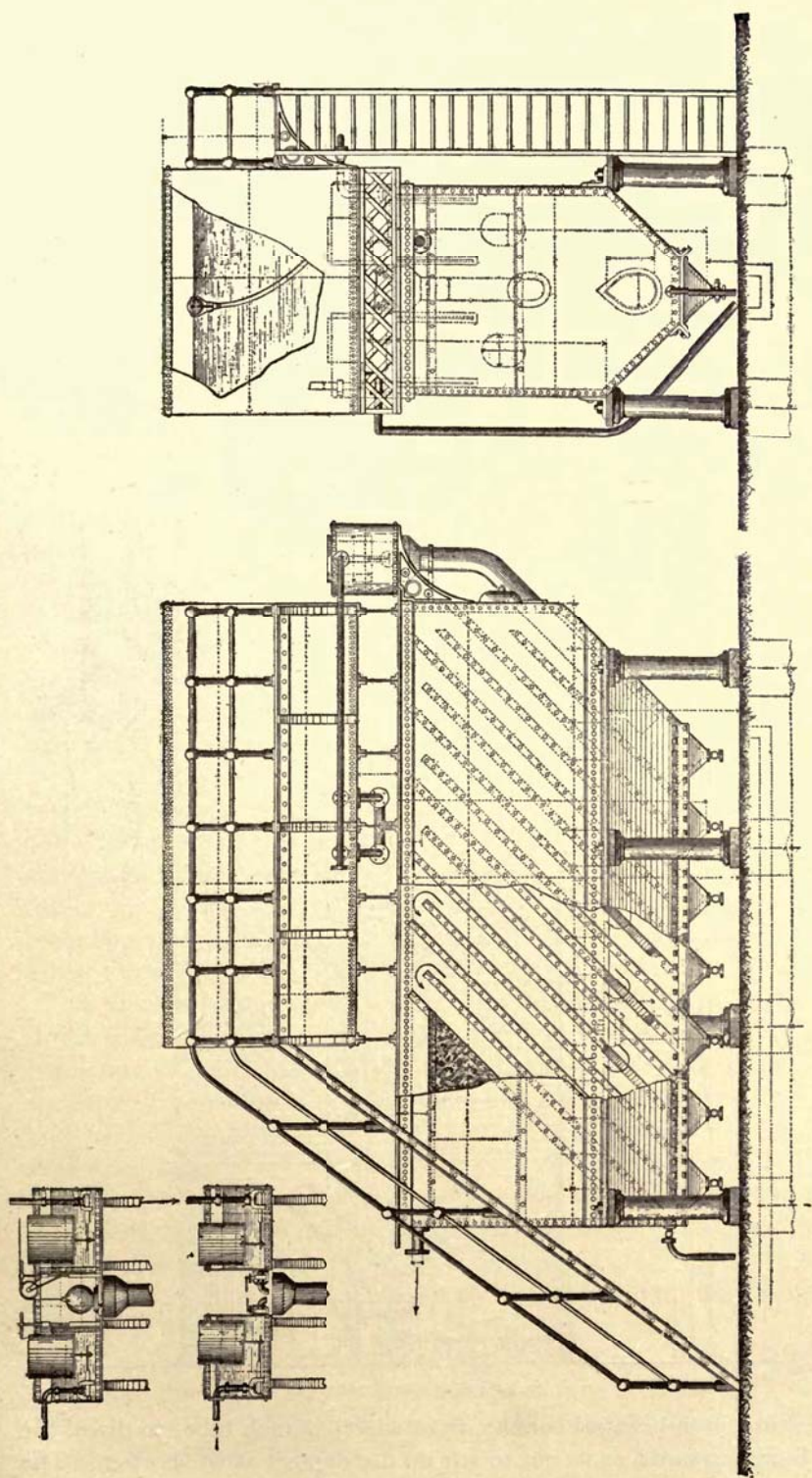


FIG. 74.—Gallet's horizontal settler (complete plant).

The water to be clarified enters the settler at the bottom through

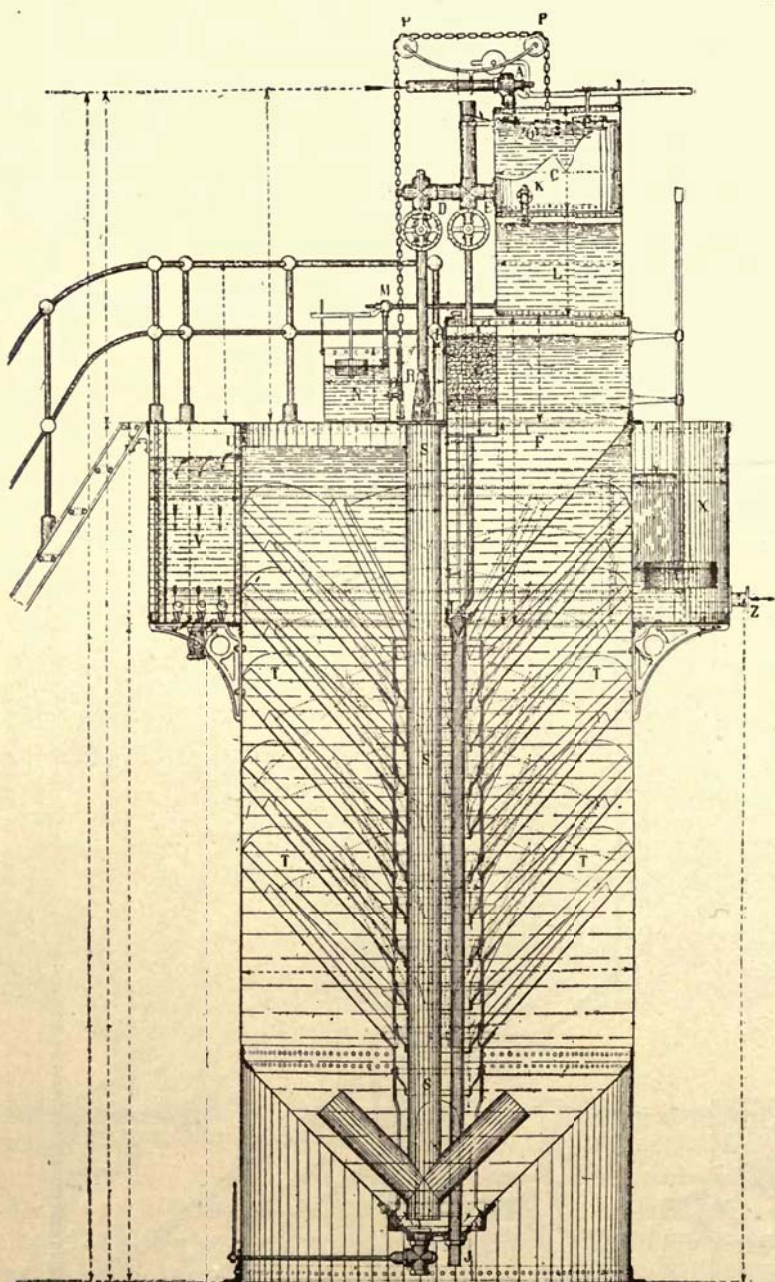


FIG. 75.—Gaillet's automatic purifier.

a tube in the central column, from which branch tubes to direct the liquid upwards, so as not to stir up the deposit at the bottom. The

water rises by the trenches of the first storey, and having traversed them meets the unperforated parts of the upper storeys, and is thus forced to pass above the deposits.

It is to be noted that the orifices in a central part correspond to the unperforated places of the contiguous parts, so that the trenches in one set of shelves correspond to unperforated parts of the contiguous sets. This arrangement changes the course of the water without abruptness, and the circulation takes place in thin streams, which favours the settlement.

As to the deposits which form on the shelves, they slide over them, and pass regularly into a central tube which takes them to the bottom of the apparatus. A filter, formed of an annular space concentric with the settler, can be divided into two parts, to enable it to be cleaned without stopping the purification. The water, on leaving the settler, passes through a channel which takes it under the filters, through which it passes to a reservoir which receives the purified water.

The apparatus for preparing the reagents is usually placed above the settler. It is terminated by a cone which penetrates into the settler. It communicates by an outlet valve and a pipe with the base of the latter, which receives the deposits from it.

If lime only is used in the purification of the water, a distributing vessel ensures a properly proportioned flow of reagent and water, but if other reagents are employed, such as soda, ferric chlorides, aluminate of soda, etc., they are introduced into reservoirs on the top of the purifier, and with automatically regulated outflows. It must be noted that Gaillet contemplates, in his apparatus, the combined use of lime and soda.

In the preceding figure, which represents a section of a cylindrical purifier with an external filter, the water is introduced by a regulating valve A, worked by a float B, according to the level of the water to be purified, which is poured into the distributing vessel C, and leaves it by another valve D, leading to the purifier. Another regulating valve E takes some of it into the reagent saturator.

The automatic lime-water saturator F communicates with a receiver G, where the lime is slaked automatically. It has at its bottom an emptying valve I and an opening J for cleaning it. Thus prepared, the lime-water leaves by the channel H into the supply tube S of the purifier.

A tap K, fixed to the distributing vessel G, leads a part of the water into the soda-reservoir L or into reservoirs of other reagents. It then passes by the regulating valve M into a distributing vessel N for soda or other reagents.

The output of soda is regulated by an automatic valve O, or stopped by the arrangement P P, in which a float Q, the position of which depends upon the level of the water in C, regulates the ball-cock O. The reagents are then mixed in a receiver R whence they pass into the supply tube S of the purifier T, provided with its shelves and emptying tap.

After having deposited its sediment on the shelves, the water passes by the channel U into the compartment V, then underneath the filters by the openings W. The water is collected after filtration in a special reservoir X. A float Y regulates the starting and stopping of the action. The water leaves by the opening Z after having been purified and filtered.

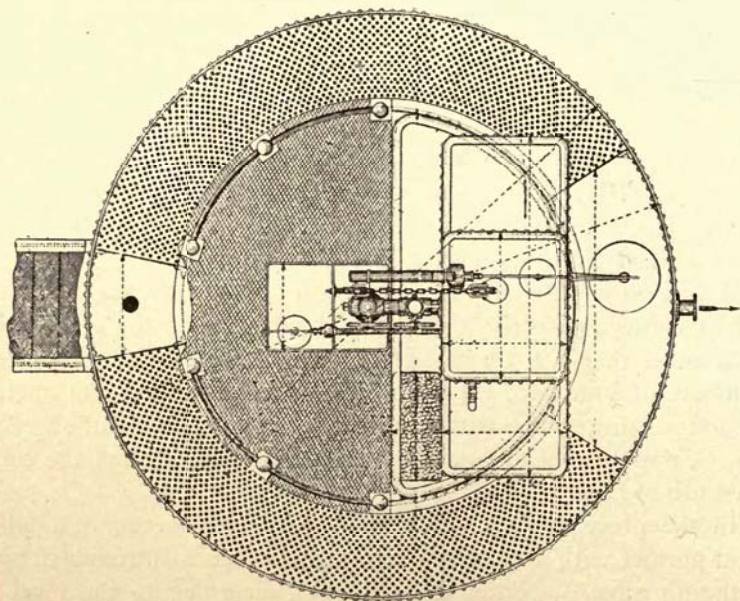


FIG. 76.—Gaillet's cylindrical purifier (plan).

Berenger and Stingl's Apparatus.—This consists of a series of purifiers, generally three, that number being usually sufficient.

The water to be purified, and also the reagents, pass by two pipes governed by graduated taps into a metal receiver where they are mixed together. The mixture of water and reagents then overflows into an outer concentric cylinder which terminates below in a vertical pipe.

The water mixed with the reagents descends by this vertical pipe into an inverted metal cone supported by a tripod, and overflows the cone into the cylindrical reservoir which contains it.

The water deposits part of its precipitated matter, which falls

into the cylindro-conical lower part of the reservoir. The mud is expelled by means of a tap at the bottom.

The overflow from one purifier passes into the next by a gutter communicating with the upper part of the first purifier and leading into a horizontal pipe. Leaving this horizontal pipe, the water descends the vertical pipe which comes after the horizontal pipe and passes into the second purifier, where it gets rid of its suspended matter which settles at the bottom. The water passes from the second into the third purifier in the same way.

On leaving the third purifier the water is filtered by passing

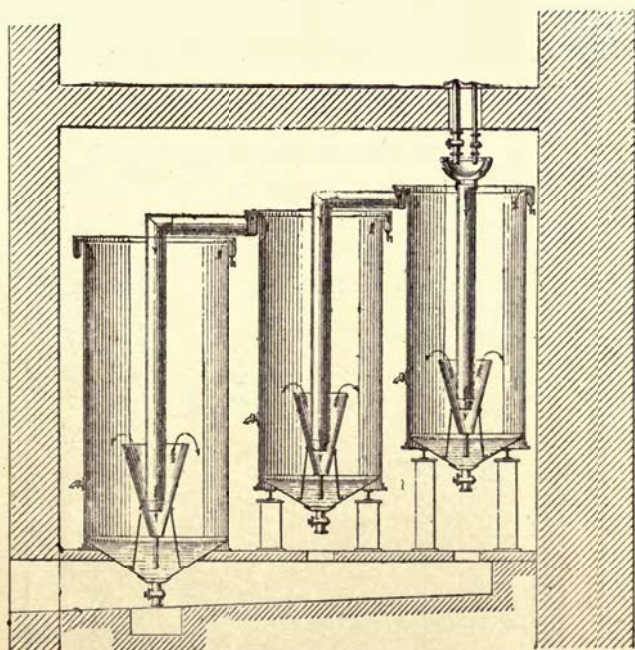


FIG. 77.—Eerenger and Stingl's apparatus.

upwards through a layer of wood-fibre or other filtering material enclosed between two pieces of wire netting. The purified and filtered water then flows into the feed-reservoir.

H. Desrumaux's Automatic Purifier.—In the Desrumaux purifier (fig. 78) the water enters by a pipe A, and passes into a distributing vessel B, from which the water to be purified falls, in quantities regulated by the valve C, upon the water-wheel E, and thereby driving the stirrer of a saturator J. The water leaving the water-wheel, or hydraulic motor, passes by the channel F to the settler M.

The various reagents are prepared in a reservoir G, and their outflow from it is regulated by the ebonite float I. On the left side

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of the distributing vessel B is placed a valve D, which serves to

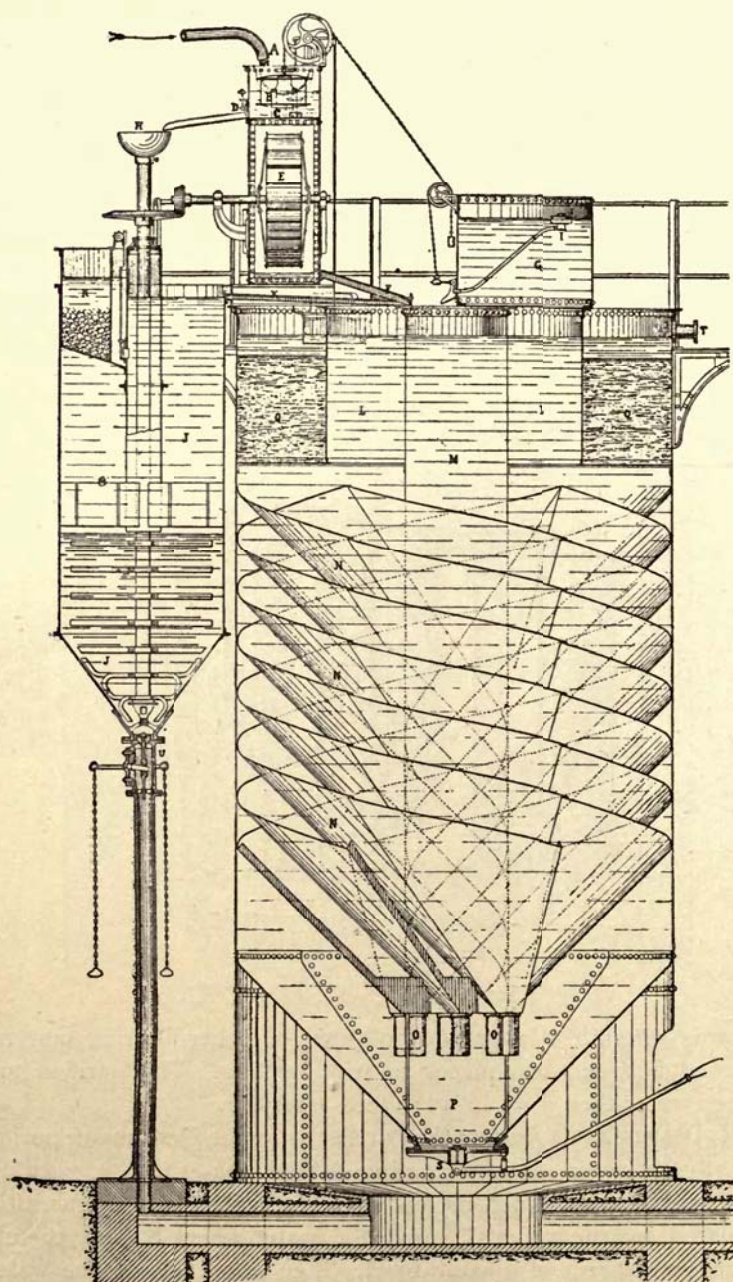


FIG. 78.—Desrumaux's automatic purifier.

regulate the flow of water to be made into lime-water, and which passes by the funnel H into the saturator J. This saturator is

provided with an automatic lime-slaker R, and a discharging valve U at the bottom of it.

A channel K brings the concentrated lime-water into the central column M of the settler, which can be cleaned by means of the free annular space LL.

Helico-conoidal plates N form a continuous depositing surface,

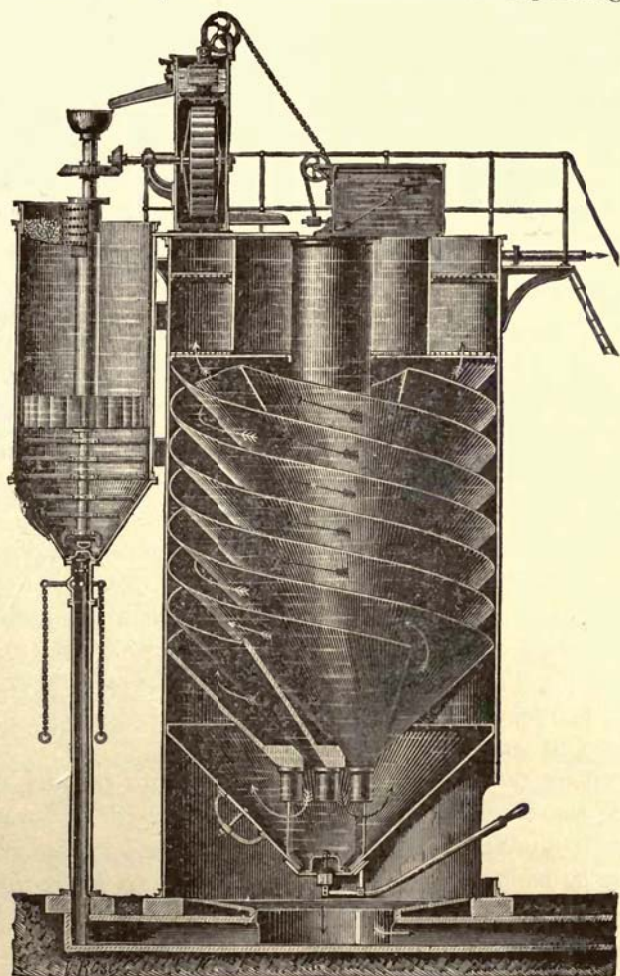


FIG. 79.—Desrumaux's purifier (interior view).

which can be cleaned without taking the apparatus to pieces, simply by turning in a stream of water by the annular space LL.

The helico-conoidal shape of these surfaces directs the mud to the lower part of the apparatus, into the collection OO, and thence, finally, into the mud-reservoir P, which is provided with a valve S for emptying it.

A filter QQ completes the apparatus, and the purified water leaves by the pipe T.

We see then, in the Desrumaux purifier, two perfectly distinct kinds of operation carried on: (1) The precipitation of the salts dissolved in the water by appropriate reagents prepared in special reservoirs, and (2) the separation of the precipitate formed and also of suspended matter, such as oxide of iron, sand, iron and organic debris of all kinds.

The reagents soluble in water are distributed easily enough, in proportion to the volume of water to be purified, but the regularity of the distribution requires the use of a specially constructed apparatus. The regular distribution of the reagents is secured by taking the solutions by means of a regulating float of ebonite into which they enter by a hole pierced in the central tube of the regulator.

This central tube is connected by a side tube to a flexible discharge pipe, and is kept by the annular float at a constant distance from the surface of the liquid. In this way a regular and constant flow of liquid is secured.

By raising or lowering the central tube of the regulating float, the flow from the reagent reservoirs can be reduced or increased at pleasure. The regulating floats being made entirely of ebonite are not attacked by acid or alkaline reagents.

As to the preparation of the concentrated lime-water, it presents rather more difficulty, for the lime is always mixed with foreign matter, so that different proportions of it have to be used to get complete saturation.

The preparation of this reagent is based upon the fact that water, in the presence of an excess of lime, dissolves about $1\frac{1}{4}$ grammes of it to a litre.

Everything then, in obtaining a fixed weight of lime, depends on taking the corresponding volume of saturated lime-water.

There is no necessity to prepare lime-water by stirring up lime and water by hand, for the Desrumaux apparatus is provided with a lime-water saturator, in which the water is saturated with lime by means of an automatic stirrer driven by a water-wheel set in motion by the water to be purified.

The lumps of lime are put into a semicylindrical vessel, where it is slaked with water. The water used in preparing the reagent is brought by the central tube, which it leaves at the lower end.

To charge the apparatus the lime is put into the stirring-chest by means of a rack and pinion valve which governs a central pipe whereby the bottom of the slaker communicates with the stirring-chest.

After saturation and clarification, the lime-water leaves the saturator at the top, mixes with the water to be purified which falls from the water-wheel, and mixes at the same time with the other solutions coming from the reagent-reservoir on the top of the settler.

As soon as they come into contact with the water to be purified the reagents precipitate the salts dissolved in it, and the precipitates have to be collected, and the water rapidly clarified to finish the operation. This is done in a settler with helico-conoidal surfaces, and consisting of a large vertical cylindrical vessel, closed below with a conical bottom provided with a discharge valve.

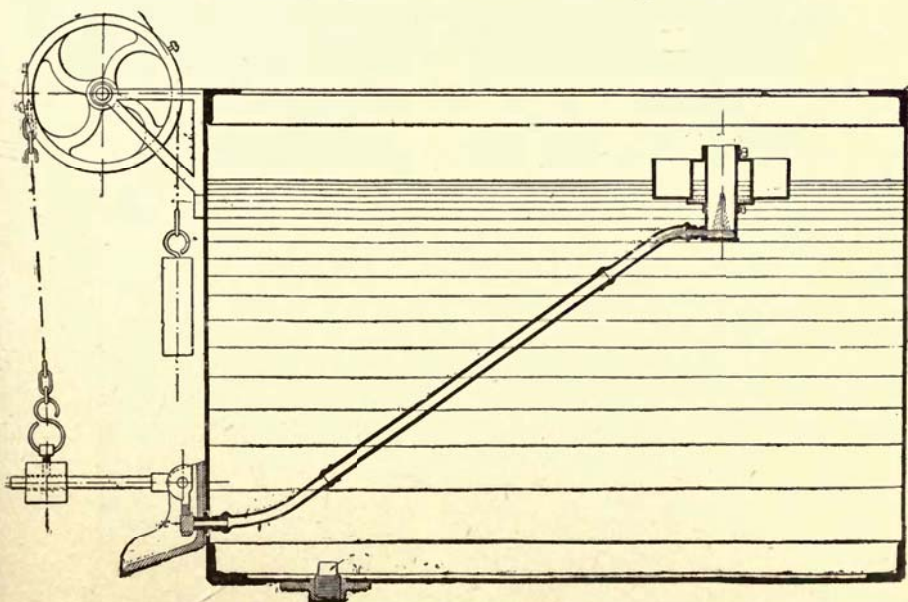


FIG. 80.—Reagent tank of Desrumaux's purifier.

In its central part there is a cylinder open at both ends, round which are rolled several ranges of metal plates, which slope like the sides of a cone and are drawn out into a spiral. This is why their surfaces are called helico-conoidal.

By reason of this shape the plates cause a rapid descent of the solid particles, precipitated or in suspension, which are led into the sludge drum. The purified water passes finally through a filter consisting of wood-fibre lightly compressed between two perforated iron plates.

Dervaux's Cold Purifier.—This purifier is constructed to receive any two reagents intended for purifying water, but its constructor contemplates the use of soda and lime.

In consequence, the apparatus consists of a lime-water saturator, a distributor of soda-solution, a settling reservoir, and, finally, a filter. A distributing vessel A, divided into two compartments R and Q, contains the water and the crude lime.

The water to be purified arrives into the reservoir R by a pipe,

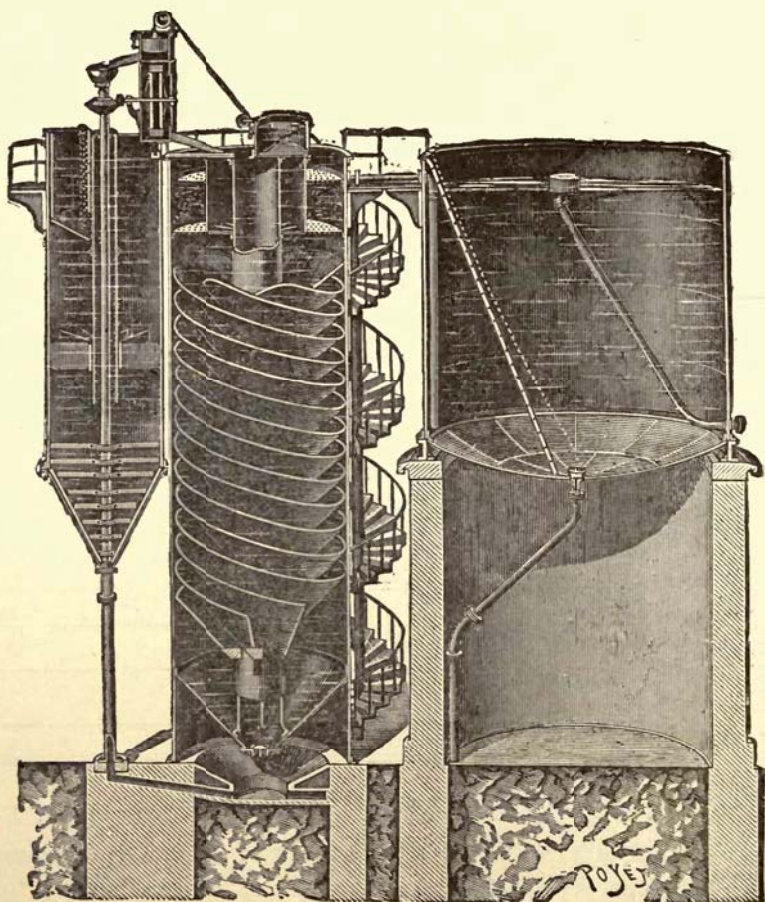


FIG. 81.—Desrumaux's purifier as installed on the stations of the Jaffa and Jerusalem Railway.

and is thence distributed by the openings V, M, P, and their corresponding pipes, into the receivers S, N, D.

The openings V, M, P are regulated by gauges in accordance with the composition of the water to be purified, so as to pass larger or smaller quantities. The crude lime is in the reservoir Q, and has previously been slaked and freed from stones. When it is transformed into milk-of-lime, it can be used. It is run, once

a day, into the receiver S, through the pipe O which goes to the bottom of S, by opening the tap G.

This receiver S, or automatic conical lime-water saturator, is composed of a conical receiver, furnished at its base with a discharge valve for the exhausted lime.

The water to be purified, brought by the pipe K, whose opening V is regulated by a gauge according to the composition of the water, mixes with the milk-of-lime brought by the pipe O.

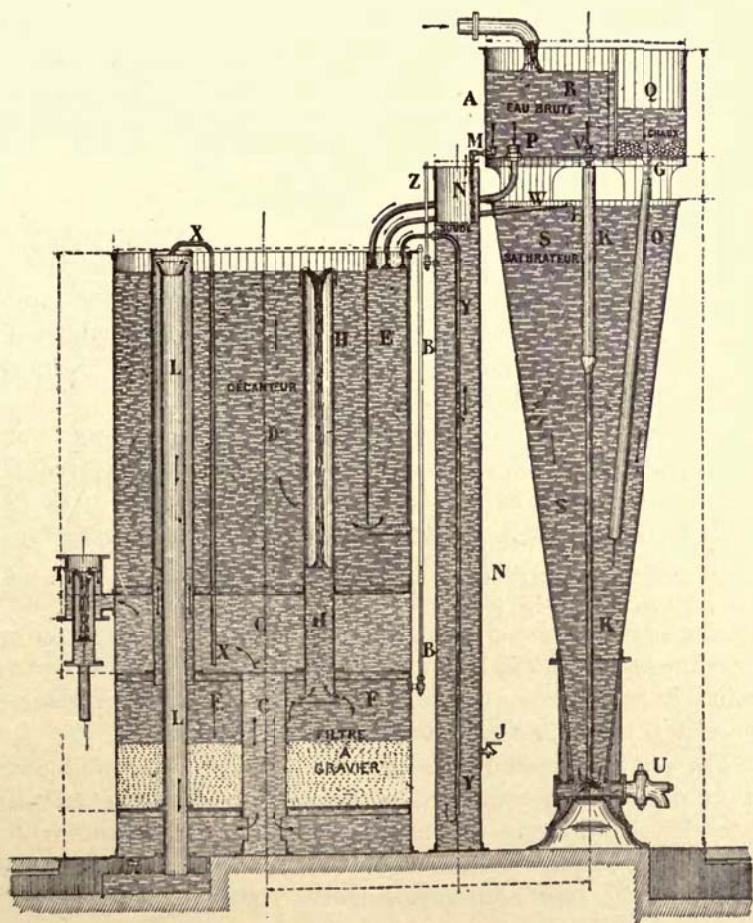


FIG. 82.—Dervaux's automatic purifier.

Owing to the conical form of the saturator, and to its consequent progressive widening, the rate at which the liquid ascends diminishes in proportion as it rises, and causes the saturation and the clarification of the lime-water. The lime-water thus saturated is clear, and passes by a pipe W into the chimney E, into which pass also

soda and the water to be purified. The automatic soda-distributing column N is formed of a cylindrical receiver or column, into which the water is introduced by the pipe M regulated by its gauge.

A pipe Y, going to the base of the column, serves to direct, by an ascending movement, the solution of soda which is poured every day into the upper part of the cylindrical receiver, into the shaft E.

The mixture of lime, soda, and water to be purified, in the proper proportions known from the analysis of the water, takes place in the shaft E. Thus the liquids descend into the settling reservoir D, where the mud settles to the bottom.

The purified water descends by the chimney H into a filter F, provided with an automatic cleaning syphon, and consisting of a layer of gravel supported by a perforated iron plate. The water passes down through the gravel into a reservoir G.

Thus purified and clarified, the water leaves the apparatus by the pipe T. If the deposit is so great that the water cannot get through the gravel, the water to be filtered rises from the reservoir F into the annular space of the pipe T and returns into the pipe L.

The water of the reservoir C is then drawn up, and, passing through the gravel from below, drives the mud out of the gravel and out of the apparatus.

Finally, in Dervaux's purifying system, the saturating cone S, the reagent-column N, and the automatic filter E, can easily be separated from one another.

Clarke Atkins and Porter's Apparatus.—This apparatus is mostly used in England.

The reagent is prepared in a special lime reservoir, the water entering from below and saturating itself with lime. A stirrer promotes the operation. The water saturated with lime rises, leaving behind it the excess of lime, and passes into another reservoir where it is stirred up with the water to be purified.

The purified water leaves this reservoir at the top, and passes into a filter press, composed of a series of perforated cast-iron plates, between which is the filtering medium, such as cotton.

The water, charged with reagent and precipitated matter, enters the filter by a pipe and traversing the filtering medium issues at the other end of the filter-press from a pipe which communicates with a channel traversing the plates of the filter.

The water leaves its solid matter in the filter and issues clear and pure. The filtering medium has to be cleaned about every fifteen hours. To effect this water is driven through the filter in the opposite direction to that in which the water to be filtered comes.

Demailly's Apparatus.—This apparatus may be used in purify-

ing water for industrial use but it is often used for purifying boiler-feed, and is then placed between the feed pump and the boiler.

The apparatus consists essentially of two metal cylinders, A and B. In the receiver A there is milk-of-lime. The water to be purified is brought by a pipe T, which is connected both with the principal pipe V and a small tube L.

A portion of the water is taken up by this small tube which transfers it by a series of openings into the reagent cylinder A.

The milk-of-lime is thus diluted; the water saturates itself with lime and rising through a filter F, passes by the central tube, and finally falls on to a helical wheel E which brings it into contact with the main mass of water brought by the pipe V.

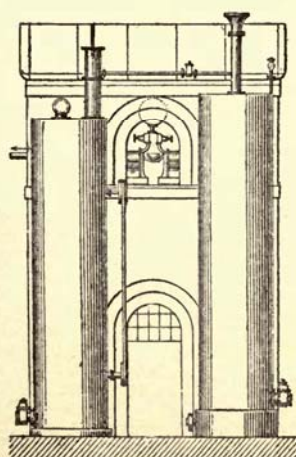


FIG. 83.—Clarke Atkins and Porter's purifier (front view).

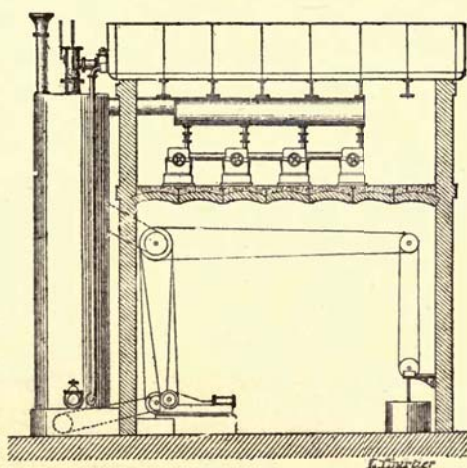


FIG. 84.—Clarke Atkins and Porter's purifier (side elevation).

A pipe R brings the liquid into the reservoir B, where the lime-water, reacting with the water to be purified throws down the carbonates of the alkaline earths.

The water once purified traverses the filter F, and goes out by the central pipe into the pipe Z.

To prevent the filter in the reservoir getting choked by the deposit, a bush rubs against the filtering surfaces. To eliminate sulphates, appropriate reagents must be introduced. In this way the mixture of water to be purified and reagent circulates over the baffles, traversing the whole surface of each of them, and always in an opposite direction from one baffle to another.

By this arrangement the suspended and precipitated matters are readily deposited, and this is still further facilitated by putting

wood-fibre between each pair of baffles. The purified water flows from the bottom of the compartment C into the bottom of the compartment C₁, and as it rises it passes through an asbestos partition to clarify it.

Finally, the purified water leaves by the side pipe S. A float *n* follows the rise and fall of the purified water, and at the same time regulates the taps *c* and *b*, which admit reagent and water to be purified.

There is a discharge tap for clearing out mud.

Purifier of the Maignen Filter Co.—This purifier consists essentially of a reagent preparing vessel M, having a pipe *f* at the base to lead the reagent into the storage reservoir N.

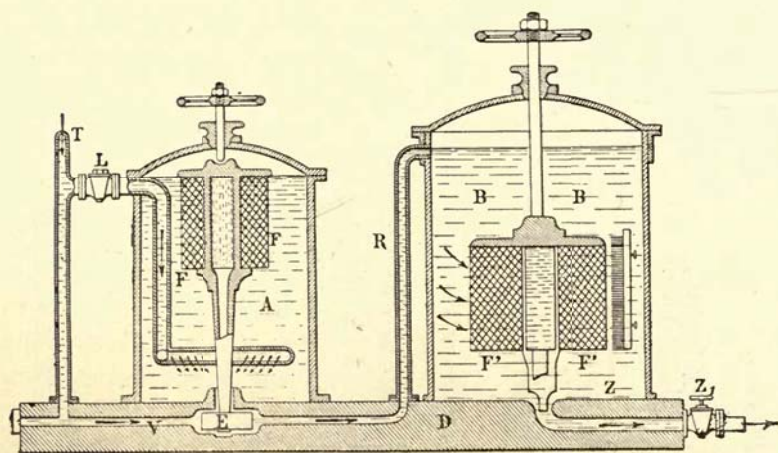


FIG. 85.—Demailly's apparatus.

The flow of reagent into the reservoir N is stopped automatically, according to the level of liquid in it, by the ball-cock *e*.

At the lower part of the reservoir N, a pipe *f* leads the reagent in quantities regulated by the tap *a*, into a channel G, and here it mixes with the water to be purified, coming by the pipe A in quantities governed by the tap *a*. The mixture of water to be purified and reagent leaves the end S of the channel G to fall into the compartment C of the reaction and clarification reservoir O, where the precipitated and suspended matters settle. A series of plates with lightly turned-up edges, and lowered at opposite ends in Z shape, are placed as baffles.

Each of these baffles is notched near one end, to allow the water to pass from one to another, but two consecutive baffles have their notches at opposite ends.

Buron's Cold Purifier.—In this purifier the impure water arrives

by a pipe A into a vessel N which distributes it by two taps 3 and 4. Tap 4 allows water to run on to lime placed in a metal basket to keep back stones and insoluble particles.

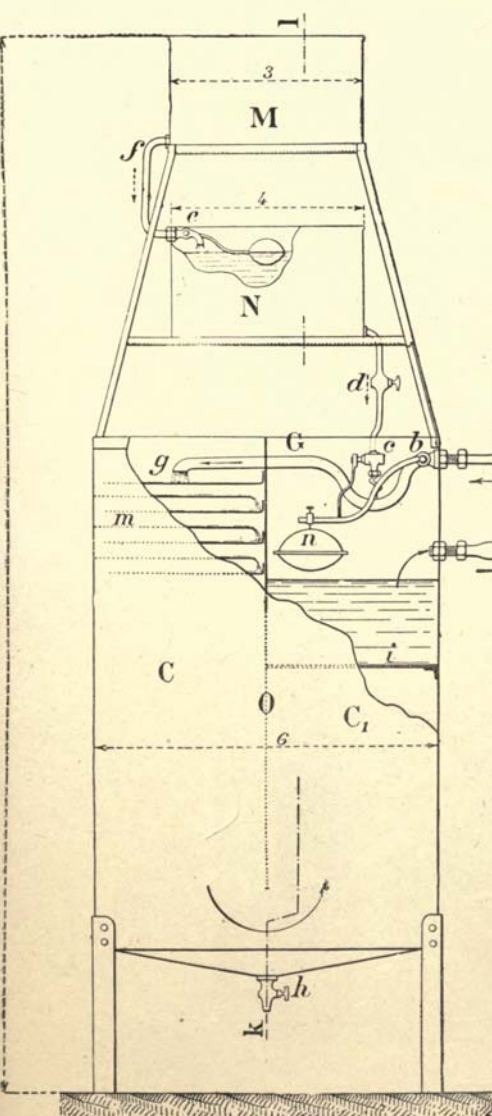


FIG. 86.—Maignen filter (elevation).

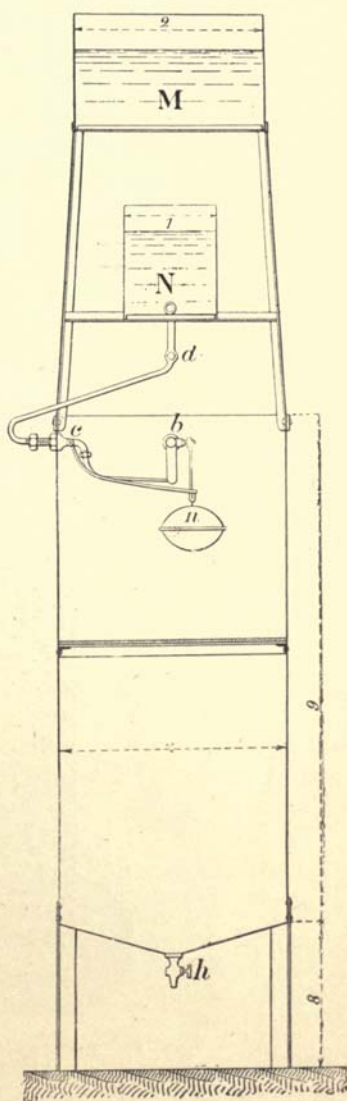


FIG. 87.—Maignen filter (side view).

The lime is taken by the water into the central tube of a saturator D where it is stirred energetically by a stirrer, with two blades revolving in it. This stirrer is driven by a water-wheel K,

moved by water from the tap 3 of the distributing reservoir N. Thus stirred, the milk-of-lime reaches the base of the saturator by the central tube and rises in the intermediate space formed by the outer cylinder, and passes into the upper part by the pipe T.

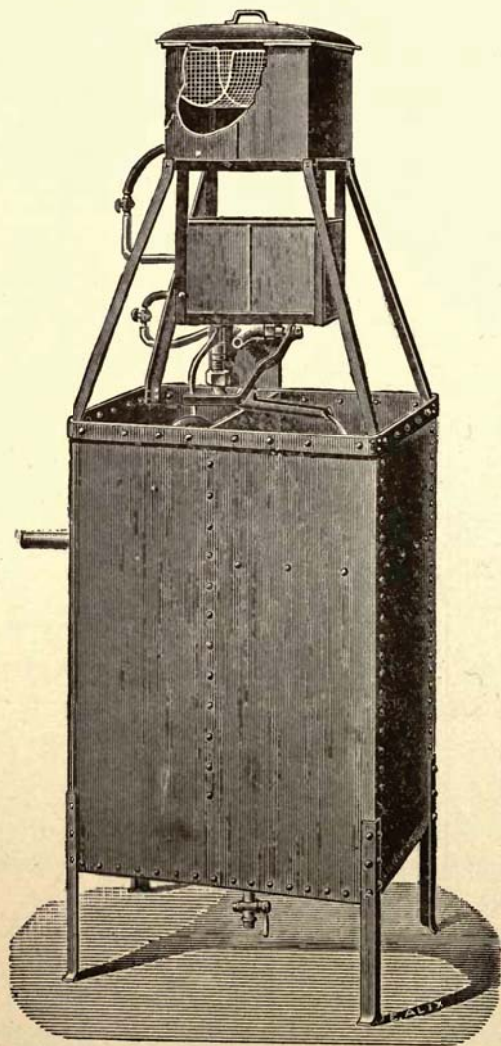


FIG. 88.—Maigen filter (exterior).

In the compartment M of the distributing reservoir a solution of soda is put every day, and is distributed from the small reservoir G by a tap into the pipe R.

Hence the milk-of-lime and the soda arrive into T and K through their respective pipes, and into contact with the water to

be purified, which escapes at S into the upper part of a central column, whence it enters the mixer, where the reactions take place and the salts are precipitated out of the water.

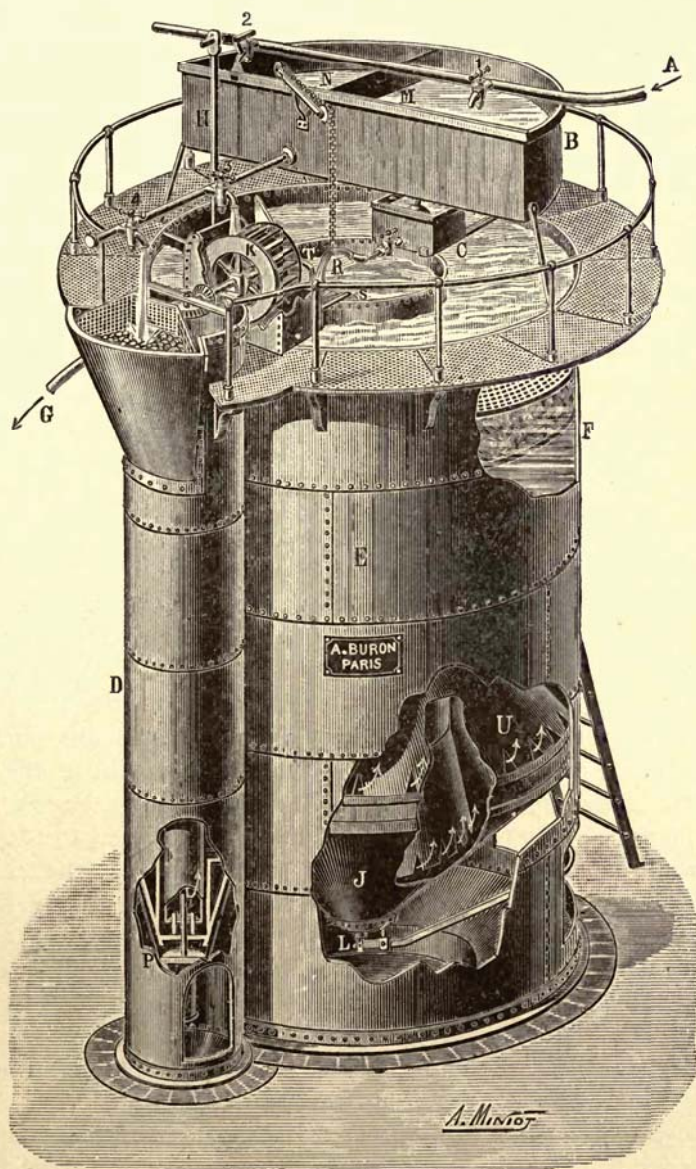


FIG. 89.—Buron's cold water purifier.

The water descends to the lower part of the apparatus and then reascends in the space formed by the external cylinder, meeting

with baffles which retard the upward movement and so facilitate the settlement of the precipitates. Finally the purified water is clarified in a filter F and passes clear from that into a special reservoir which it leaves by the opening G. It will be noted that all flows of water or reagent are regulated by a principal float H which commands the various ball-cocks.

As to the deposits formed they are removed by the discharge valve L at the bottom of the apparatus.

Henri Carpentier's Cold Purifier.—This purifier is formed of a cylindrical reservoir A in which moves a float C, which follows the rise and fall of the purified water in the residue, and commands the inlet tap B of the unpurified water. This runs through the pipe D into the principal pipe distributing the water into the central reservoir L by the descending column D, and into two measuring vessels E.

The water flows from the measuring vessels into two reagent-cisterns F provided with stirrers. The prepared reagents flow by the overflow pipes to the bottom of the central reservoir L.

This reservoir, then, receives the reagents and the water to be treated, which mix together, and overflowing, pass into an exterior reservoir M surrounding the first, and, supported by a tube N, descend to a certain distance from the bottom of the reservoir A.

Baffles O are disposed inside this tube N, in which the water under treatment circulates, depositing the precipitated bodies, which go to the bottom of the reservoir and are removed by the outlet cock *p*. The water rises again slowly and finishes its treatment by a filtration upwards through the filter bed R, and runs, purified and clarified, out at the pipe S. By the arrangement of the tap float, the water only comes in when that contained in the reservoir has diminished to a determined quantity. This allows the flow of the reagents to be properly regulated in proportion to that of the impure water, the measuring vessels E being filled at the same time as the central reservoir L by the descending pipe D.

Howatson's Cold Purifier.—The reagent, lime-water, is prepared continuously in a special saturator K, shown on the left in the figure. This saturator K, of cylindrical form, contains another cylinder M, which contains in its upper part a perforated vessel in which is placed the lime used in preparing the reagent.

An automatic tap A, governed by a float, allows the water to be purified to enter the compartment B, whence it is passed by a valve B, governed by a float, into a pipe opening at F, the size of which is regulated according to the flow required.

The water used to prepare the reagent passes beyond the point F and leaves by the opening G, which is regulated according to the

quantity of lime-water needed for the purification, and thence falls on the lime and carries it into the internal cylinder M.

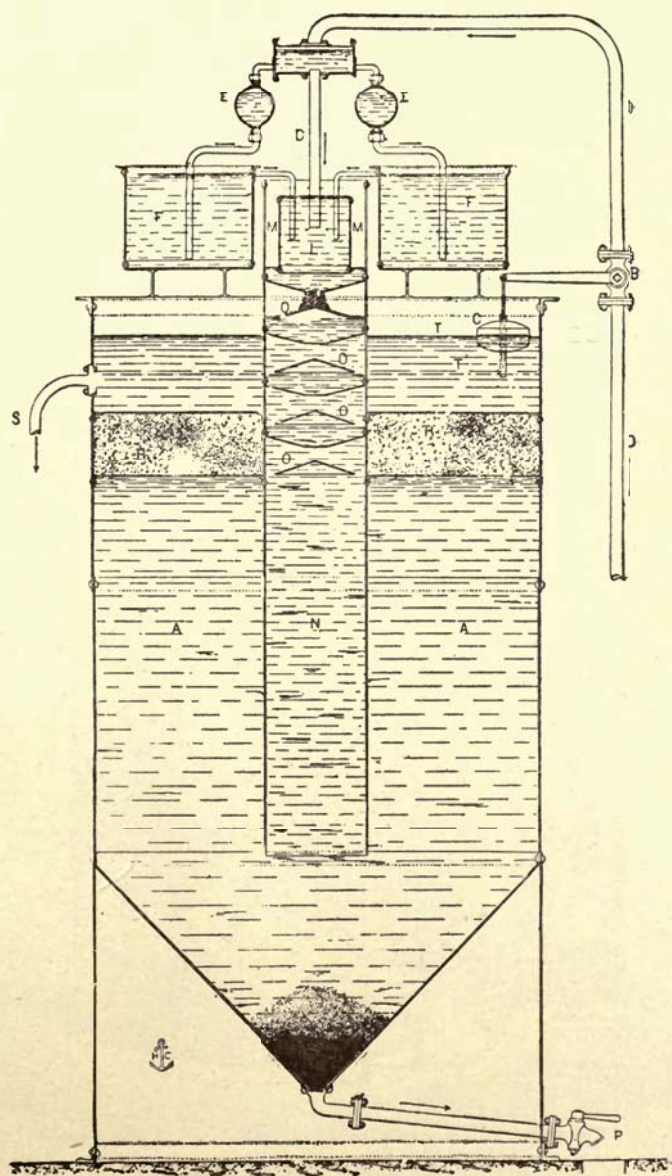


FIG. 90.—Carpentier's cold water purifier.

As for the water to be purified, it goes from the orifice F on to a water-wheel which by means of an endless screw and a cog-wheel drives a vertical shaft following the axis of the saturator K.

This shaft has blades the object of which is to suitably stir the mixture of water and lime. The solid particles fall to the bottom part of the cylinder M and settle down there. The lime-water becomes clear, and rises through the annular space between the two

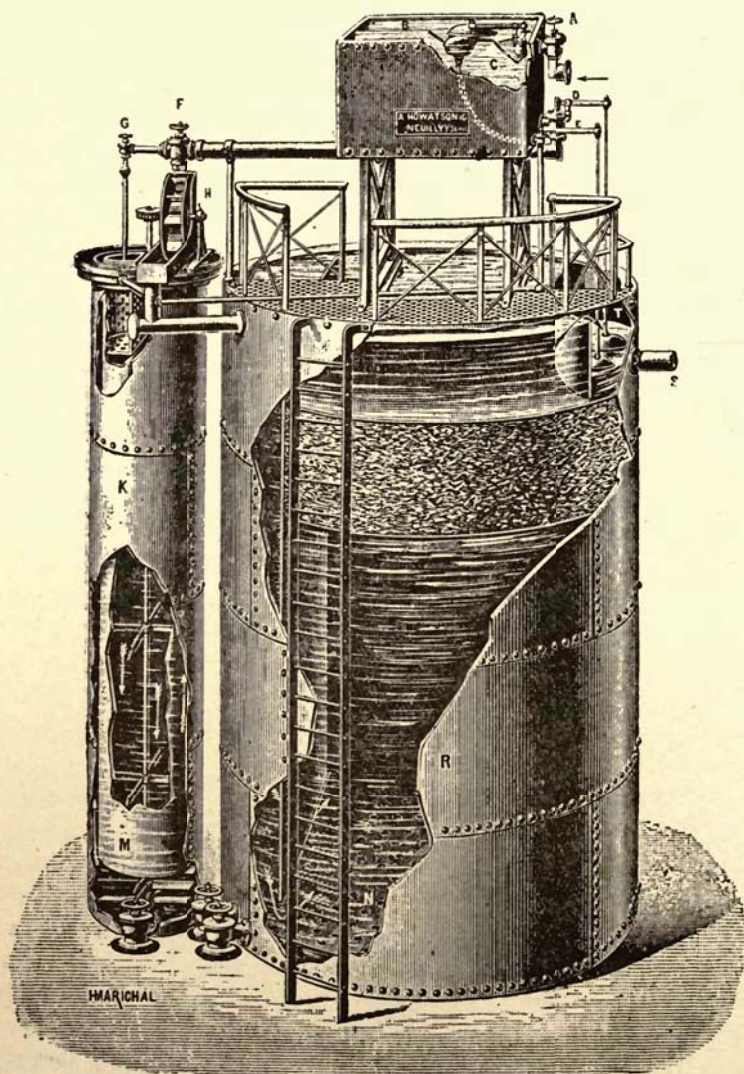


FIG. 91.—Howatson's cold water purifier.

cylinders M and K and passes through the upper part of the saturator K into a side pipe which brings it into the same T-shaped pipe as the water to be purified enters after leaving the orifice F and falling on the water-wheel H.

Thus mixed with the lime-water the water to be purified throws down its dissolved salts and passes into the upper part of the big settling cylinder R.

After having got rid of its salts in the settling cylinder R, the water traverses a thick layer of wood-fibre, where it leaves its solid matter in suspension and thus undergoes complete filtration.

The purified and clarified water finds itself shut up in the upper part and leaves by a special pipe S. If the nature of the water requires the use of a second reagent, carbonate of soda for example, the preparation of that reagent is effected automatically in the compartment C of the upper reservoir, and it would be poured as wanted into the T-shaped tube which provides for the mixing of the water to be purified with the lime-water. The flow of the water to be purified, and also that of the lime-water or carbonate of soda, is managed automatically by the taps D and E, regulated by floats according to the variations in the level of the liquid.

Finally outlet valves provide for the removal of the mud deposited in the saturator and in the settler.

Froitzheim's Purifier, for Mixed Treatment.—The Froitzheim purifier is specially constructed for the mixed treatment of water, not only with reagents, but also with steam.

A float S following the variations in the water level in a large reservoir I admits the water to be purified by the pipe W, whence it falls into a double-balanced bucket M, which it moves by its weight. The rocking movement of the buckets is transmitted by two levers to a horizontal shaft, which controls an elevator H.

This carries buckets which bring up the solution of reagent, in this case carbonate of soda, and pour it in small quantities into a funnel *l*, from which it runs by a pipe into the large reservoir I.

The flow of soda from the buckets, the motion of which is regulated by the balanced double bucket at M, is thus proportional to that of the water to be purified.

To complete this chemical purification a heater *pp* based on the counter-current principle, receives exhaust steam from the pipe A, in the direction shown by the arrow.

On leaving the heater, the water falls into the large reservoir I which is divided by a diaphragm Z into two compartments V and W, so as to reduce the speed of the flow and to facilitate the deposition of the precipitates. As to the solution of carbonate of soda, which pours through the funnel *l* into the reservoir I, it is mixed thoroughly with the water to be purified by means of a jet of steam regulated by a valve B.

Finally, after having got round the diaphragm, the water is

clarified by a filter composed of a series of frames filled with canvas, which can be removed separately for cleaning purposes. On leaving the filter, the purified and clarified water flows out by the pipe S.

COMPLEMENTARY NOTES ON SOME APPARATUSES FOR TREATING WATER WITH STEAM.

In the second part of this work, in the chapter concerning boiler-feed water, we examined a certain number of apparatuses

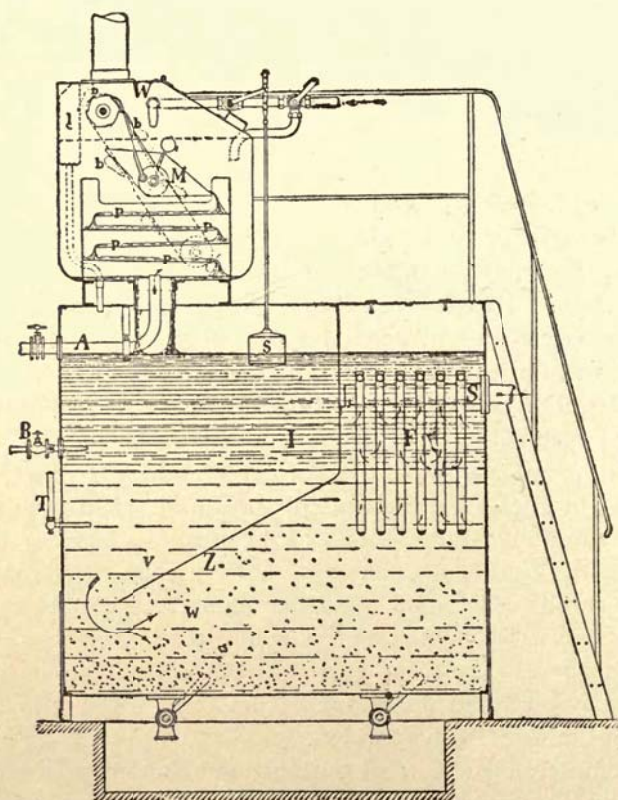


FIG. 92.—Froitzheim's purifier.

for the preliminary treatment of water by steam. As some of these apparatuses could not be put in the chapter at the time of going to the press, we shall now study them in a complementary note.

Paul Barbier's Heater and Purifier of Feed Water.—The feed-water purifier of Paul Barbier is composed essentially of a series of shallow cast-iron cylinders, having movable perforated iron bottoms. They are piled one on another, and are provided with

filtering layers of some thickness, consisting of such substances—*e.g.*, coke, pumice, slag, smithy scale, etc.—as give the greatest facilities for contact with the steam, and for keeping back the precipitates.

The water enters the apparatus by an inlet valve C governed

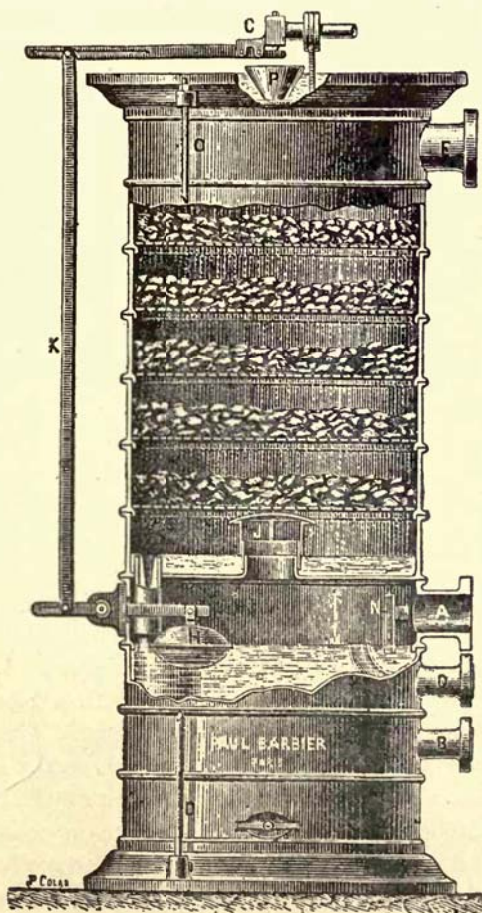


FIG. 93.—Barbier's heater and purifier.

by the float H according to the movement of the water in the apparatus by means of the vertical rod K.

On leaving the tap K, the impure water flows into the funnel P which distributes it as uniformly as possible by means of a special arrangement over the uppermost filter, from which it passes through the other filter beds into the lower chamber forming the water-reservoir. The exhaust steam from the engine comes by the outer tube A through a chest where it deposits its oil, and then passes

over the water in the reservoir and rises through the filters accompanied by the steam from J.

The water is thus clarified and its precipitated matter is run off by a discharge valve in the lower part of the apparatus.

The heated and clarified water is driven by a pump through the pipe B, which is in the middle of the water-reservoir. An overflow D prevents the depth of water in the latter from exceeding a fixed amount, and the apparatus can be cleaned by removing the plug M. The taking-down of the filter-rings is facilitated by three rods, O, with nuts, which keep them pressed together and permit of easy access to the plates and filter-beds for cleaning purposes.

Henri Carpentier's Heating Purifier.—The impure water reaches a large reservoir A by the principal pipe T.

From here it falls into a feeding chamber through pipe O, the lower opening of which is provided with a tap governed by a float which follows the fluctuations of the water in the chamber.

The exhaustion from the engine is sent towards the feed-chamber, into a small chest R, in which it leaves any lubricating oil it may have brought with it.

This oil flows slowly out by the pipe D, and is caught in a little reservoir F. Thus freed from its grease, the steam rises by a pipe H into another catcher B of large capacity, and formed of a vertical cylinder with a cone at each end. The upper cone has an opening at the point and communicates with the open air by a pipe passing through the water in the reservoir A.

The lower cone communicates at its tip with a pipe P going to the drains, and provided with a discharge valve. The water to be purified is sent by a small centrifugal pump L to the lower part of the feed chamber, and then, driven into the column E, is poured like rain into the catcher B where it meets the steam coming from the pipe H. The salts in the water (carbonates of the alkaline earths) are decomposed and settle in the lower cone of the catcher B.

The lower part of the cone of this catcher therefore fills with purified water, which passes by the pipe N into the feed chamber and thence to the engine by the pipe M.

Dervaux's Automatic Boiler and Purifier.—Dervaux's automatic boiler and purifier is intended to drive the water to be purified in a column into a long straight boiling tube, in the opposite direction to a *current of steam*.

The apparatus consists of a vertical boiling tube B open to the air and receiving the impure water from a reservoir at a higher level by means of the valve S.

A column of water is formed, which in flowing down the narrow boiling tube B meets a current of steam coming from a pipe V in the opposite, *i.e.*, the ascending, direction.

The current of steam, passing through the water, decomposes the carbonates of the alkaline earths, and takes the carbonic acid to the surface of the water, where it escapes freely.

In the upper part of the boiling tube, the steam, coming into

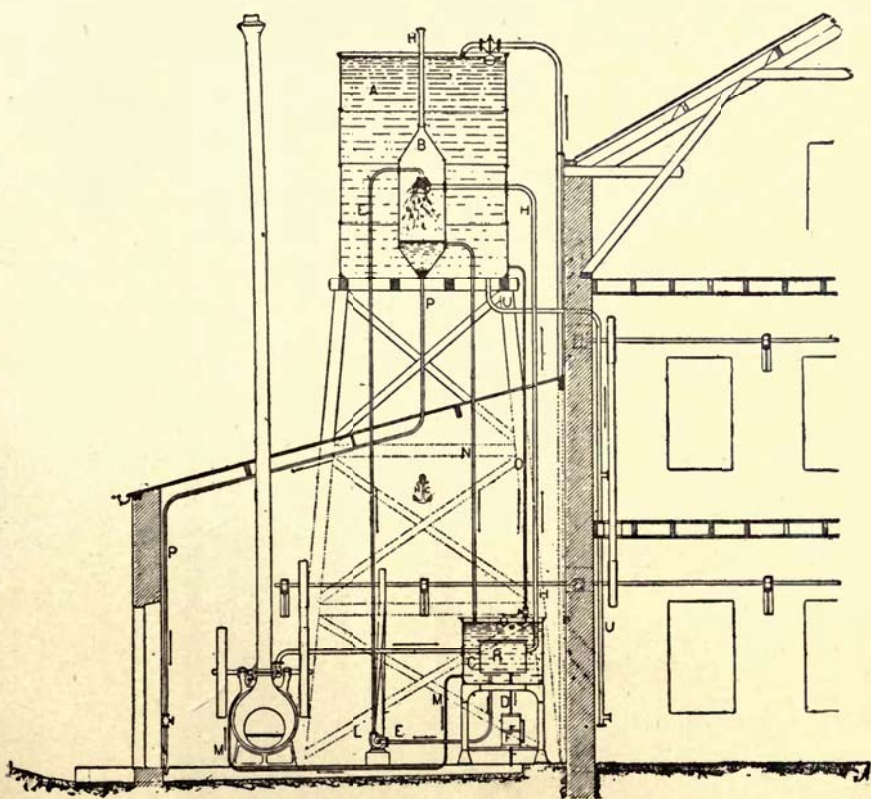


FIG. 94.—Carpentier's heater and purifier.

contact with the cold impure water which is constantly renewed, is condensed, and the precipitated carbonates are deposited.

The hot purified water passes by the lower pipe C into a settling reservoir D, in which it slowly deepens, throwing down the precipitated carbonates.

Finally, the purified water escapes by the overflow E into any suitable reservoir. A simple float F, regulating the admission valve S of the water, permits of the intensity of the ebullition and the output of purified water being regulated. To clean or inspect the

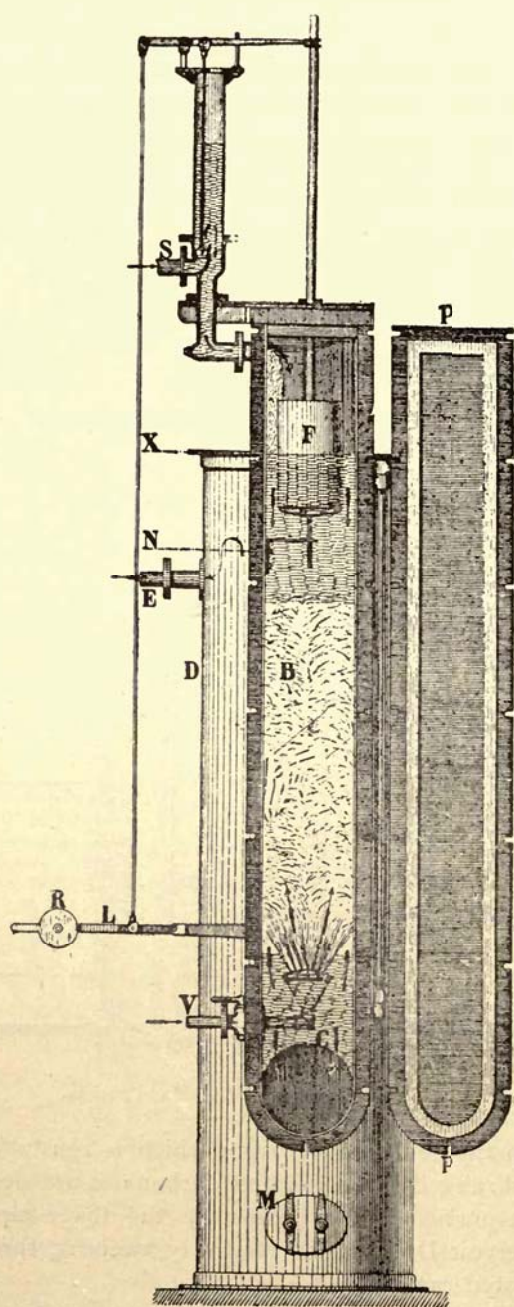


FIG. 95.—Dervaux's automatic boiler and purifier..

boiling tube, the door P may be opened; as for the deposits in the settler D they are withdrawn at intervals by the door M.

Granddemange's Heating Purifier.—Granddemange's heating purifier, built by Mazeran and Sabron, is formed of a series of reservoirs or vessels of iron one on the top of another, and is the essential element of the purifier intended to receive the deposits of tartar. A series of rings *b* kept together by rods O and screws, form, when placed one above another, the outside of the apparatus.

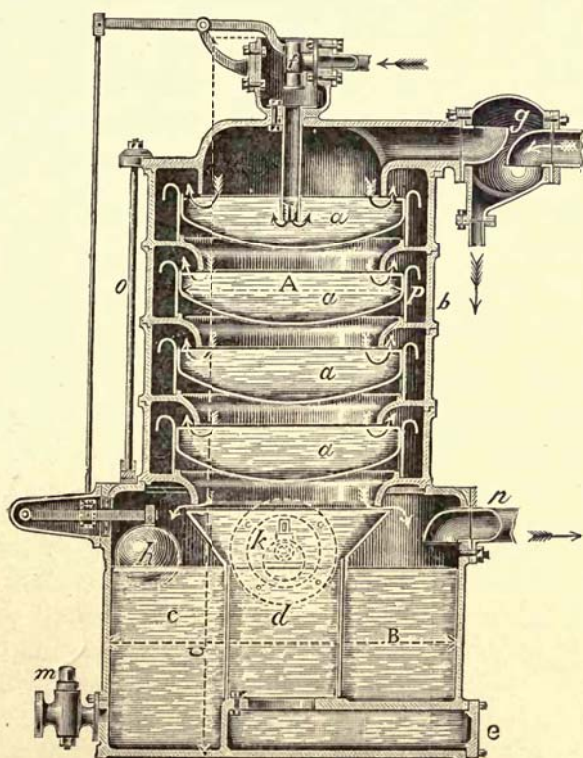


FIG. 96.—Granddemange's heater and purifier.

The cold water to be purified enters the apparatus by the tap *f*, following the level of the purified water contained in the vessel *c*. The steam enters the apparatus and gets rid of any grease by means of a catcher *g*.

On arriving at the first plate *a*, and spreading out in a layer, the water meets the steam, which heats it, and brings it to the temperature which decomposes the salts of the alkaline earths, which begin to settle in the upper decarbonating vessel.

The water heated passes above the first vessel *a*, and traverses

the space enclosed between that vessel *a* and the section of an envelope *b*, and so on, up to the last vessel *a*.

In its course the water meets the steam, and salts settle in the series of decarbonating vessels *a*. Finally the water falls into the settling vessels *d*, the width of which causes a slackening of speed, so that the salts settle.

The purified water, run off hot, leaves by the overflow *K* to pass into the reservoir *c*, whence it is taken for distribution.

By the tube *n* the excess of steam escapes, and the deposits which are left in the settler *d* may be taken out by removing the cleaning plug *e*.

Remarks.—1. The different apparatuses for treating water which we have examined in this work are serviceable not only for steam boilers, but also in the various industries which need pure water.

2. By the treatment of water by steam the carbonates are precipitated. As regards the sulphates, they may be precipitated by adding soda or any appropriate reagent in the purifier.

CHAPTER XXI.

INDUSTRIAL FILTERS.

A FILTER is an apparatus in which liquids are passed through porous bodies capable of arresting and retaining all matter in suspension, thus clarifying the liquid.

As filtering material, mineral, animal or vegetable substances may be used. Gravel, ground flint, coke and sand are the principal mineral substances used in industrial filters, and to these may be added pumice stone, porous calcareous stones and asbestos fibre or cloth.

As regards animal substances, use is made of felt, sponges, woollen cuttings or cloth and bone black. Among vegetable substances, tow or oakum, sawdust and wood fibre, straw, charcoal and raw cotton are especially employed.

Industrial filters are filled with one or several of these filtering materials and the water to be filtered traverses them either upwards or downwards.

David's Filter.—David's filter is essentially a cast-iron vessel with two taps, one at the top to admit the water and the other at the bottom to run it off when filtered. The filter is closed with an iron cover, bolted on, and is filled with layers of various filtering materials each enclosed between perforated iron plates. Commencing at the top the first layer is a bed of sponge, then a layer of grit, next shreds of woollen cloth. After this a bed of bone black or charcoal powder and finally sand or fine gravel.

To clean the filter the direction of the current of water is simply reversed.

H. Desrumaux's Filter.—In this apparatus the water is introduced by a pipe which leads from the main upwards to a funnel at the top of the filter and in the centre.

The water falls on a distributing plate which spreads it over a layer of flints spread over a metal plate supported by a hollow iron pillar. In traversing the layer of flints it leaves behind all the

particles of suspended matter and runs off clear through the hollow iron pillar to be distributed according to requirements.

The deposit of suspended matter of course accumulates in the layer of flints, and at the end of a certain time the filter must be cleaned out. In its passage through the flint layer the water finds an obstacle in the accumulated deposit. It therefore commences to fill the upper part of the filter and at last actuates a float which turns off the arrival tap automatically.

To clean the filter the arrival tap is first turned off and the rest of the water is run off by a two way tap under the layer of filtering matter. The current of water is then reversed and traverses the layer of flints from the bottom upwards. While the water is forced

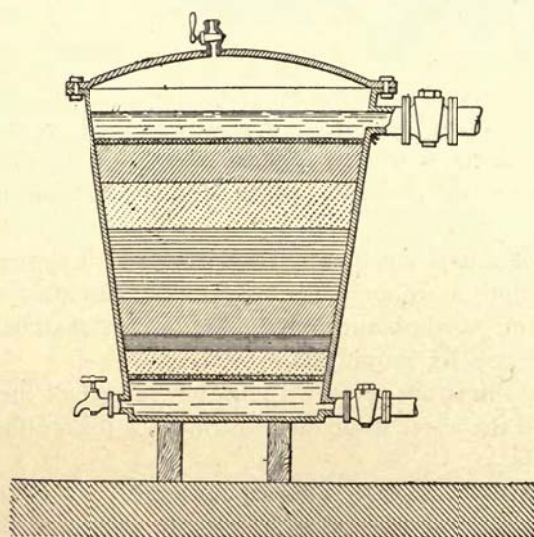


FIG. 97.—David's filter.

through the flints a handle is turned which revolves a large disc with bars which stir up the flints in every direction. This disc is mounted on the central hollow pillar.

All the deposited solid matter is thus stirred up and kept in suspension and is drawn off at the top of the apparatus, thus leaving the filter clean and ready for use again.¹

Dervaux's Automatic Continuous Filter.—In this filter the water is led by a pipe A in the tube B to a closed chamber C and passes through a bed of gravel F on a perforated iron plate P.

Having filled the reservoir V the water rises in the pipe K into

¹ The French author describes this filter by the aid of a lettered diagram which does not appear in the work.—Tr.

the reservoir R, and when it reaches the level N it runs by the escape D and out by the filtered-water tap P.

If the accumulations of deposit become too great the cleansing process commences automatically.

Not finding a passage through the filtering material the water mounts in the tube L communicating with the closed reservoir C.

When it mounts to J it falls into a central tube S forming a

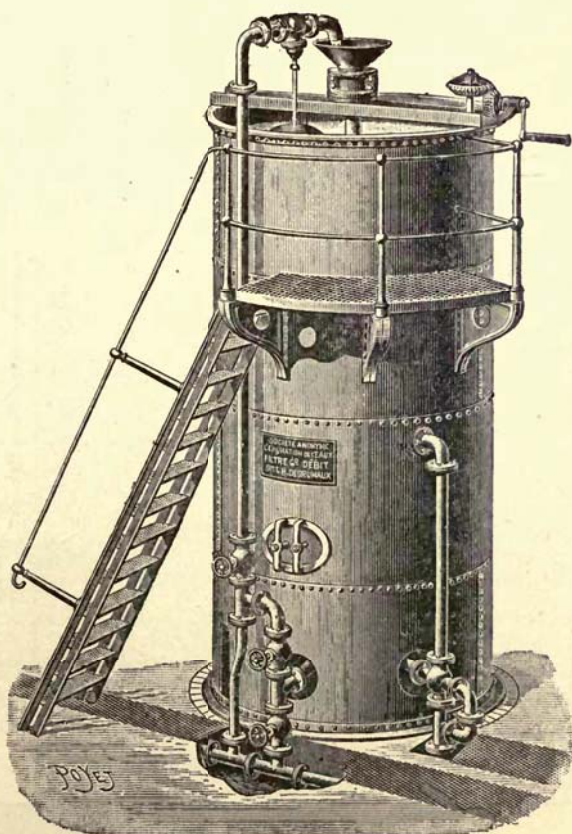


FIG. 95.—Dervaux's filter.

syphon, and when once the syphon action is set up the water runs with force, and first sucks up all the sediment into the evacuation tube S and next the filtered water from the reservoir R which is drawn through the filtering layer from the bottom to the top bringing with it the deposit which is run off by the tube S.

The upper part of the tube L forming a syphon with the tube S communicates with the reservoir R at this level M by a curved tube M. When the level of the water in the reservoir R falls to

M the syphon is thrown out of action and the filter, cleansed automatically, resumes its normal functions.

Delhotel and Morides Filter.—This filter is a closed cylinder of cast iron two-thirds filled with quartz sand.

Curved pipes lead the water into the filter and cause a gyratory movement. Thus the water stirs up the upper layer of sand, retard-

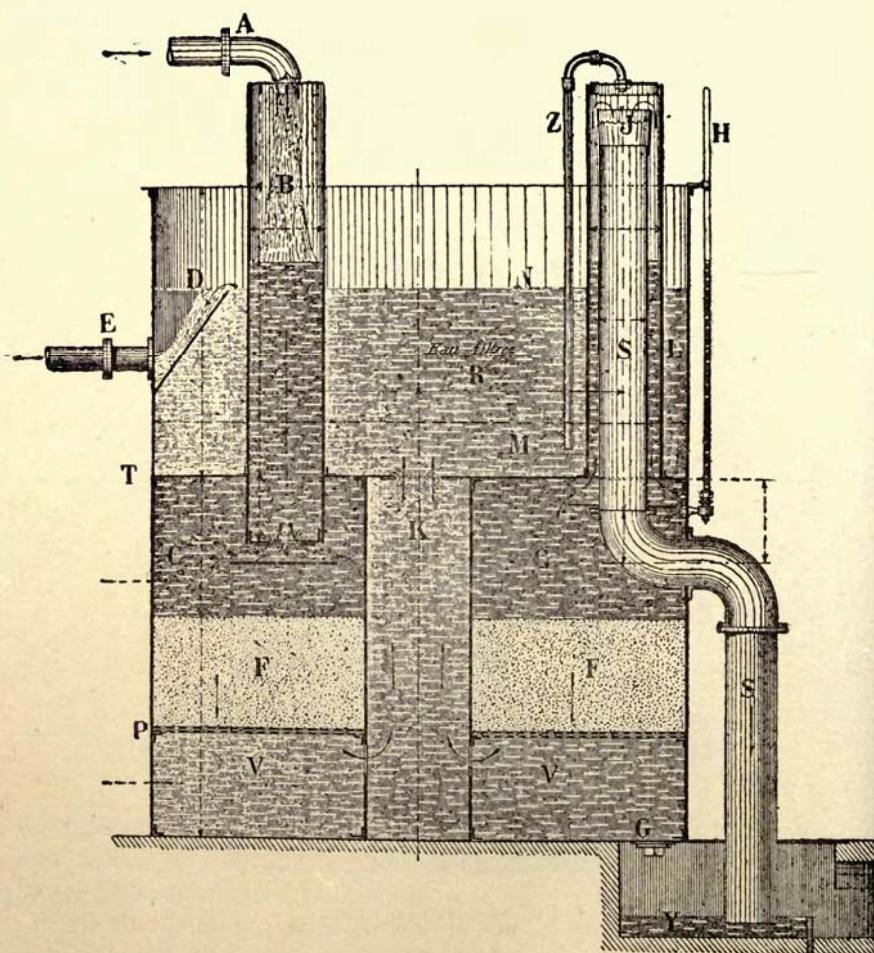


FIG. 99.—Dervaux's filter (section).

ing the deposit of slime and matters in suspension and therefore the action of the filter lasts a longer time.

To cleanse the upper part of the filter it is merely necessary to turn on a tap at the bottom communicating with a central pipe. The water rushing violently down this central tube into a funnel carries with it the solid particles of deposit in the filtering

material and when the bottom tap is turned off the filter functions normally. To clean the lower layers of the filtering bed a tap is turned on which leads an inverse current under the sand; the filter bed is thus stirred up and the deposited matter is brought into suspension and evacuated.

This tap is then shut off and the filter is ready for action as before. A special run-off tap is turned on to run off the turbid water and when it runs clear the filtered water is run into a receptacle provided with a tap for the purpose.

M. Moride in his work on soap-making recommends this filter for use in soap works. It is provided with a system of pipes and

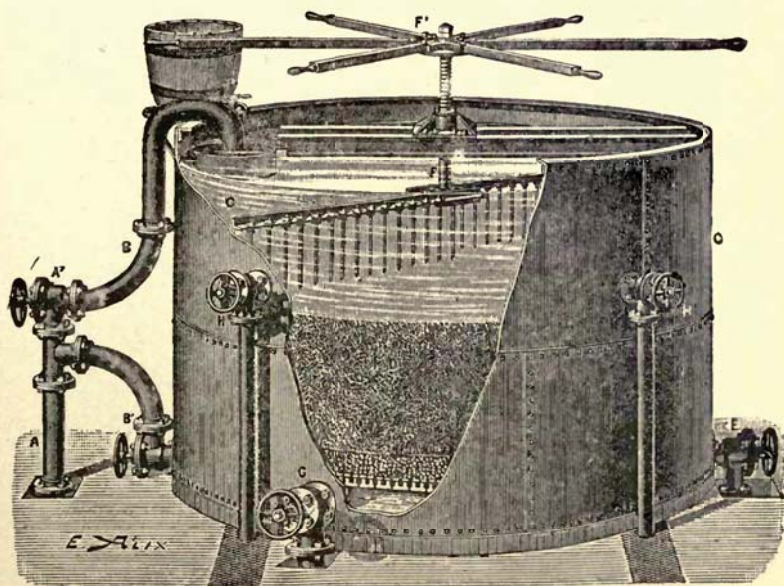


FIG. 100 —Howatson's filter.

taps which allow it to be cleansed either with water from the main or filtered water.

Howatson's Filter.—The filter of Howatson is a metal cylinder C into which the water is forced from the main by the tube A with a tap A¹.

The water traverses a bed of crushed flints, of suitable size, resting on a grooved double bottom of cast iron which is perforated with a large number of holes of 4 mm. in diameter. The total area of these is equal in dimension to that of the draw-off cock E.

Passing through the filtering bed the water is freed from matters in suspension and is drawn off clear at E ready for use.

The cleansing of the filter is done by shutting the tap A¹ and

opening the tap B^1 . Then the water rises into the upper part carrying the sediment with it down the pipes H , kept open for the purpose. The degagement of the deposit is facilitated by means of a stirring device F set in motion by a capstan F .

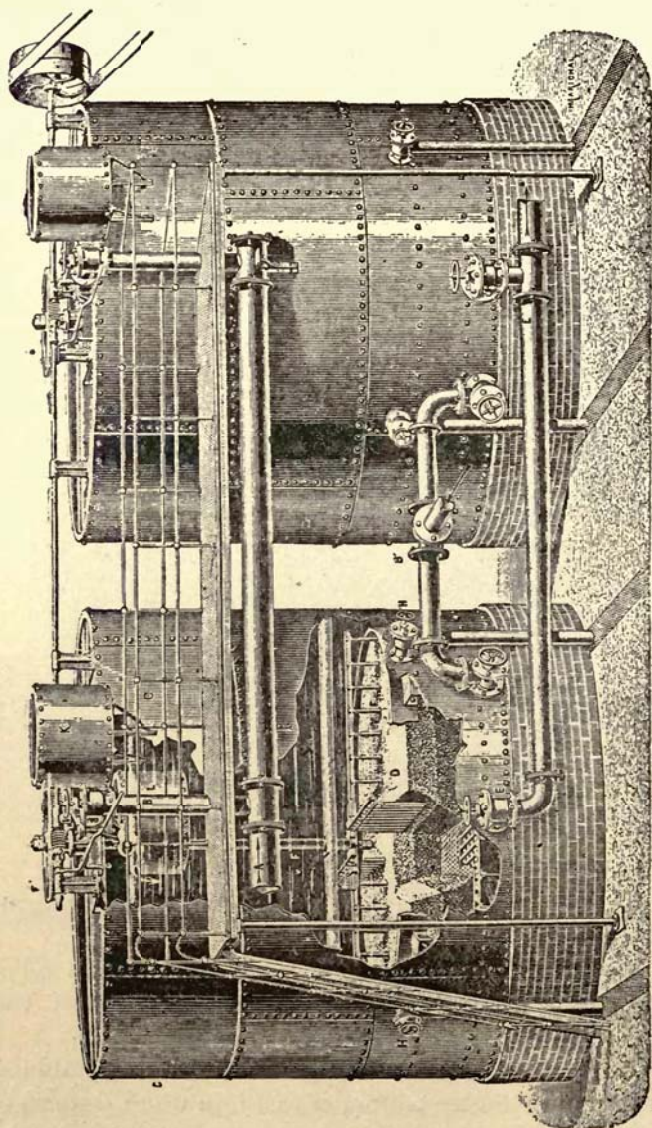


FIG. 101.—Howatson's filters coupled.

This stirrer is a free screw on which are fixed arms bearing paddles. These are lowered for the cleansing operation and raised when the filter is in working order.

When the filter is clean the tap B^1 and the draw-off cocks H

and H^1 are shut. The draw-off cock C is opened to evacuate the wash water and when this is shut the filter is ready for work again. It is merely to reopen the tap A^1 to run the water into the apparatus.

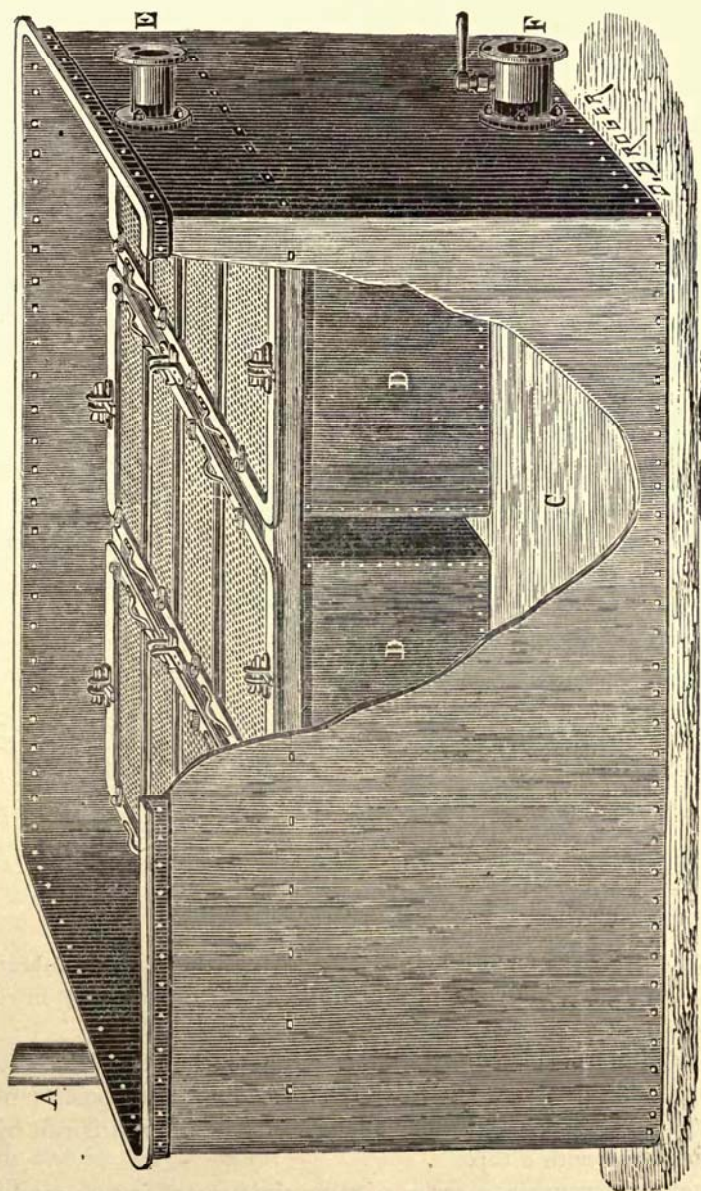


FIG. 102.—Buron's filter.

Buron's Industrial Filter.—This filter is a metal vat into which the water is forced at the lower part C by the pipe A. The current has a minimum pressure of 1 metre.

The water traverses the compartments D containing the filtering materials which are packed in firmly and held down by a metal grating. After filtration the water is run off at an outlet E at the top of the reservoir. Every two months, or thereabouts, the filter is cleaned. To do this the outlet E is closed and the water is forced upwards as far as possible. The tap from the main A is then shut off and the draw-off cock F in the lower part is then opened.

The water rushes through the filter bed and escapes with force at F carrying with it the impurities, the slope of the bottom of the filter aiding the operation. The taps are again set as before and

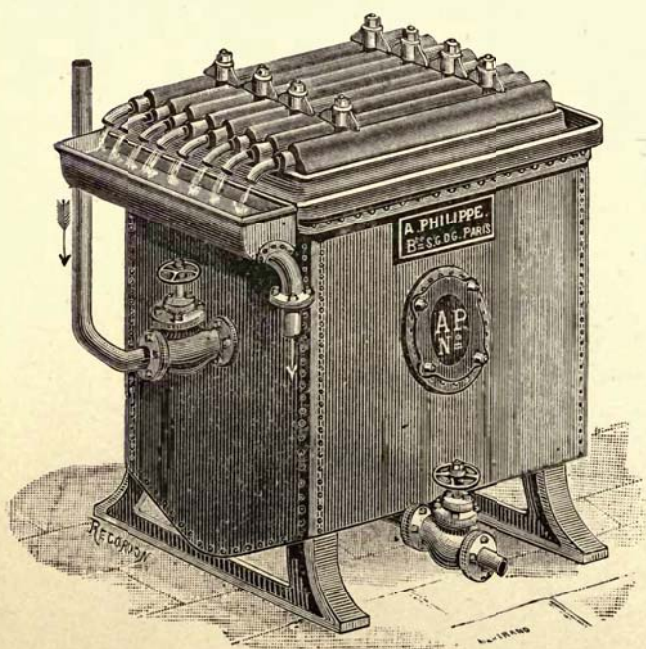


FIG. 103.—Philippe's filter.

the filter is ready for work again. To cleanse the filtering material thoroughly it is removed from the inner cases and washed in running water.

A. Philippe's Mechanical Filter.—The mechanical filter of A. Philippe differs completely from the preceding. It consists of a reservoir of metal A into which the water to be filtered is run by a pipe furnished with a tap.

The water traverses a series of removable metal frames made of a peculiar metal trellis-work covered with pockets of filtering cloth of cotton, woollen or asbestos, according to the nature of the liquid to be filtered.

The upper part of the pockets D is open, and is furnished with a supple tag F by which the pouches and their metal frames E are fixed to the cover B, forming an exterior joint. The cover B has openings by which the pockets D or filtering bags are introduced. The water traverses the filtering material and freed from its impurities rises in the pockets and flows into a movable cap G.

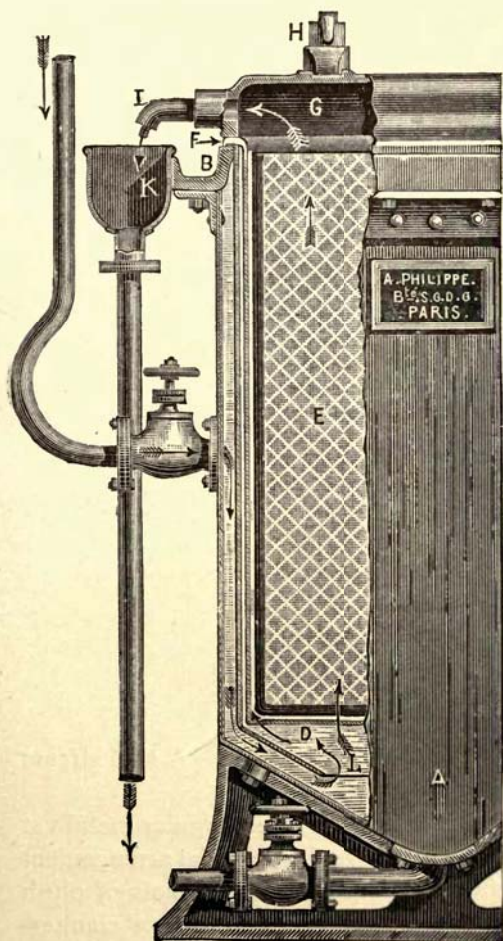


FIG. 104.—Philippe's filter (transverse section).

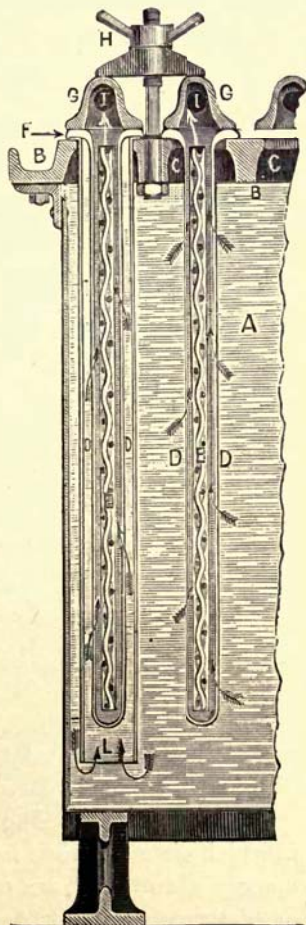


FIG. 105.—Philippe's filter (lateral section).

Each of the bags is provided with one of these which is fixed on while the filter is in action.

The filtered water runs off through the tubes I in the caps G to a collecting funnel K from whence it is carried to its destination. The caps are held in place on the upper tags F of the pockets by the screws and nuts H.

To change the pockets it is merely necessary to shut off the arrival tap, slightly slacken the screws H and take off the caps G. The pockets can then be drawn out and easily replaced.

The impurities caught by the filtering tissue are only lightly adherent. They fall to the bottom of the reservoir A, whence they are evacuated by the draw-off cock at the bottom. As for the frames they can be easily cleansed by taking them and washing them in running water.

The arrangement in the form of a gutter round the cover B prevents any mixture of the filtered with the non-filtered water; in fact if the movable caps G are not fixed, accidentally or purposely, the non-filtered water cannot run off by the tubes I. It is diverted into the gutter round the cover and runs off on the outside. This

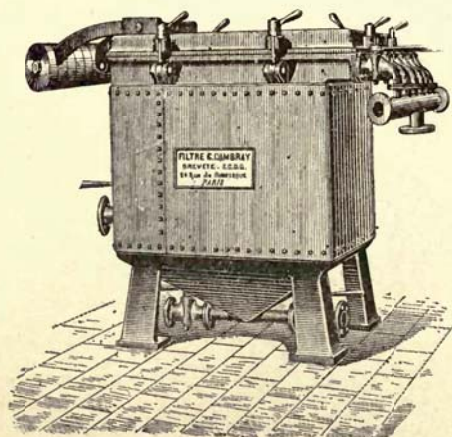


FIG. 106.—Muller's filter.

makes the operation of the filter a simple matter. A thin stream of liquid is sufficient in working with this filter.

Muller's Filter.—The filter of Muller is a rectangular metal vat in which are suspended from the iron cover by a special arrangement a series of two, four, six or more quartettes of flat pockets of plush or of smooth tissue. A movable cover, furnished with a counterweight, is hermetically closed by means of a rim of indiarubber. This cover has grooves or gutters making a communication between the pockets and a flanged pipe B which is a part of the movable cover and thus preventing the unfiltered liquid from mixing with the filtered.

The water from the main is led into the filter by the tap A at the side and traversing the pipes rises in the interior of the pockets and runs off clear by the pipe B. The heavy sediment falls into

the lower part of the reservoir and is evacuated by the draw-off cock D. To clean the pockets the current is reversed. The taps A and B are first shut, then, after emptying the filter by the draw-off cock D, the wash-water is forced in through the tap at B and the impurities are washed off the pockets and, falling to the bottom, run off with the water at D.

The taps are then turned to their first positions and the filter is in working order again.

Filters with Sponges.—Sponges, which we have mentioned

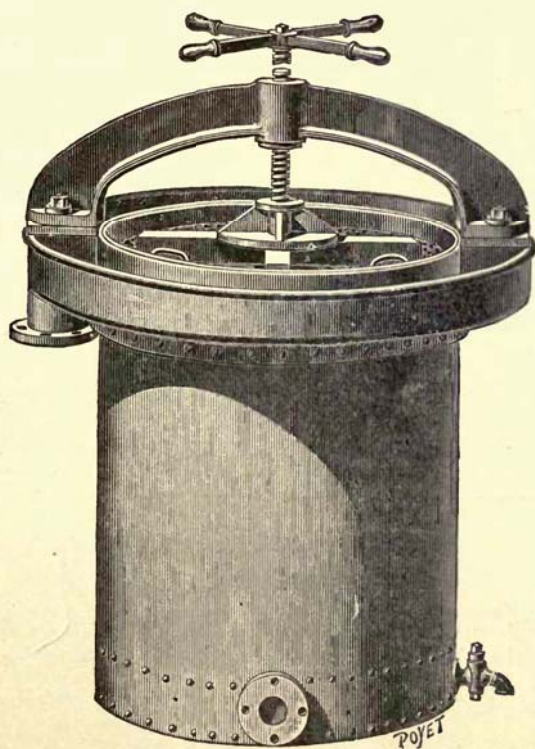


FIG. 107.—Desrumaux's sponge filter.

among filtering materials, are used in a large number of industrial filters. It is easy to arrange the apparatus so that the sponge, or analogous material such as cotton or wadding, can be compressed and thus its filtering qualities can be improved. By allowing the sponge to expand the filter can be rapidly cleaned by forcing the water through it from the bottom upwards and running it off with the impurities. The sponge filter of H. Desrumaux is well arranged for this purpose. Perret's filter is a long trough of cast iron in which cotton is packed as the filtering agent.

The cotton is in the form of cloth tightly held in the frames of perforated cast iron and resembles the leaves of a book.

The water passes from one end to the other and is freed from its impurities by the cotton cloth or by sponge, if that be substituted. The filtration is commenced by allowing the deposit to settle mechanically. The water is then decanted into the apparatus and the filtration is completed by the physical effect of the porosity of the material.

Filter Presses.—The principle of the filter-press depends upon the fact that the filtration is the more rapid the larger the filtering surface and the greater the pressure used.

Filter presses, although they are employed chiefly in distilleries, candle-works, sugar-works and breweries, are also used in purifying water and in separating out the precipitates in residuary waters.

The water to be filtered is pumped into a series of vats the

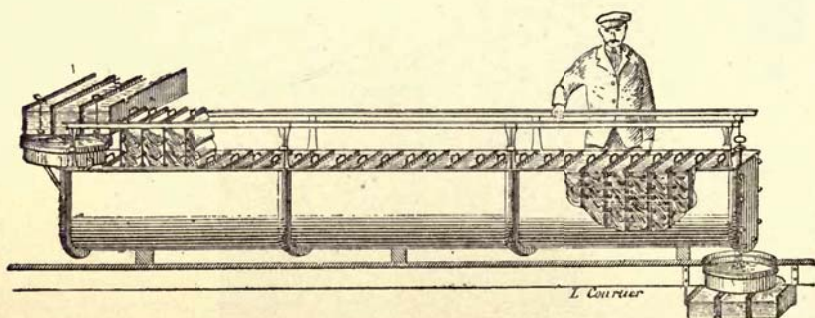


FIG. 108.—Perret's sponge filter.

lateral sides of which have perforated plates covered with the filtering cloths. In this way the mass to be filtered is forced by the pressure through the filtering cloths and the liquid part is separated out.

As for the solid matter it remains in the vats and is emptied out in layers. The filter press of G. Cambray has frames and grooved plates which obviate the employment of perforated sheets.

These plates have no outlet and the filtering cloth is placed over them saddle fashion.

In order to make the work easier the plates and frames have handles. The squeezing action is obtained by means of a central screw worked by a system of cog-wheels. Taps are arranged at the front end and at the back of the press to allow the air to escape.

G. Leclair's filter press made by the Société des Etablissements Métallurgiques d'Onnaing has a series of plates kept in position

during work by rigid parallel bars. The plates are driven in a carriage way by means of a screw.

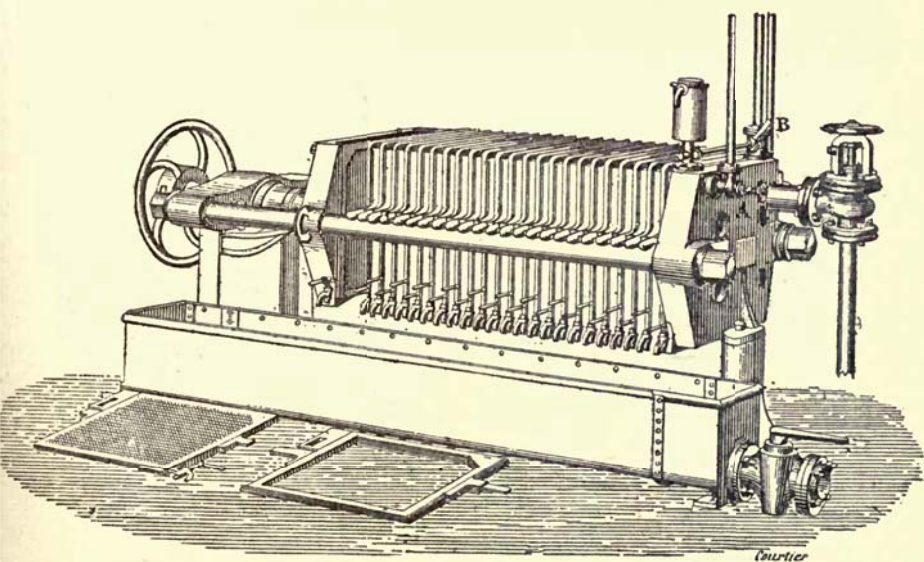


FIG. 109.—Ordinary filter press.

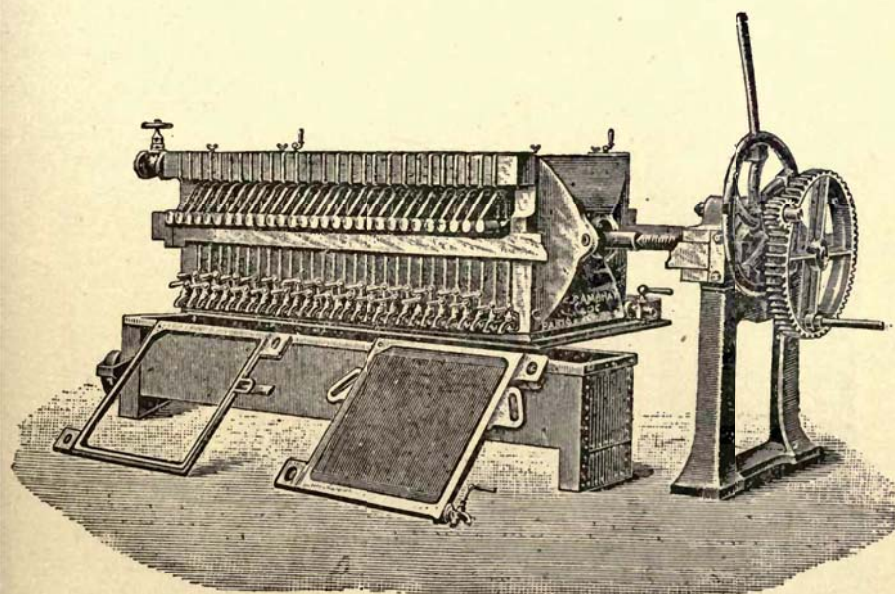


FIG. 110.—Cambray's filter press.

The easy run on the carriage way allows one man to work the machine, and by the system of squeezing a very energetic pressure

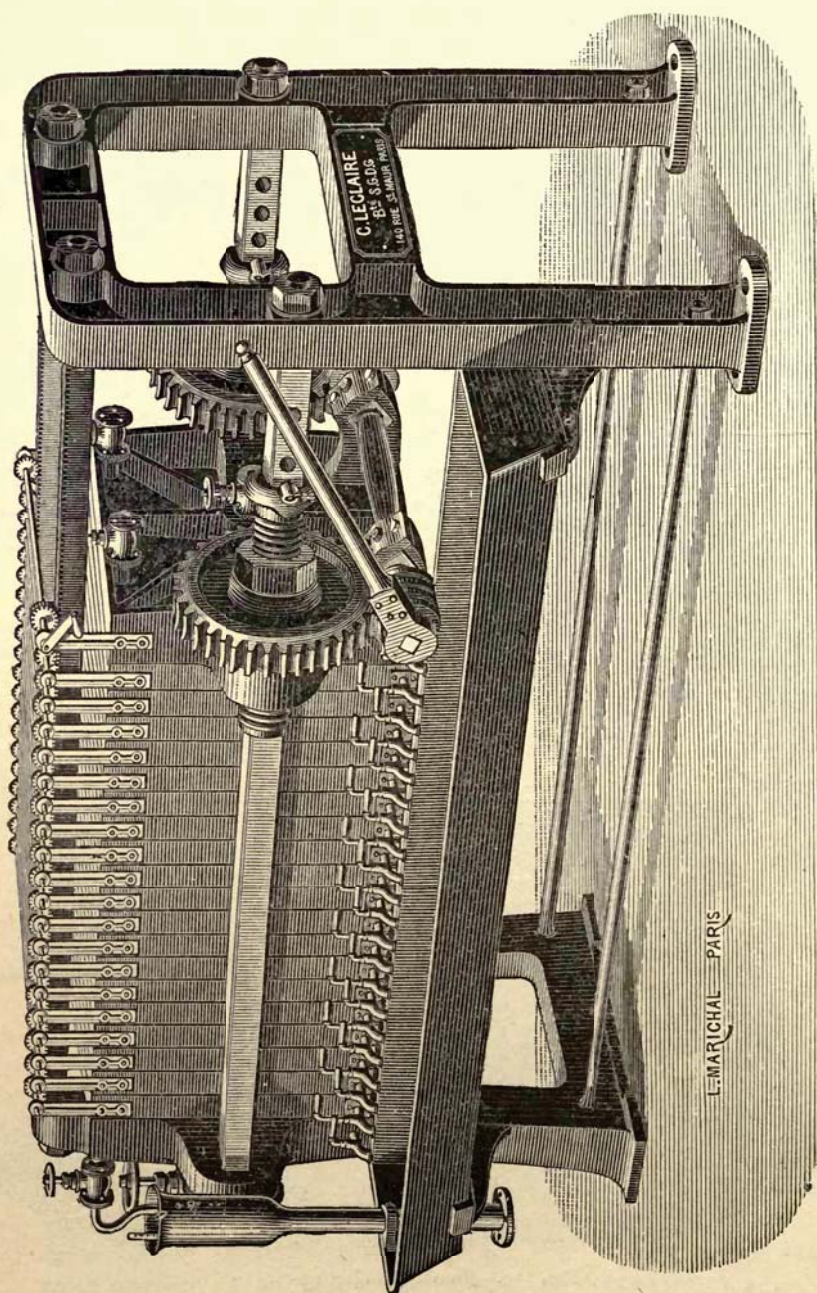


FIG. III.—Leclaire's filter press.

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is assured. The filtered liquids run off by a series of taps communicating with the various plates and are collected in a reservoir.

This filter can be fitted with an arrangement by which the filtration is effected by means of compressed air; in this case an air-pump is used.

The liquid to be filtered flows into the air-pump and is driven back into the filter press by the pressure of air. We give here an illustration of an installation comprising one of Leclaire's membrane air-pumps and regulator connected with a filter press like the last

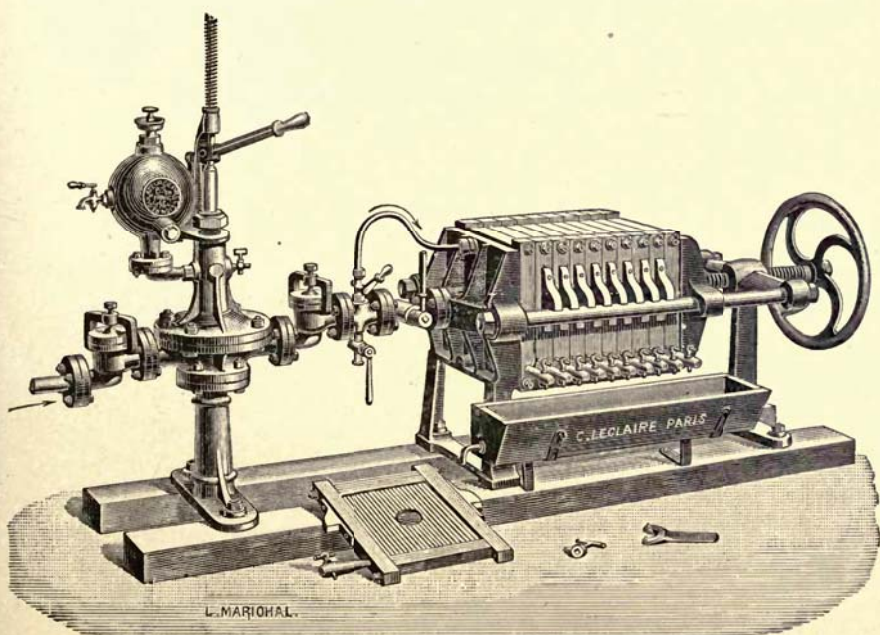


FIG. 112.—Plant for Leclaire's filtering system or membrane pump and regulator.

described. By means of the regulator the pressure can be exactly determined and a constant force assured.

When the pressure is at its maximum in the filter press the membrane of the pump becomes immobile; the plunger continues its alternative movement and forces the water to pass from the body of the pump to the regulator.

At each stroke of the piston the pump is automatically filled.

Solden's Special Filter for Greasy Waters.—This apparatus is used in America for filtering greasy waters from steam engines; its utilisation in the navy has been described by M. Ortolan.

The filter is a series of eleven compartments. The first of these is filled with lime which enters into combination with the oleic acid

in the greasy water, and the oleate of lime thus formed rises to the surface and is skimmed off.

The second compartment contains coke held in position between two sheets of copper. In the third and fourth compartments are frames covered with felt. The fifth contains coke, the sixth, seventh and eighth frames of felt and the ninth coke. The tenth compartment is reserved for the purified water.

CHAPTER XXII.

INDUSTRIAL STERILISATION OF WATER.

IN the manufacture of various beverages, mineral waters, for instance, and of ices, it is necessary to sterilise the water.

Two methods of sterilisation may be employed :—

1. Physical action.
2. Chemical action.

1. STERILISATION BY PHYSICAL ACTION.

By Filtration.—We need not describe here the very numerous filtering appliances which are constructed on the principle of retaining the micro-organisms by means of porous bodies. We will merely insist on the necessity of keeping these filters absolutely clean. The filter must be cleansed as often as necessary, otherwise the micro-organisms will accumulate in the pores of the filtering matter and it will become a veritable colony of microbes.

By Heat.—Numerous experiments have proved that a sufficiently high temperature is destructive to microbes. We will instance the experiments of Miquel and Wada in proof of this.

Experimenting with the water of the Ourcq, which contains 460,800 microbes to the cubic centimetre, Wada obtained the following results, showing the bactericidal power of heat.

Temperature of the water. Degrees C.	Duration in minutes.	Microbes per c.c.
14	10	460·800
50	10	600
60	10	60
70	10	88·8
80	10	62·4
90	10	26·4
100	10	0·5
100	20	0·0

It is sufficient therefore to raise the temperature of the water to 100° C. for ten minutes to kill almost all the germs it contains.

But Pasteur proved the remarkable fact that whereas water

raised to 100° C. loses nearly all its germs, if the temperature is raised from 110 to 120° C. no organism remains. It is evident therefore to ensure complete destruction of the germs the water must reach a temperature of about 115° C.

A number of apparatuses have been invented to sterilise water by heat. We will cite to begin with the perfected apparatus of M. Jules le Blanc, a Paris engineer, the inventor of the well-known steam-disinfecting apparatus. The steriliser of M. Blanc has proved

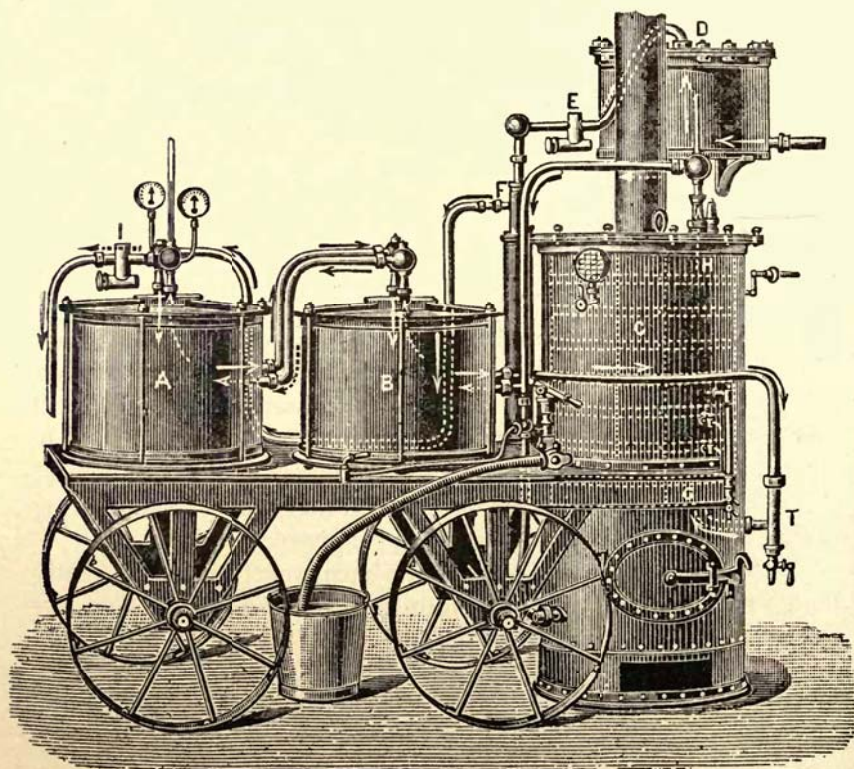


FIG. 113.—Vaillard and Desmaroux's steriliser.

in experiments made before several Commissions on Hygienics that the perfect sterilisation of water can be obtained under particularly advantageous circumstances.

In the steriliser of Vaillard and Desmaroux the water to begin with is clarified in a filter D, then passes to a pressure regulator E, then to a temperature regulator F which stops the circulation of water in the apparatus when the necessary temperature is not reached.

The water leaving the regulator F enters a special vessel A

called an interchanging recuperator, and from there it flows into a second interchanging recuperator B, like the first. From here it is conducted by the pipe T which is in connection with a coil of tubing inside the boiler C composed of eight rings superposed and interchangeable.

The water circulates in the boiler C at a high temperature the necessary time to sterilise it completely, then rises to the top of the apparatus and runs down the tube, following the arrow in the figure, into the recuperator B and from thence into A, thus reversing the first order. Finally the water leaves A completely sterilised.

It will be noted that in its first passage the cold water receives

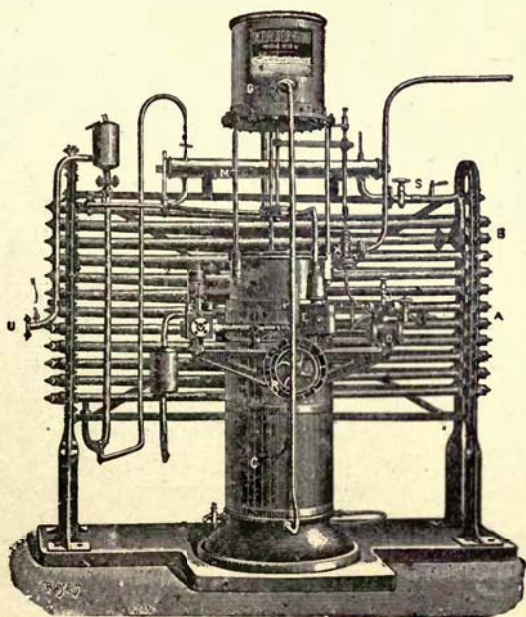


FIG. 114.—Houdard, Egrot and Grange's new pasteuriser.

in the recuperators A and B the heat of the sterilised water leaving the boiler C. Thus it enters the boiler at a temperature of about 100° C. and the boiler need only raise this a little to obtain complete sterilisation. Thus robbed of its heat by the entering cold water the sterilised water leaves the apparatus at the normal temperature.

Houdard, Egrot and Grange's steriliser or pasteuriser, much used for wine and the juice of grapes, can be used for any liquid and is very suitable for water. It is composed essentially of two parts:—

1. A system of tubes forming the recuperator and heater.
2. The accessories, that is to say, a motor, pumps, warm water reservoir and regulator.

The liquid to be sterilised is rapidly forced by the pump at a certain pressure into the lower part of the system of tubes, and in rising into the upper part is heated by contact with the hot liquid already sterilised and circulating in the opposite direction.

By a special arrangement of the tubes this exchange of temperatures is easily effected. The tubular recuperator is formed of pairs of straight tubes; each of these contains a removable series of smaller tubes ending in a box which puts them into communica-

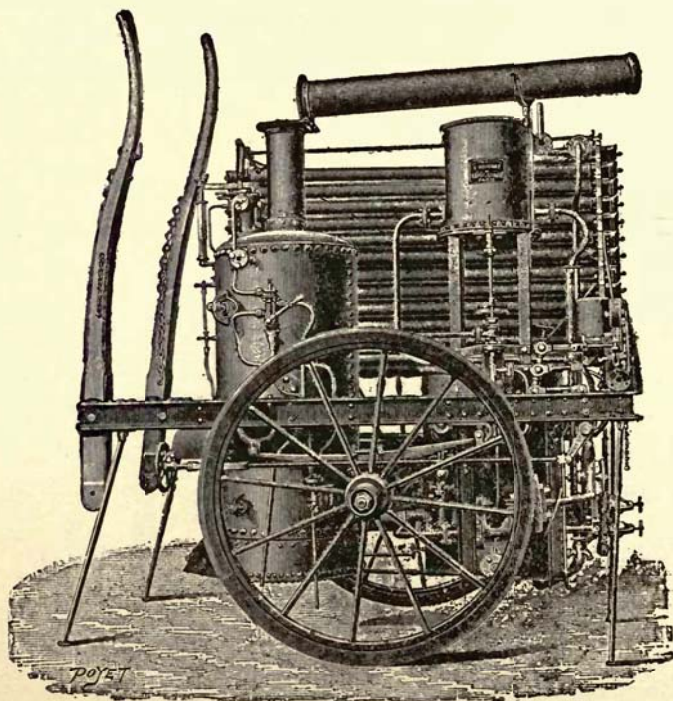


FIG. 115.—Houdard's steriliser on wheels.

tion. In this way two circulations are set up, one outside the smaller tubes and the other within.

After leaving the system of tubes the liquid rises into the heater composed of tubes arranged like the others. These complete the sterilisation at the necessary temperature which is obtained from a hot-water boiler below. This boiler is heated by steam from the boiler of the motor which works the pumps.

The hot water is led to the upper part of the reservoir by a special pump and forced at a certain pressure into the heater, to return again to the lower hot-water boiler by the intermediary of a vat mounted on the upper part.

Regulators control the delivery of the liquid and the amount of heat necessary.

The Houdard, Egrot and Grange steriliser, when sheltered from the air, allows a sterilising temperature of from 115° to 130° C. to be attained.

One type of pasteuriser is mounted on wheels for easy transport. This type is especially employed for sterilising casks and heating wines.

2. STERILISATION BY CHEMICAL ACTION.

The processes of chemical sterilisation depend upon the action of agents capable of an energetic oxidising action.

Chloride of lime, iodine, bromine, permanganate of potash, permanganate of lime, peroxide of chlorine, and ozone have been suggested for the sterilisation of water.

By Permanganate of Potash.—Permanganate of potash is rich in oxygen as shown by its formula, KMnO_4 . It possesses the power of oxidising organic bodies.

This enables it to act as a steriliser by destroying the micro-organisms. In using permanganate of potash it is simply added little by little to the water until the pink tint produced no longer disappears.

One of the drawbacks of using permanganate of potash is that the hydrate of potash remains in the water after treatment.

By Permanganate of Lime.—Ch. Girard and Bordas suggested the use of calcium permanganate. This agent in the presence of organic matter in the water is decomposed into oxygen, oxide of manganese and lime.

The permanganic acid set at liberty oxidises the organic matter and is reduced to oxide of manganese. As for the carbonic acid arising from the oxidation of the organic matter it combines with the lime and forms chalk. It is necessary to get rid of the excess of permanganate of lime; this is done by transforming it into bin-oxide of manganese by the aid of a lower oxide of manganese. The bin-oxide of manganese thus formed may be reduced in its turn by the organic matter in the water, passing into the lower oxide which may be used again to reduce the excess of permanganate which again becomes bin-oxide.

A little charcoal may be added to the lower oxides used in order to facilitate agglomeration.

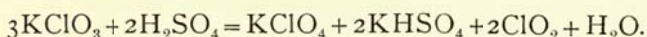
It has been shown that permanganate of lime in a neutral or slightly acid solution sets up a physical action. It has the tendency

to form a sort of lake with the organic matter and thus this is deposited and destroyed together with the micro-organisms of the water.

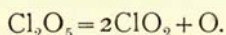
By Peroxide of Chlorine.—Water may also be sterilised with peroxide of chlorine, a process invented by H. and A. Berge. The peroxide may be used either as a gas or in solution.

To prepare peroxide of chlorine chlorate of potash is acted upon at about 15° C. by sulphuric acid of 1·711 S. G.

Peroxide of chlorine, perchlorate of potash and water are thus obtained :—



This reaction is complex and the peroxide of chlorine is formed by the decomposition of the chloric anhydride, which comes from the chlorate of potash :—



It will be seen that in this reaction free oxygen is also obtained.

In sterilising water the peroxide of chlorine acts on the organic matter as an energetic oxidant without introducing basic salts into the water. By the first reaction it will be seen that a gramme of chlorate of potash gives '367 of a gramme of peroxide of chlorine.

For ordinary water an average of from 1 to 2 grammes of peroxide of chlorine is needed, that is to say 1 to 2 milligrammes per litre. According with the theoretical formula therefore a quantity of chlorine varying from '0035 to '0070 per litre is added to the water. This is from 20 to 40 times less than water which passes as only slightly chlorinated.

In practice the peroxide of chlorine is added to the water in slight excess in order to ensure the complete destruction of all germs. As a test a solution of iodide containing starch is used. When the addition of this to the water produces quickly a blue coloration sufficient peroxide of chlorine is present.

By Ozone.—Ozone as a sterilising agent has been experimented upon for the past few years by Drs. Roux, Calmette and Van Ermengen and by Houzeau and de Luynes.

By the reports of these experiments, published in the *Annales de l'Institut Pasteur*, it is evident that ozone must be looked on as a powerful germ destroyer. The ozone not only destroys completely all microbes and organic matter, but also improves the water very considerably by its energetic aeration which does not rob it of any of its useful mineral constituents.

By ozonisation the water acquires keeping qualities which preserve it from ulterior pollution. We may add that even waters

polluted by decaying matters from middens or water-closets have been rendered wholesome by a treatment with ozone.

The industrial treatment of waters by ozone has been practised:—

In France by G. Séguy, Otto, Eck, Abraham, Marnier, de Saint-Martin, Andréoli, and Patin.

In Holland by Baron Tindal, Schneller and Van der Sleen. In Germany by Ohlmüller, Siemens and Halske.

In 1895 Tindal exhibited an apparatus for sterilising water by ozone at the Health Exhibition in the Champ de Mars at Paris. The Municipal Council of Paris voted £5,000 for the installation of a plant at Saint Maur to deal experimentally with the water of the Seine by ozone and capable of treating 500 cubic metres of water in twenty-four hours at a maximum expense of $2\frac{1}{2}$ centimes per cubic metre of sterilised water.

Recently experiments have been made in Germany on the ozonisation of the waters of the Spree at Berlin and the results obtained have been most conclusive.

The sterilisation of the water is done either by direct ozonisation or by filtration followed by treatment with ozone.

The laws which regulate the production of ozone according to a communication of Gaston Séguy to the Academy of Science in 1885 presented by M. Schützenberger may thus be stated:—

The quantity of ozone produced is:—

1. In direct ratio with the tension of the current used.
2. In direct ratio with the number of producing surfaces.
3. In inverse ratio with the thickness of the di-electric body interposed between the two poles and with its conductivity.
4. In ratio with the number of passages under the influence of the current, it being given that three is the maximum number to effect supersaturation.

M. G. Séguy must be credited as the inventor of the first apparatus for the industrial production of ozone and also as the first experimenter on this method of sterilising water.

The generator of M. Séguy, known as the ozone supersaturator, allows large quantities of ozone to be produced and supersaturated owing to a device which makes the oxygen pass several times under the influence of the electric current in the course of its transformation into ozone.

Séguy's apparatus is composed of a dynamo J producing a continuous current which is transmitted to the transformers E. The alternations are regulated by a vibrator F.

The high potential current is led to the ozonising tubes by the

rings B and B². The air to be ozonised enters at M and the ozone produced comes off at A. The ozone generator works with a transformer of very high potential and produces 154 milligrammes of ozone per minute.

The oxygen, transformed into ozone, runs in bubbles on a sort of sieve of aluminium which distributes it in the water to be sterilised. A gasometer is provided to collect the ozone when it

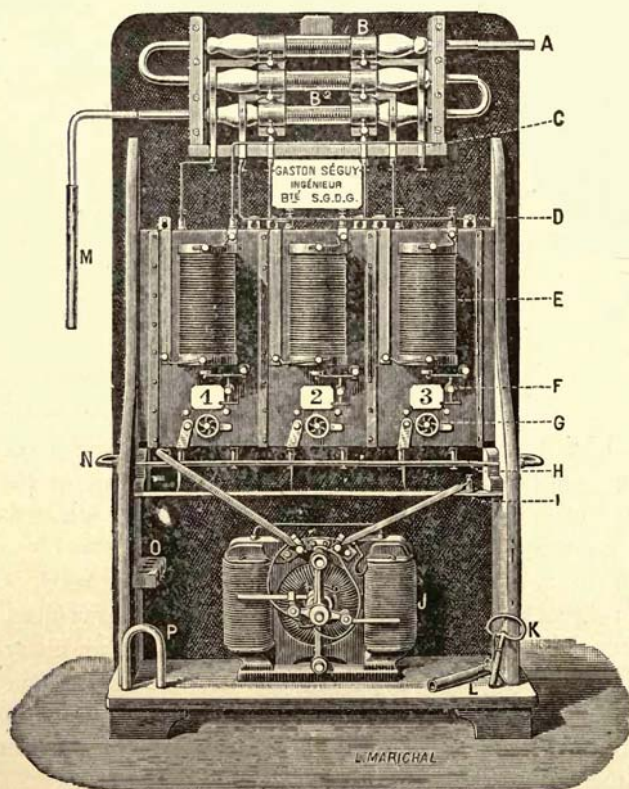


FIG. 116.—Séguy's ozone generator.

has done its work. It is then in the form of oxygen which may be retransformed into ozone by the electric current.

In a note to the Academy of Science and a communication to the French Society of Civil Engineers, M. Otto describes the phenomena of phosphorescence which are produced when the microbes and organic matter are destroyed by ozone.

He shows that :—

1. In certain conditions there is a vivid luminosity when the ozone comes in contact with the water.
2. This luminosity is proof of the destruction of the germs as

it is not produced in pure water. The apparatus for the sterilisation of water on a large scale described by M. Otto is characterised by the employment of emulsifiers serving to produce a perfect contact of the ozone with the water by forming a perfect emulsion of the sterilising body with the water to be sterilised.

This emulsifier is formed of two cones running side by side with the apex of the one against the base of the other.

The ozonised air is led by a pipe to one of the cones and the water to the other. It is delivered in a thin stream and is thus quickly acted upon by the ozone. On leaving the emulsifier the action of the ozone is completed by contact with the water in a special form of steriliser.

These sterilisers are formed of a number of flat surfaces of large area, the number of these varying as a rule from 20 to 50, according to requirements. The water already ozonised is spread in a thin sheet on the highest plate of the apparatus. The plates have outlets surrounded by rims which keep a layer of water constantly on the plate.

On leaving the emulsifier the ozone escapes at the upper part and enters at the bottom of the steriliser, traversing the first plate by the outlet just described, then the second plate in the same manner, and so on to the last. The outlets in the plates are so arranged that the water in passing from one to the other takes a zigzag course from the top to the bottom, meeting the ozone, the current of which is flowing from the bottom to the top, where it escapes by an outlet pipe.

The sterilised water runs into a reservoir below, from whence it is drawn by a system of pipes.

The Compagnie de l'Ozone at Paris have a series of apparatus specially constructed for the preparation of table waters and sterilised ice. In sterilising table waters the empty bottles are brought by endless carriers into position in the filling and stoppering apparatus against a bar of bronze.

The water is saturated with ozone in a special form of mixer, which consists of three glass cones running in the same bearing. This works exactly in the same way as the emulsifier which we have just described. The water is forced into the bottle, charged with a large quantity of ozone, and thus not only the water is sterilised but also the bottle.

When filled the bottles are led away by an endless cloth.

In the preparation of sterilised ice, the apparatus used works in a similar manner, but it is arranged so that the stoppering of the bottles is done automatically.

In 1898 experiments were undertaken by Marmier and Abraham at the forcing station for the water of the Emmerin at Lille, with a view to sterilise it with ozone.

The installation consisted of three plants :—

1. For the production of the electric current.
2. For the production of the ozone.
3. For the sterilisation of the water.

The electric current produced passes into a transformer of high potential, capable of giving 40,000 volts and more.

The ozone is produced by two apparatuses—by an ozoniser and a deflagrator. A series of sparks play between the branches of the deflagrator, assuring a regular potential between the poles of the ozoniser.

As for the ozoniser, it consists of a metallic electrode, a sheet of glass, a space, a sheet of glass, an electrode, a sheet of glass, a space, and so on. The first electrode is in communication with one pole of the transformer, and the second with the other pole, and so on, and the electric current flows in the spaces between the glasses.

Leaving the ozoniser, the ozone passes on to a large column in stonework, in which the water, to be sterilised circulates. This after treatment collects at the base of this column.

The patents of Abraham and Marmier are worked by the Société Industrielle de l'Ozone. Trials made with the apparatus for the production of ozone of Eck and Patin show that more than five cubic metres of Seine water can be sterilised for each horse-hour employed. Andréoli has made an aluminium ozoniser, producing 100 grammes of ozone or thereabouts per horse-hour with a slight rise of temperature. The great germ-destructive power of ozone should make application of this gas as a steriliser one of the most important questions of the day.

PART IV.

RESIDUARY WATERS AND THEIR PURIFICATION.

RESIDUARY waters vary in composition not only according to the class of industry producing them, but also according to the particular methods and processes used in the works and the quantity of water employed. Some works can extract useful matter from the residuary waters economically and profitably.

The treatment of course varies with the circumstances, but the purification methods adopted may be broadly classified as (1) Purification by the soil; (2) Chemical purification, and these are sometimes combined.

In studying soil filtration, which has given such satisfactory results in the treatment of sewer water, we are face to face with the great question of the sanitation of towns. The soil does not always lend itself to the necessities of the case, and the residuary waters must often be treated by chemical or electro-chemical processes.

After having passed in review the processes in general use as for instance in sugar-works, distilleries, starch-works, paper- and board-mills, tan-yards, etc., we will point out the method of recovering certain residues in dye-works and from the waters used in soap-making. We will then consider the treatment of soapy waters, which are the principal residuary liquors in a large number of industries, as for instance in woollen factories. The treatment of these is generally very profitable.

The treatment of these soapy waters must be considered under two circumstances, at the works themselves or at a central collecting station like that of Grimonpont, which deals with the waters of the Espierre, the great drain of the north of France.

The purification of the water of the Espierre, an acute Franco-Belgian question, has been the object of numerous experiments for many years past, and it will be useful to consider these as they throw a light on other problems of the purification of residuary waters.

Finally, we will finish the third part of this work by describing how certain profitable substances are extracted from soapy effluents.

CHAPTER XXIII.

SOIL FILTRATION.

PURIFICATION by the soil or by irrigation cannot always be employed. Certain waters, such as those of the Espierre, are freed with difficulty from the foreign matter which they contain, and soil filtration is extremely troublesome.

The nature of the soil is an important factor, and is often an obstacle in this method of purification, as for instance in the East, in the districts around Roubaix and Tourcoing. The divers international and inter-communal commissions which have sat to consider the question of the Espierre, have pronounced categorically against soil filtration.

On the other hand, irrigation is one of the best means of treating sewer waters, as for instance the effluent which is diverted over the plain of Gennevilliers.

In the period between 1887 and 1895, taking an average of analyses, the results obtained have been as follows :—

	Oxidibility.	Organic Nitrogen.	Ammoniacal Nitrogen.	Nitrites.	Chlorine.
Drained from Clichy	39'1	5'4	18'7	4'1	61
„ St. Ouen	56'6	6'3	25'5	3'6	92
„ Grésillons	1'3	—	—	21'3	72
„ D'Épinay	1'3	—	—	22'6	69

On an average, during the year 1895, these drain waters showed the following number of microbes per cubic centimetre :—

Clichy	13,250,000
St. Ouen	16,870,000
Grésillons	880
D'Épinay	8,380

In the peninsula of Gennevilliers the diverted waters do not exceed 40,000 cubic metres to the hectare, and have the following composition per cubic metre :—

	Grammes.
Phosphoric acid	45
Nitrogen	18
Potash	27

According to M. Duclaux, 1 cubic metre of sewer water contains the same quantity of fertilising principles as 10 kilogrammes of farm manure. The sewer water spread over the plain of Gennevilliers therefore may be estimated as equal to 400,000 kilogrammes of manure, which is twenty times more than is necessary, as the highest culture does not exact more than 20,000 to 25,000 kilogrammes. A large part of the population of Paris is supplied from the agricultural products obtained. The vegetables are most excellent in spite of the prejudices of the public when they know that they come from Gennevilliers.

The matters in the sewer water are transformed under the influence of microbes into substances which form a part of the natural food of plants, and the prejudice is a mistaken one, as the agricultural products are not impregnated with the primitive substances.

The results obtained have been so satisfactory at Gennevilliers, that a considerable enterprise has been carried out in diverting the sewer waters of Paris on to the plain of Achères.

The plain of Gennevilliers, formerly uncultivated land, has become extremely fertile, for, in treatment by the soil, the water filters through the permeable strata, leaving behind it the matter that was in suspension, the organic matters are then submitted to the influence of oxygen and of the ferments which assist in their nitrification.

Nitrates are thus produced assimilable by the plant, and the water is purified by the abandonment of its fertilising principles to the profit of agriculture. Sewer water contains these principles in large proportion. The soil is also employed for filtering purposes by works in country places near cultivated fields. Starch works and distilleries, for instance, treat their effluents in this way.

Two considerations are involved in the method of purification by irrigation, filtration and oxidation. Both these phenomena must be considered in examining this method.

As the filtration depends upon the permeability of the soil, this must be sufficiently permeable to permit a rapid filtration, and the degree of purification of the water also depends largely upon this permeability. In its passage through the soil, the water is freed from the various organic and mineral matters which it holds in solution or in suspension, and also abandons part of the organic germs which it contains.

This filtration is best effected in soils which have a uniform permeability, and which consist of sand or gravel, or a mixture of these with a little clay. The oxidation should proceed rapidly, the

organic matters being oxidised under the influence of nitrous and nitric ferments.

The water to be purified should be as much as possible in contact with the oxygen of the air. This is why the irrigation method requires a large surface area.

A good permeable ground will purify an average of from 60 to 100 cubic metres of water per hectare in twenty-four hours.

Some manufacturers have a certain practice which should be absolutely condemned. We have seen some distilleries deal with their effluent from the filter presses by draining it into an uncovered pit, from which the liquid was diverted into the stream. The filtration was done in a deplorable way under the worst possible conditions for health.

These decanting pits rapidly fill with stagnant matter and become cesspools. The putrid fermentations set up make them a source of infection, dangerous to the public health, and moreover the liquid is run off into the stream in a state of active fermentation.

If soil filtration properly employed frees the water from the soluble organic substances in it, and destroys the living organisms, it cannot be applied, it will be seen, in all districts or to the residuary waters of all industries.

To meet this difficulty the effluent is often submitted to a mixed treatment. A chemical purification is first resorted to and the irrigation process then finishes the purification. Residuary waters are also treated by chemical processes alone, and we will proceed to describe these.

CHAPTER XXIV.

PURIFICATION BY CHEMICAL PROCESSES.

RIVERS and streams being protected by statutes, by-laws and regulations, manufacturers cannot run their effluent into them without first bringing it into the desired condition.

Works carrying on dangerous or insalubrious manufactures are especially bound by rigorous regulations in the matter of their effluent. Sometimes, as in the case of the Espierre district, the neighbouring works run their water directly into a collector. Thence there are two methods of purification, the one consisting of the treatment of the water at the factory itself, in order to run it off clean and wholesome, and the other in treating the effluents of many works at a common collecting basin.

These two methods are both in operation in the Espierre district, as some of the manufacturers find it to their advantage to treat the waters at their own works, in order to recover the useful substances they contain.

Woollen-works in particular can purify their effluents very profitably, extracting from them potash and suint, in a proportion that much more than covers the cost of treatment. Waters containing fats free or in combination are subjected to recovery processes, which of course are only profitable if the cost of treatment is less than the value of the recovered substances.

If the matters extracted from residuary waters do not pay the cost of treatment, manufacturers are content to purify the effluent by ridding it of these substances or by transforming them into harmless matters before running off the effluent into the stream.

I. PURIFICATION OF RESIDUARY WATERS FROM DIVERS SOURCES.

Schloesing's Process.—Three essential principles are found in midden waters: phosphoric acid, potash and nitrogen in combination. The phosphoric acid is almost entirely contained in the solid

matter ; the nitrogen is in the ammonia and this in particular must be extracted from the midden waters.

By Schloesing's process this ammonia is precipitated in the form of a phosphate of ammonia and magnesia which is very useful as a fertiliser. Instead of obtaining this substance by using phosphates or magnesia salts, which are expensive products, phosphoric acid and magnesia, free or combined, are used.

By adding phosphoric acid to sludge containing magnesia a precipitate of tri-basic phosphate is at once obtained which after settling can be easily filtered through cloth and precipitates ammonia in the state of phosphate of ammonia and magnesia. This reaction is produced by the exchange between one molecule of magnesia of the tri-basic phosphate and one molecule of ammonia which is present in different states in the midden water.

Sea water contains salts of magnesium in large proportion, and a product can be prepared from it capable of precipitating the ammonia from the waters containing it.

The sea water is simply treated with lime and the precipitate is allowed to settle for twenty-four hours. After decanting off the clear supernatant liquid, the sludge thus obtained is mixed with a solution of phosphoric acid, and a precipitate falls down which is collected and is ready for use in the treatment of residuary waters.

Process used at Coventry.—On leaving the collector the water to be purified passes into a kind of wheel with gratings to facilitate the separation of the solid matter.

The matters retained in the wheel are thrown out into a basket to drain and then carried off by an archimedean screw which conducts them to a filter press, and after pressing the solid sludge is used as manure. The water on leaving the wheel is stirred up mechanically with solutions of alumina and iron and finally with milk-of-lime. Filtration finishes the treatment, and the waters are then run off into the river.

Lechatelier Process.—The use of salts of iron and of aluminium has been suggested by M. Lechatelier, who employs Picardy pyrites, containing salts of aluminium and iron, or bauxite, which he treats with sulphuric acid.

When sewer water is treated in this way, soaps of alumina and of sulphide of iron formed by the sulphuretted hydrogen are obtained. The iron thus acts as a disinfectant. This action of the iron ensures oxidation and the regeneration of the reagent. Numerous trials have been made by Lechatelier on sewer waters and residuary waters from divers works, in particular the effluent

of sugar-works, which has given good results on purifying with perchloride of iron combined with lime or dolomite.

The albuminoid matters and the phosphoric acid are precipitated by the perchloride of iron acting as an oxidiser.

As regards the use of sulphate of alumina proposed by M. Lechatelier, the experiments of Durand-Claye, made on the sewer water from Clichy, have given good results, using 200 grammes of sulphate of alumina per cubic metre of water.

The result of these experiments was that the water running off after treatment was absolutely limpid and colourless, so that a printed page could be read under a layer of it 10 centimetres thick. Fishes were able to live and thrive in the water thus purified. The sludge which remained after treatment was odourless and dried easily when spread over the soil.

Putting the price of the reagent at 11 francs the 100 kilogrammes, this treatment would cost about 2 centimes per cubic metre.

A. and P. Buisine's Process.—In this process use is made of ferric sulphate, obtained economically by roasting pyrites.

When ferric sulphate is introduced into sewer water the alkaline salts and the salts of the alkaline earths which are always in the water decompose the iron salt and ferric oxide falls down as a precipitate. The precipitate of ferric oxide carries down with it the matters in suspension, and they form compounds with the albuminoid and greasy matters. The colouring matters form lakes and the sulphuretted hydrogen is fixed by the iron.

Most of the micro-organisms are eliminated by the precipitation of the hydrate of the ferric oxide, enveloped in some way by the lakes formed with the organic substances.

Trials made on the Paris sewer waters gave the following results. The water, after a preliminary decantation, gave 1053 kilo. of dry matter containing 1.08 per cent. of nitrogen per cubic metre. It was then treated with ferric sulphate, in the proportion of 100 grammes per cubic metre.

After the addition of the ferric sulphate a precipitate was obtained which on drying weighed 318 grammes and contained 2.18 per cent. of nitrogen. The organic matters in solution were sensibly diminished by this treatment, and water which contained 600 gramme of organic matter in solution before purification contained no more than 0.65 after treatment.

Thus nine-tenths of the organic matter in solution is eliminated, the whole of the matter in suspension, and moreover a proportion varying from 60 to 90 per cent. of the micro-organisms primitively contained in the water.

The treatment gives a clear, limpid and colourless water, containing so small a quantity of organic matter in solution that it may be looked upon as imputrescible.

Putting the figure at 100 grammes of ferric sulphate the process costs about half a centime per cubic metre of the water treated.

Sillar's Process.—This process, which has had a certain vogue in England, employs a mixture of three principal reagents, known as A, B, C alum, blood and charcoal.

In addition to these three reagents other products are usually employed: Clay, manganate of potash, earth containing salts of lime and magnesia, and the chlorides of sodium, and of magnesium, so that the mixture is very complex. This reagent precipitates the salts in solution, but the nitrogenous matters which are the cause of putrefaction, are treated in an absolutely imperfect manner.

Moreover, from trials made at Leicester¹ it has been shown that the waters contain more ammonia after treatment than before.

Compared with the lime process the sludge contains more ammonia as it is acid, whereas in the lime treatment the sludge being alkaline is in a good condition to throw off the ammonia, and in drying allows it to escape.

Anderson's Process.—Anderson's process consists in allowing the water to be purified to drip over scraps of cast iron, contained in a horizontal cylinder revolving on its axis.

In absorbing the oxygen dissolved in the water the iron is transformed into the protoxide and dissolves. The water running from the cylinder passes into a wide shallow open conduit, in order to give the air free contact with it, and thus produce oxidation. Finally it passes into an open reservoir built of cement.

As a result of the peroxidation of the iron by the oxygen the hydrate of ferric oxide is precipitated, carrying with it the organic matter in solution. It is allowed to settle a little and finally filtered through sand. Trials of this process made by M. Schutzenberger show that the dissolved organic matter and the microbes have largely disappeared, but not altogether.

Suvern's Process.—This process, which gives an incomplete purification, is especially employed in England. It consists in treating the waters with a mixture of:—

	Parts.
Slaked lime	100
Chloride of magnesium	15
Coal tar	15

Defosse's Process.—The process of Defosse is in three stages.

¹ We believe that the author means Manchester.—Tr.

1. Decantation and preliminary precipitation with three reagents, sulphate of alumina, permanganate of potash, and lime.
2. A rapid filtration through peat.
3. A final filtration through a layer of iron ore and limestone.

The water to be treated is to begin with decanted into a basin filled with baffles and a stirring arrangement. In this the greater part of the fat rises to the surface of the liquid by reason of the agitation, and the different fatty bodies in the upper part of the water are drawn off and collected.

These fats can be treated by special processes of purification, and used commercially. On leaving the decanting basin, the waters are run into a trough and mixed with sulphate of alumina, permanganate of potash and lime in different proportions according to the nature of the liquid to be treated. This mixture of reagents is regulated and delivered automatically by means of floats in the water to be purified, adjusting the delivery of the reagents.

The precipitates formed and the matters in suspension are deposited in the form of sludge in the basins, which are filled and emptied alternatively. These deposits are evacuated from the lower part of the basins by a pipe leading into tanks below.

The supernatant sewage from the decanting basins is spread over layers of turf, and passes on to a layer of artificial iron ore, which is extremely porous, and then on to a bed of limestone.

The artificial iron ore is made specially for this process and is a combination of iron, manganese, and charcoal.

According to M. Defosse, this ore, in contact with the water containing organic matter, forms carbonates and hydrates which are subsequently peroxidised. As after the passage through this ore the waters carry with them a certain quantity of iron in solution, they are taken on to a bed of limestone in order to precipitate it as carbonate of iron.

The iron ore being used very slowly and gradually, its expense is very slight. The process employs 120 grammes of reagent (permanganate of lime and charcoal) per cubic metre of sewer water.

The greasy matters obtained are treated by the processes of Souffrice of Saint Denis, by which industrial fats and stearine are obtained from greasy waters from various works and from the scum of the Seine.

The sludge is used in making illuminating gas, which has much better lighting qualities than coal gas, and the residue left in the retorts, which is a compound of potash, soda, carbon and a certain amount of phosphate, is ground up and sold to the farmer as a fertiliser.

Scott's Process.—Instead of using lime alone a mixture of lime and clay is added to the sewer water.

The organic matters form about a third of the deposit, and on calcining the residue, not only lighting gas is obtained but also cement.

Bird's Process.—The sewer waters are treated with a mixture of clay and sulphuric acid, and the treatment is terminated by a filtration through coke.

Trials made at Stroud, in Gloucestershire, show that nine-tenths of the matter in suspension is precipitated in this way, and the nitrogen in solution is reduced by half.

Howatson's Process.—This process consists in mixing by degrees the residuary waters with a product which the inventor calls ferrozone, the preparation of which varies according to the waters to be treated. It invariably contains, however, a large proportion of ferrous and ferric salts. Two samples of ferrozone show on analysis the following composition :—

	A.	B.
Anhydrous ferrous sulphate	1'33	0'80
Anhydrous ferric sulphate	1'00	0'05
Anhydrous aluminium sulphate	36'29	30'13
Insoluble matter (including a little carbon).	32'40	26'56
Water, etc.	28'98	42'46
	<hr/> 100'00	<hr/> 100'00
Sulphate of alumina	69'00	} 85'1 per cent. soluble.
Ferrous sulphate	10'50	
Ferric sulphate	5'60	
Ferric oxide	12'50	} 14'9 per cent. insoluble.
Alumina and silica	2'40	
	<hr/> 100'00	

The soluble salts which this product contains rapidly precipitate the solid matters in suspension, and prepare the putrescible substances for ulterior oxidation.

When the precipitation is finished the liquid is decanted off and passed through special filters which retain any particles in suspension still remaining after decantation, and in addition aerate the water.

The water is then poured over a material known as polarite which has a powerful oxidising action, and which is intended to destroy the organic matters.

Polarite is a black, hard, very porous, insoluble and inoxidisable substance, which has the property of retaining oxygen in its pores. Its composition is as follows :—

Magnetic oxide of iron	54
Silica	25
Lime	2
Alumina	6
Magnesia	7
Alkalies	6
	<hr/>
	100

The organic matters in suspension or solution are oxidised and transformed into carbonic acid and nitric acid. After its passage through the polarite, the water is sufficiently clear and limpid to be run off into the stream.

In treating residuary waters a preliminary decantation should be effected in order to retain the matters in suspension as far as possible. The sludge resulting from the ferrozone treatment is treated in filter presses in order to free it from liquid and transform it into solid matter.

Piet and Dumas' Process.—The water is run into a reservoir containing 1 kilo. of quicklime for each ton of water to be purified. The albuminoid matters and the sulphate are precipitated.

After decanting, hypochlorite of soda or of lime is added to the liquid in the proportion which ensures the presence of 1; litres of chlorine gas per cubic metre of water. This is allowed to react for six hours, then carbonic-acid gas is bubbled through the liquid to precipitate the lime, and a decantation and filtration terminate the treatment.

Webster's Electro-Chemical Process.—In Webster's electro-chemical process an electric current is passed through the residuary or sewer water, by the aid of a dynamo communicating by wires to ordinary iron electrodes.

In the case of Paris sewer waters it is sufficient to use a current of .05 ampère-hour per litre. Residuary waters require a more intense current, and although they are incompletely purified they become clear and inodorous enough.

There is no necessity to use any reagent, as the electrolysed waters contain chlorides, especially those of sodium and of magnesium, which are decomposed under the influence of the electric current and release chlorine which comes off at the positive pole. Ammonia, soda, potash and magnesia form at the negative pole.

The chlorine and oxygen formed act energetically on the organic matter, which is rapidly oxidised. In combining the two gases form hypochlorous acid with the water and oxides of chlorine. The acid thus formed attacks the iron of the electrode, and compounds

of acids with the iron are produced, amongst which, according to Webster, hypochloride of iron is in the largest proportion.

This hypochloride of iron produced at the positive pole comes

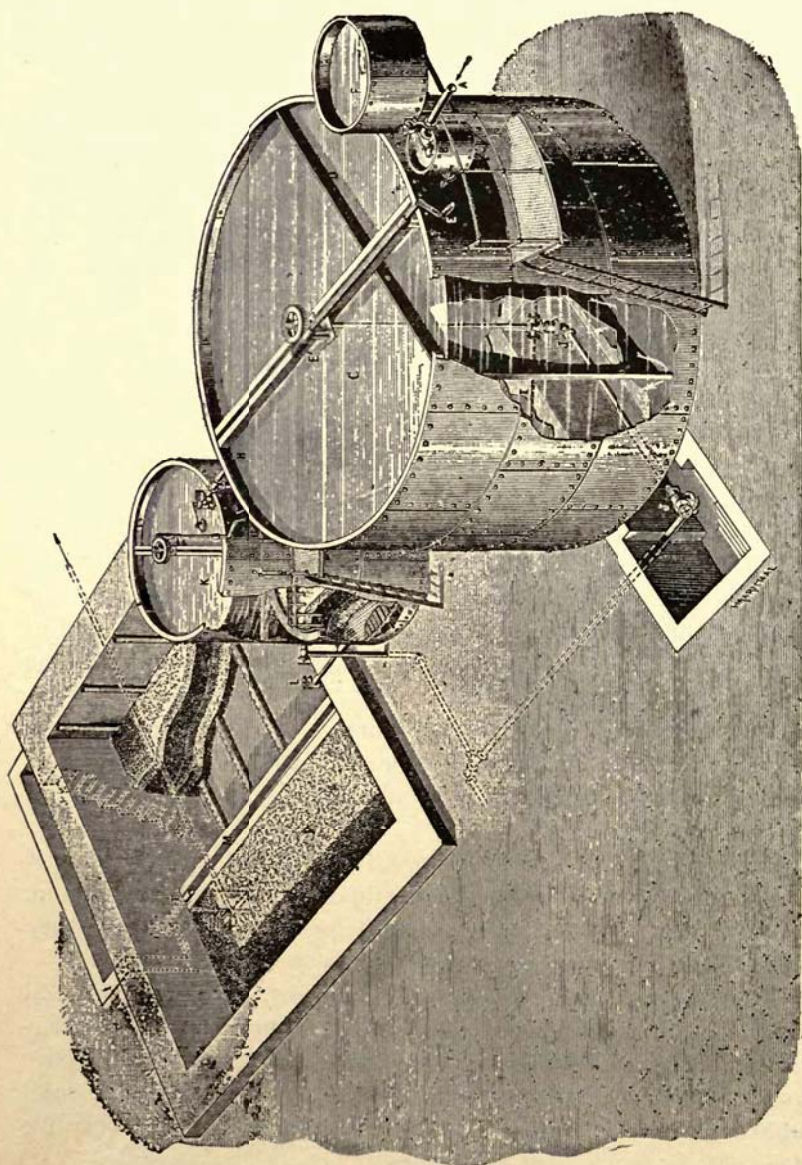


FIG. 117.—Howatson's process for purifying residuary waters.

under the action of the free ammonia, soda, potash and magnesia, and causes the precipitation of a hydrate of the oxide of iron which combines with the organic matters. The hydrate of the oxide of iron and the hypochloride of iron formed attack not only the matters

in suspension, but also those in solution. The bubbles of hydrogen escaping at the negative electrode carry up the solid matters towards the surface ; but these are quickly reprecipitated.

Hermite's Electro-Chemical Process.—Hermite's electro-chemical process for the purification of residuary waters depends upon the following principle. If an electric current be passed through a solution of a chloride, preferably a mixture of the chlorides of magnesium and of sodium, as for instance sea water, the water and the chloride are decomposed.

In consequence a very unstable compound of chlorine and oxygen is formed at the positive electrode, and this has great oxidising power and consequently is an excellent disinfectant.

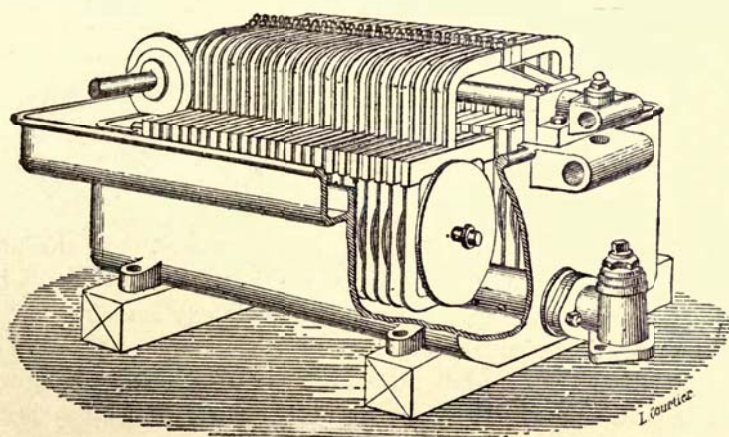


FIG. 118.—Hermite's electrolyser.

An oxide is formed at the negative pole which is capable of precipitating certain organic matters.

The result of the electrolysis is thus to form a liquid capable :—

1. Of bringing about the destruction of the organic matters resulting from putrefaction, and of destroying the microbes and the gases, such as sulphuretted hydrogen, hydrosulphate of ammonia, and the carbides of hydrogen.

2. Of precipitating certain bodies, such as the albuminoid matters.

Two methods can be used in the electro-chemical treatment of residuary waters—the direct and the indirect method.

The direct method consists in passing the residuary water into the electrolyser with the mixture of chlorides to be electrolysed, and the water leaves the apparatus after having been purified.

The indirect method consists in preparing a liquid containing

the oxides of chlorine by electrolysing a chloride in the apparatus, the resultant liquid being then added to the water to be purified.

The electrolyser used in either case is composed of a vat of galvanised iron, in the lower part of which is a tube perforated with holes and furnished with a zinc tap to allow the passage of the liquid to the electrolyser, that is to say the chloride alone or mixed

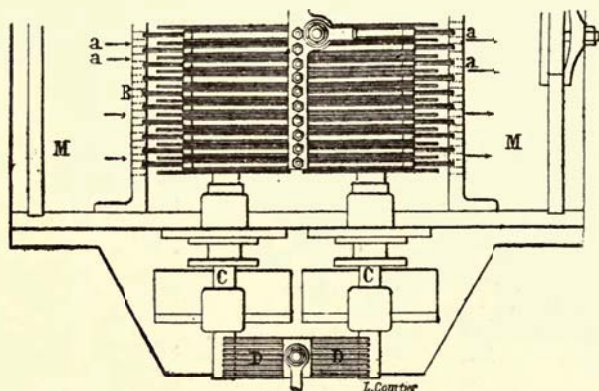


FIG. 119.—Hermite's electrolyser (plan).

with the liquid to be purified. The vat has a rim on the upper part forming a reservoir, from which the liquid is carried off by a tube arranged so as to give a constant circulatory current.

The negative electrodes are a certain number of zinc discs, mounted on two horizontal and parallel shafts, and turning slowly.

The positive electrodes were formerly represented by a sheet of

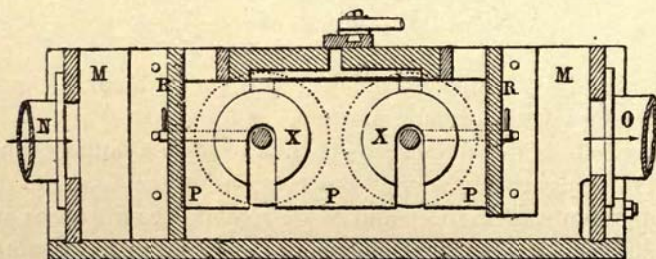


FIG. 120.—Hermite's electrolyser (transverse section).

platinum held in an ebonite frame, but are now slates pierced with holes in which are platinum wires.

The positive electrodes are placed between each pair of zinc discs, and soldered to them at the upper part is an armature of lead, bringing them all into communication with a bar of copper which traverses the electrolyser.

This bar of copper representing the positive electrode is there-

fore in communication with the positive pole of the dynamo. The current passes to the platinum wires, then to the discs of zinc, forming the negative electrode, and in communication by means of the cast iron of the vat with the negative pole of the dynamo.

Finally, flexible blades of ebonite placed on the positive frames press against the zinc discs and keep them clean by friction.

The chlorides preferably employed are to begin with the chloride of magnesium or this mixed with chloride of sodium or potassium, then sea water, then chloride of sodium, chloride of aluminium, and chloride of iron. A current of 1,000 to 1,200 ampères is generally passed through the electrolyser with a force of 5 volts.

When several electrolyzers are employed they are arranged in series.

Oppermann's Process used at the Sugar Refinery at Lambres, near Douai.—In this process a mixture of perchloride of iron and

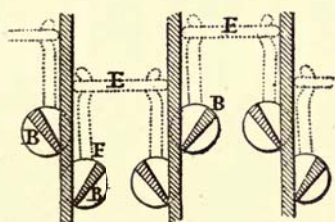


FIG. 121.—Hermite's electrolyser : arrangement of the blades.

calcined dolomite is the reagent used in treating the residuary waters.

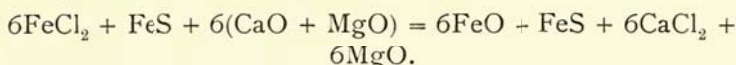
This reagent is largely used in Germany in dealing with the waste liquids of sugar works and has given excellent results. M. Manoury has given the process a trial in France at the Lambres Sugar Refinery, near Douai, and its success has been perfect. Manoury has communicated the results he obtained to the *Journal des Fabricants de Sucre* and the official inspector of roads and bridges has also reported on them to his chiefs.

The process so far seems to have been used in sugar works only, but its employment would doubtless be efficacious in the treatment of other effluents.

Having prepared a solution of sulphide of sodium it is poured into a solution of perchloride of iron and a part of this becomes sulphide of iron. The mixture thus obtained is put into a cask with a tap by which the outflow can be regulated. The mixture is drawn off into a tank containing the water to be purified, and when mixed some milk of dolomite, which is calcined dolomite stirred up

in water, is dropped into it from a height of a few yards above the tank in order to bring about the precipitation of the impurities.

The action of the protochloride of iron in the presence of the sulphide of iron and of the milk of dolomite brings about the following reaction :—



Thus hydrate of the protoxide of iron, and of the oxide of magnesium, sulphide of iron and chloride of calcium.

The greater part of the lime is combined with the chlorine giving chloride of calcium and the carbonic acid turns the rest into carbonate of lime. The magnesia alone remains, which being only slightly soluble in water is less troublesome than the lime, and as it is only weakly caustic it does not dissolve the organic matter, or only to a negligible extent.

Hydrate of the protoxide of iron and sulphide of iron are formed together with the magnesia, the protoxide is quickly oxidised by the air and becomes peroxide. In the presence of the peroxide of iron the sulphide of iron is oxidised in its turn, and as sulphate of iron enters into solution burning up the organic matters by rapid oxidation and by parting with its oxygen is precipitated as sulphide of iron.

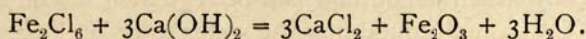
This iron sulphide is of course again in contact with the peroxide of iron and the cycle of reactions already described continues. The purification of 40,000 hectolitres of waste liquids per day at the Lambres Sugar Refinery is estimated at 100 francs.

M. Oppermann has recently combined the treatment with dolomite and the ozone process and has applied the combination to sewer water purification.

Gaillet and Huet's Process used at the Central Sugar Refinery at Flavy le Martel.—This process used for the residuary waters of divers industries and especially for the spent liquids of sugar-works consists in treatment with perchloride of iron and lime.

A cask is filled with a solution of perchloride of iron to begin with and its contents are poured into a tank containing the waters to be treated by a regulating tap. The water treated is run off and in its course milk-of-lime is poured into it from a mixing tank which is kept constantly supplied with fresh quicklime.

A precipitate of oxide of iron is formed by the following reaction :—



By its weight which is considerable this precipitate carries down

with it the coagulum of lime and organic matters in suspension. A limy sludge results from this which is rich in fertilising properties and can be used as manure.

According to M. Vivien the cost of this treatment at the Central Sugar Refinery of Flavv le Martel may be estimated as follows:—

The cost of daily treatment at Flavv le Martel in dealing with 14,000 hectolitres of waste liquid is 56·775 fr., that is to say 0·004 centimes per hectolitre.

Recovery of Residues in Dye-house Spent Liquors.—If the exhausted dye-baths and wash waters are run into the dye-house drains there is a certain loss of substances which may be profitably recovered by treating the dye-house effluent.

In addition to the recovery of carbonate of potash from raw wool, which will be considered later in dealing with soapy waters, the dyer can very profitably recover the tin from the bichloride of the metal used in weighting silk. After having been mordanted and squeezed or wrung the silk is then rinsed in plenty of water, and during this washing the bichloride of tin decomposes a part remaining in the bath and the rest becoming fixed on the fibre. To recover this lost tin Martineau saturates the wash liquors with lime. On stirring, the oxide of tin is precipitated and can be collected by filtration through cloth.

A paste containing 15 per cent. of oxide of tin is thus obtained from which the metallic tin may be extracted or reconverted into bichloride by treating the paste with hydrochloric acid.

In indigo vats there is often a considerable amount of unused indigo in the deposit, either because the indigo has been badly ground or because the vat has been badly worked. It is of course profitable to recover this indigo.

For this purpose M. Garçon advocates the treatment of the deposit with hydrochloric acid in excess; the lime and the oxide of iron are thus transformed into soluble chlorides. The residue is collected on cloth and washed and the indigo which it contains is dissolved out with hydrosulphite of sodium.

2. SOAPY WATERS AND THEIR PURIFICATION.

Residual waters containing soap require especial attention from manufacturers as they are the most profitable to deal with.

Potash and fatty bodies can be extracted from them which are of great commercial value and are always in demand.

All waters containing soap in more or less quantity come under this head, but we shall here deal with the effluents which result

from combing and spinning wool, milling cloth, degumming and boiling-off silk, bleaching fabrics, Turkey-red dyeing, and from spent dye-baths generally. The water used in treating raw wool is specially advantageous to deal with.

Three classes of these effluents may be distinguished.

1. Wash Waters.—These solutions result from the washing in cold water of wool in suint. They contain potash which is extracted by evaporating to dryness.

Maumené and Rogelet's process of extracting the potash is still in use. It consists in using the water for washing fresh batches of wool until it shows 10 to 12° B.

It is then evaporated to dryness and the residue calcined in retorts gives a gas which may be used for lighting purposes.

The residue left in the retorts is dissolved in water and gives a crude potassic salt containing about 70 to 80 per cent. of pure carbonate and giving a yield of 5 to 7 kilogrammes of crude salt for each 100 kilogrammes of wool in suint.

The manufacturers thus find it to their advantage to give a preliminary washing, as not only does it yield a profit but it considerably facilitates the chemical purification.

2. Scouring Waters.—These result from the hot scouring of the wool or hides with soap.

These are the most abundant in wool manufacture, and as they contain large quantities of putrescible matters they need the most careful purification.

3. Waters from Working the Wool.—In these waters the oil remains which is used in combing the wool, and the soap which has been used to form an emulsion with the oil.

There is no difficulty in treating these waters. The addition of hydrochloric acid produces a magma which on pressing yields a fatty matter which can be used in soap-making and is worth 60 to 80 francs per 100 kilogrammes. The waste waters from wool scouring are the most difficult to purify. Their composition is very variable as it depends upon the concentration of the water, the nature of the raw material and the processes it passes through.

In practice the scouring liquors should be looked upon as containing:—

1. Organic matters, fatty bodies and other substances.
2. Soluble and insoluble mineral substances.

Before running these waters off into the river two methods may be used in purifying them, at the works producing them or at a central collecting station dealing with the effluent from all the works in a manufacturing district.

The treatment of the effluent at the works themselves has the advantage that it can be done regularly with a knowledge of special circumstances and furnishes valuable by-products to the manufacturer. As a matter of fact the effluent of each works is almost always charged with the same matters, and has therefore a known composition for which a recovery process can be exactly elaborated, and as the amount of fat contained is usually fairly large the recovery is certain to be profitable.

When the effluents of a manufacturing district are run into a common collector for treatment, as in the case of the towns of Roubaix and Tourcoing, the composition of the liquid, coming as it does from all kinds of works, is not only complex but very variable. The recovery of the by-products becomes in this case problematic for the yield is frequently too small to pay the cost of the process. We will examine several processes used at the works themselves to deal with soapy waters, especially the effluents of the woollen industry. Then we will pass in review the experimental processes at collecting stations dealing with divers effluents, taking as a type of water that of the Espierre.

(A.) PURIFICATION OF SOAPY WATERS AT THE WORKS.

Vohl's Process.—This process has been specially recommended by the soap-boilers for dealing with the liquors resulting from the boiling-off of silk and from Turkey-red dyeing.

The soapy waters are treated with chloride of calcium until precipitation is complete, the precipitate is collected, pressed and put into lead-lined vats where it is decomposed with commercial hydrochloric acid which must be free from sulphuric acid.

A jet of steam is then blown in and the excess of this with the gas resulting from the reaction is passed through a box filled with lime and escapes by the chimney.

The unwholesome gases and bad odours are destroyed and the fluid fatty acids float on the surface of the liquid. It is allowed to settle for six hours and then the lower contents of the tank are drawn off by means of a tap at the bottom. As this liquid contains chloride of calcium it can be utilised over again.

Water acidulated with hydrochloric acid is then added to the contents of the tank and after turning on the steam for half an hour the whole is allowed to settle.

The clear acid liquid is drawn off and the layer of fatty acids in an emulsion are ready for special treatment, either to get rid of the water or to do this and bleach the fat at the same time.

The water is driven off by heating the emulsion with the addition of sea salt over the open fire or with a steam coil.

If it is required to bleach the fats also and thus increase their volume after washing with hot water the hot fats are put into a lead vat with a stirring arrangement and heated by a steam coil. A solution of chromate of potash in sulphuric acid is added and the contents are stirred for half an hour, after which they are allowed to settle for six hours to separate out the fatty acids.

The lower layer of liquid is chrome alum. It is drawn off and the operation is repeated five or six times according to the degree of bleach required.

Finally the fatty acids, after settling and the drawing off of the clear water, are freed from water by distillation. For this purpose they are put into a still with 14 to 15 per cent. of mineral oil and distilled.

The mineral oil can be recovered and used again. If the separation of the solid fatty acids is required, the mixture of fatty acids still hot, freed from water and bleached, is put into a vat and allowed to cool slowly to 9° C. The concrete fatty acids collect at the bottom of the vat and crystallise. They have only to be collected and cold pressed and the separation is effected. In order to avoid the formation of alkaline sulphate by impure hydrochloric acid containing sulphuric acid, which renders the separation difficult, M. Vohl proposes to replace the chloride of lime by chloride of calcium.

Treatment with Chloride of Sodium.—Like the preceding one this process is used for treating soapy liquors of a certain purity.

Sea salt is added to the liquor until it is saturated; the soap comes to the surface in clots and after collection is treated with sulphuric acid to separate out the solid fatty acids.

Treatment with Carbonate of Soda.—The treatment with sodium carbonate is used, preferably, in the same case as the preceding processes. The carbonate of soda is simply added to the soapy liquor and it is heated to about 60° C. for half an hour.

A scum forms on the surface of the liquid. This is collected and treated with hydrochloric or sulphuric acid to separate out the fatty acids.

Purification at Holden's Woollen Works at Croix.—The method used at Holden's works, the great wool-combing factory at Croix, in the north of France, is also used at Seydoux's works at Cateau.

The soapy waters to be purified have the following composition per cubic metre:—

	Kilos.
Fatty matters	9'500
Organic matters	3'841
Soluble and insoluble minerals	7'082
	<hr/> 20'423

They are run into a cast-iron tank lined with lead and 5 kilogrammes of commercial hydrochloric acid of 22° B. per cubic metre are introduced. The greasy matters are decomposed into fatty acids and a magma floats on the surface of the liquid which contains the major part of the fats and the earthy matters.

This magma has the following composition :—

Fat	43'30
Organic matter	18'83
Earthy matter	37'87
	<hr/> 100'00

After settling the clear liquid is run off and this still contains :—

	Kilos.
Fatty matters	1'100
Organic matters	1'672
Mineral matters	1'145
	<hr/> 3'917

As the water that runs off is acid, on neutralising this acidity with lime a precipitate is obtained which according to M. Goblet contains 1'390 kilogrammes of fat and organic matters per cubic metre. In this precipitate is also found a large proportion of the mineral matters. Usually this precipitate is thrown away and the water is passed through lime or decanted and run off into the Espierre collector.

The cost of this treatment per cubic metre, as regards reagents, may be put at :—

Commercial hydrochloric acid, 5 kilogr. at 4 fr. the 100 kilogr.	0'20
Lime	0'02
	<hr/> 0'22

The magma obtained by the hydrochloric acid is hot pressed. It yields a non-saponifiable fat. The residue containing fatty matter is treated with bisulphide of carbon.

At Holden's works the fat recovered is estimated as worth 25 francs the 100 kilogrammes, and as 6 kilogrammes are extracted per cubic metre the treatment furnishes 1'50 fr. of fat per cubic metre. Taking into account the cost of reagents, *i.e.*, 0'22 fr., the remaining 1'28 fr. is amply sufficient to meet the cost of working and to leave a profit.

J. Mollin's Process.—Clay purifies residual waters by forming a coagulum with certain of the substances in the water.

In soapy waters, where the soap is simply in solution, an abundant precipitate is not obtained. The clay sinks to the bottom of the liquid and the water remains turbid. If however the water contains fatty acids in emulsion on adding clay mixed up in water a voluminous precipitate is deposited.

In the case of the waste waters from wool combing soured with hydrochloric acid an emulsion of grease is obtained which treated with 1 gramme of blue or potter's clay per litre of water gives a voluminous flocculent precipitate which falls down rapidly and carries with it a great part of the nitrogenous matters in solution.

The magma formed is collected and yields from 1.5 gramme to 1.7 per cent. of a product that on treatment with bisulphide of carbon gives 30 per cent. of a light-coloured fat melting at from 34 to 35° C. and resembling good suint.

The fatty matter of this magma need not be extracted and the whole mass may be retorted for illuminating gas. In the treatment by bisulphide of carbon the cakes after the grease is extracted have the following composition :—

Water	4.40
Organic matter	28.00
Ash	67.60
	<hr/>
	100.00

These cakes contain 1.19 per cent. of nitrogen, which proves that the clayey-greasy precipitate has eliminated a considerable proportion of the nitrogenous organic matters.

Using 1 kilogramme of clay per cubic metre of water, 787 grammes of the organic matter is eliminated thus :—

Organic matters	Kilo. 0.4570
Divers and nitrogenous organic matters	0.3304
	<hr/>
	0.7874

The elimination of these 787 grammes of organic matters requires 1 kilogramme of clay at 2 francs per ton, that is to say the cost is 0.002 fr. Naturally this cost is calculated for clay alone and as concerning the purification of waste acid liquors from wool combing. In this way the greater part of the fatty bodies which have escaped precipitation from the soapy water by hydrochloric acid are recovered. This treatment with clay therefore necessitates that the fatty acids should be in a free state, and consequently, if they are not, the fatty matters must be decomposed to begin with by the addition of hydrochloric acid to the water to be purified.

Purification at the Woollen Factory of MM. Delattre at Dorignies les Douai.—This question of the purification of waste water from wool combing being very important we will examine minutely the methods of treatment employed at the factory of MM. Delattre at Dorignies les Douai. We will describe the process formerly used at the Dorignies factory and the process as improved by M. Delattre.

1. *Old Process.*—The wash waters are run into decanting cisterns, as soon as one cistern is full the water is turned into another.

The solid matter is deposited as sludge. Wooden grids superposed from bottom to top of the cistern collect the sludge and drain it sufficiently to allow it to be scooped out. They are removed successively in the course of the work with this object.

This sludge contains much wool and mineral substances which allow it to be used as a fertiliser. The water is diverted into a tank and a reagent of perchloride of iron soured with hydrochloric acid is added. Thus the fats are decomposed into fatty acids and being set at liberty float on the surface of the liquid. They are skimmed off and are ready for use. By treating the fatty acids by steam pressure oil is extracted from them from which a very brilliant illuminant gas can be obtained. The water after treatment in the tank passes into a circular vat in which milk-of-lime is continually dripping. The contents of the vat are kept in agitation by a mechanical stirrer.

The result is that the acid water is neutralised, oxide of iron is precipitated, carrying with it the organic matter and the water is turned into decanting cisterns where it deposits the precipitated matters. The water runs off clear from the upper part of the decanting cisterns and is allowed to escape into the river. The calcareous sludge can be pressed into cakes.

This process formerly used at the factory of MM. Delattre, and devised by M. Gaillet, allows wash waters from wools in suint, containing about 30 kilogrammes of residue per cubic metre, to be treated so that 72 per cent. of the volatile organic matter and 50 per cent. of the fixed organic matter is eliminated. At Dorignies 1,000 cubic metres of water is treated every twenty-four hours and the same process has been employed at Fourmies.

2. *New Process.*—In the woollen industry the wools in suint before being spun have to undergo two operations to free them from foreign matters.

(1) Desuinting, or simple washing, to take away the soluble matter in the suint.

(2) Degreasing, or scouring, in which the insoluble fats and the

various foreign matters that adhere to the fibre are taken from it by using carbonate of soda and soap, after the simple washing. The result of these two operations is to produce enormous quantities of residuary waters, known as wash waters. These must be considered under different heads according as to whether they come from the simple washing or the scouring.

The water from the first operation is easy to treat in order to obtain potash which may be used in soap manufacture.

In this case it is sufficient to evaporate the liquor in special kiers following the process of Maumené and Rogelet. The residuary waters are thus transformed into a remunerative product.

But if the wash-liquors are easily treated this is not the case with scouring-liquors. These latter contain the most varied foreign matter in large proportion, and thus, until recently, these liquors were considered incapable of profitable treatment. Lately, owing to the constant efforts of MM. J. Delattre and Son, the residuary water at the works at Dorignies les Douai has been so perfectly treated that the effluent is sufficiently clear to be turned into the stream.

The importance of the question will be seen when it is understood that at the Dorignies factory alone 6,000,000 kilogrammes of wool is scoured and combed annually, and that the daily effluent amounts to from 1,500 to 2,000 cubic metres of residuary waters having the following composition per litre:—

										Grammes.
Insoluble matter	{	Organic	30.46	} 32.30						
		Mineral	1.84							
Soluble matter	{	Organic	2.35	} 4.45						
		Mineral	2.10							
				<hr/>	36.75					

After purification the water is run off into the canal of the Haute Deule and has the following contents per litre:—

										Grammes.
Soluble matter	{	Organic35
		Mineral	2.00
										<hr/> 2.35

In examining these analytical results the conclusion is arrived at that in the course of purification 34.40 grammes of impurities have been obtained from each litre of water. It will be seen that a mere trace of organic matter remains, and an insignificant 2 grammes of mineral substances.

As the result of conclusive trials the Administration of Bridges and Highways has allowed the effluent from the residuary waters thus treated to be run into the river, and the late Aimé Girard

reported enthusiastically on the process to the Society for the Encouragement of National Industry.

Description of the Process.—The wash-liquors are separated into two portions:—

1. The liquor from the cold wash is treated as usual to recover the potash.

2. The scour-liquors are submitted to a special treatment.

This proceeds as follows:—

(a) It commences with a preliminary decantation from a deep and narrow cistern. The sludge is deposited and used as manure; it is very rich in nitrogen, potash and ammoniacal nitrogen.

(b) The fatty matters are separated out with a slight excess of sulphuric acid, and this is subsequently neutralised with lime.

(c) The greasy sludge is treated to extract "suintine" from it, and the residue, rich in fertilising principles, is used in the manufacture of manures.

Method of Operation.—The wash-liquors are run into tanks having taps in the lower parts which allow the liquor to be run off with force down a sloping central conduit bearing the solid matter with it. From the conduit the water runs into a culvert which leads it by two lateral openings into one of two deep and narrow stone-work cisterns where the sludge is allowed to settle.

In each cistern troughs of wood are arranged from top to bottom, taking a long zigzag course in order to free the water completely from the solid matter. Two large sluices in each cistern allow them to be cleaned out simultaneously. The water is decanted from the upper part of the cistern and is carried off by a trough into a large stone-work reservoir.

In order to acidify perfectly the liquid mass which is a necessary condition of successful purification the water before entering the stone-work cistern meets with a large stream of sulphuric acid which runs over a glass plate. A number of baffles which force the current to wash from side to side facilitate the mixture with the acid, and it pours into the large reservoir which has a capacity of about 500 cubic metres. The sulphuric acid is diluted with water to from 20° to 22° B. in two lead-lined tanks, and the mixture is stirred mechanically. It is carried to the trough by one of Kulmann's steam acid pumps.

The acid in excess in the waters thus treated is neutralised by diverting the wash-water into a conduit where it meets a stream of milk-of-lime, prepared in a circular vat by means of slaked lime mixed with a stirrer.

In order to obtain a regular neutralisation, large liquid masses

are operated on. After this preliminary neutralisation, therefore, a second and more complete neutralisation follows in a large special reservoir.

When this is completed the purified water is limpid and clear, and can be run off into the river.

Recovery of the By-products.—The wool in suint contains :—

Pure wool	40
Potash	4'50
Fatty acids	14
Earthy matters	41'50
	<hr/>
	100

It will be seen that it must be profitable to recover the fats.

Works treating the wash-liquors from 6,000,000 kilogrammes of raw wool annually produce about 840,000 kilogrammes of fat.

Adding the oil entering into the composition of the soap employed and that used in the combing, that is to say about 110,000 kilogrammes of oil, a total of 950,000 kilogrammes is obtained from the treated wool. In the preliminary washing some part of the grease is carried off and lost, and the recovery processes may be estimated as dealing with 60 per cent., that is to say 570,000 kilogrammes of fat remains in the waste liquors.

To recover the fat the flow of liquor into the cisterns is stopped, to begin with, at the end of twelve or twenty-four hours, according to circumstances and the clear part is decanted.

The sludge is cleared out by a sluice in the bottom of the cistern into a deep cistern-well from whence it is taken successively into two sludge pumps.

A jet of steam forced into the first sludge pump mixes with the sludge, which is raised to a temperature of about 80° C.

The more liquid sludge from the first sludge pump is carried by a pipe into the second sludge pump which takes it to a filter press.

In its passage through the filter the sludge leaves 40 to 50 per cent. of fatty matter in a collecting tank, and these fats are treated with acid, as before, then washed in clear water before putting them on the market.

The residue from the filter press is taken out, dried and ground up with a view to the recovery of the 20 to 25 per cent. of fat which it still contains.

To extract this still remaining fat benzine is used.

The ground-up cakes of sludge are put into cylinders, 2 metres high by 1 broad, and treated methodically with benzine, commencing with the most exhausted sludge and finishing with the untreated



cakes. The supply of benzine is stopped with the last introduced and shows no grease when evaporated on a glass plate.

The benzine is then run into a central reservoir, and the benzine still impregnating the sludge is driven off with a jet of steam. The benzine is condensed in a refrigerator and from there returns into the central reservoir.

The whole of the benzine, charged with grease, is run into a still and the benzine is distilled over and collected in a refrigerator and from there passes into the central reservoir to be used again.

As before the recovered fats are treated with acid and washed before being put on the market.

The fat extracted from the wash liquors, or suintine, amounts to about 520,000 kilogrammes yearly and brings from 12 to 15 francs the 100 kilogrammes. About 2 per cent. of fat still remains in the sludge and the loss of benzine is estimated at 30 kilogrammes for every 3,000 kilogrammes of treated sludge.

The cakes after the recovery of the grease make excellent manure, and at the works of MM. Delattre and Sons a very substantial profit is made in combining them with superphosphate of lime and selling them to the farmers as fertilisers.

Recovery of Glycerine from the Mother-liquors of Soap-works.

The large consumption of glycerine makes its recovery of special importance in soap-works where it is obtained in considerable quantities as a by-product, unfortunately too frequently wasted.

Many processes have been proposed to effect this recovery, but very few of them have been found really practicable. The extraction of glycerine from the soapy residuary water of woollen factories requires a special process suited to the particular composition of the water, which moreover constantly changes, qualitatively and quantitatively, so that the recovery is a very difficult matter.

The recovery from the soap-boiler's effluent is much easier as the same problem is always proposed: given an aqueous mixture of glycerine, soda and chloride of soda to separate out the glycerine with economy.

A method of extraction consists in neutralising the alkalinity of the water with hydrochloric acid, then evaporating the whole in the water-bath. A syrupy mass results from this evaporation which is taken up with 90° alcohol in order to separate the glycerine from the saline matters. These latter are only dissolved in very small quantity by the alcohol.

The distillation of the alcoholic solution allows the alcohol to

be driven off and collected and the glycerine to remain behind in the still in the form of an impure brownish residue.

The process of S. W. Koppe, which is much more practical, consists in neutralising completely, to begin with, the alkalinity of the mother waters containing the glycerine. This neutralisation has an important effect on the work of separating the salts and on the purity of the glycerine obtained. The product thus treated is put into shallow vats with a large surface for evaporation and heated with the waste steam of the works. It is raised to 109°C . and concentrated; the evaporation is very rapid and as the saline matters deposit they are withdrawn with an iron rake. These saline matters are thrown into baskets and allowed to drain into vats and from this liquid the glycerine is recovered. The liquid is carried to a high temperature and finally put into a still and heated over the open fire until the temperature reaches 193°C . When this temperature is reached it is kept up by a current of superheated steam and the glycerine distils over.

(B.) PURIFICATION OF SOAPY WATERS AT A COLLECTING STATION.

As a typical collecting station dealing with soapy waters we will take that of the Espierre, as without contradiction the most numerous experiments have been made there. Moreover these waters are polluted with a variety of substances and are in huge quantity.

The waters of the towns of Roubaix and Tourcoing are turned into this collector which drains all the putrid matters in the effluents of this district. A large proportion of the effluent of the woollen-mills and dye-works of the district is turned into the Espierre, but all sorts of works use the same open sewer and it receives also the household slops and midden drainings.

It therefore contains the most varied accumulations of mineral substances and organic matters. There is a heavy proportion of fats and these are almost the only bodies capable of being extracted, other extractable substances are in too small proportion.

The Espierre with its pestilential waters has been the cause of numerous complaints by the Belgian Government, for on entering Belgium it flows into the Escaut and pollutes it.

This question brought about a diplomatic protest in 1861. A Prefectoral Decree of the 21st October, 1863, called upon the authorities of the two towns of Roubaix and Tourcoing to deal with the nuisance and prevent the Espierre from carrying infectious matters into Belgian territory. The results obtained were far from good; fresh complaints were made and the question several times

over came before the Chamber of Deputies. Several commissions were nominated, among others those of 1866, 1873, and of the 7th June, 1881. A communal commission was also appointed by Prefectoral Decree.

The nature of the Espierre water and of the surrounding soil led these commissions to conclude that chemical purification was the only possible solution of the problem. In the wool-combing establishments the extraction of the fats can be made profitable as the waters contain from 9 to 11 kilogrammes of these matters per cubic metre. In the case of the Espierre as the effluent has the most diverse origins the proportion of these bodies is of course much smaller.

Analyses of water from the Espierre made by the Faculte des Sciences of Lille on seven consecutive day in July, 1881, at seven o'clock in the morning, gave the following results :—

Mixture of the Roubaix and Tourcoing Waters taken from the Espierre at the Sartel Dam.

Contents per litre.	Day.							Average of the seven days.
	1st	2nd	3rd	4th	5th	6th	7th	
Fat	0·81	0·82	1·08	1·05	0·93	1·84	1·05	1·08
Organic matter	0·83	1·52	1·54	0·63	0·81	1·35	1·33	1·14
Sulphate of sodium	0·31	0·13	0·32	0·14	0·30	0·26	0·29	0·25
Chloride of sodium	0·22	0·18	0·26	0·11	0·17	0·20	0·20	0·19
Carbonates of potassium and sodium	0·47	0·49	0·27	0·15	0·43	0·56	0·36	0·42
Carbonate of lime	0·36	0·68	0·96	1·08	0·68	0·68	0·48	0·70
Sand, alumina and iron	0·45	0·53	0·72	0·74	0·58	0·98	0·59	0·66
Dry residue	3·45	4·35	5·15	3·90	3·90	5·90	4·50	4·44

The 0·42 of alkaline carbonates, shown as the average of the seven days, consisted of 0·24 of carbonate of soda and 0·18 of carbonate of potassium. The total nitrogen showed an average of 0·098, existing as :—

Organic nitrogen	0·090
Ammoniacal nitrogen	0·008

According to the above table the average content of fat in the seven days was 1·80 kilogramme per cubic metre.

We will now describe the works at Wattrelos-Grimonpont which have been established with the particular purpose of purifying the water of the Espierre. The lime process has been adopted at these works, but it has been established with the view of adopting any

other process which the results show to be advantageous. We will examine to begin with the principal processes which have been given a trial. At the same time we may mention that through the energy of M. Gruson, Inspector-General of Bridges and Highways, and the deep interest naturally taken in the question by the towns of Roubaix and Tourcoing, a solution of the problem has been reached in the adoption of the new process perfected by M. G. Delattre of Dorignies.

Central Works at Grimonpont for the Purification of the Waters of the Espierre.—This establishment is about 4 kilometres from Roubaix and about 2 kilometres below the confluent of the Espierre and the Truhon. With its dependencies it covers an area of 8·34 ha. and receives the majority of the residuary waters of Roubaix and Tourcoing.

The canal of the Espierre receives 30,000 cubic metres of water in twenty-four hours, of which about one-third comes from the woollen-works. The proportion of the solid matter that the water contains is extremely variable and oscillates between 5 and 10 kilogrammes per cubic metre. As we have said chemical treatment is resorted to at Grimonpont. To begin with purification by lime was tried, but the model works designed by M. Gruson, Inspector-General of Bridges and Highways, and his collaborators M. Devos the engineer, and M. Weber, have been constructed with a special view of trying any chemical treatment which might be advantageously substituted. Thus the works at Wattrelos-Grimonpont have often been put at the disposition of chemists who wished to make experiments with particular processes. To begin with the water is decanted from two tanks each with a superficial area of 2,500 metres.

Dams in the Espierre turn the water into the works. The waters to be purified are diverted into a cistern well and are treated with milk-of-lime, made as a rule with 100 kilogrammes of quick-lime to 600 litres of water. The milk-of-lime ready prepared is run into two superposed reservoirs, it is allowed to escape into the lower one, and from there is pumped into a distributing tank.

By means of a regulator the flow of the reagent is controlled proportionally to the quantity of water to be treated and its nature. In this way the milk-of-lime is mixed with the water to be purified in the cistern well. Four centrifugal pumps force the mixture of Espierre water and lime into a series of twenty decanting tanks. The water is decanted from each tank by means of two sluices and the clarified water runs off and continues its course.

The sludge is dredged out and spread over a sort of sewage farm

in the neighbourhood of the works and this rids it of the major part of its water. The case where a reagent, other than lime, is employed which gives liquid sludge has been provided for by arranging two sluices in the bottom and in the axis of each tank. By burning the dried sludge in special furnaces the lime can be recovered but it is mixed with the impurities of the precipitated matter.

Lime Process.—The lime process has been recommended by Clark, the engineer, and later by Hofmann and White; nevertheless it gives very imperfect results.

The matters in suspension and the fats are properly precipitated, but the lime does not eliminate the organic matters in solution and these are the source of putrefaction.

The Royal Commissioners, W. T. Dennison, E. Frankland and J. Chalmers Morton, in reporting on the pollution of the Mersey and Ribble, described the water after treatment with lime as black and foul, with putrid matter floating on its surface. For the Espierre water 3 kilogrammes of lime are used per cubic metre, which makes the expense for this reagent 3 centimes.

The purification of the Espierre water by lime is very imperfect. The water is alkaline and favours the caustification of the organic matters and their consequent entrance into solution. The lime takes oxygen from the air and becomes the carbonate, and the purified water becomes the source of still more active putrefaction. Using 2 kilogrammes of lime per cubic metre the analytical results of 1 litre of purified Espierre water are as follow:—

Residue	1,350 milligr.
Colour of residue	Yellowish green.
	Milligrammes.
Calcined residue	920
Loss at red heat	430
Ammoniacal nitrogen	25
Albuminoid nitrogen	12.24
Alkalinity (CaO)	84
Sulphuric acid	237
Chloride of sodium	187
Total lime	129
Oxide of iron	40
Hydrotimetric deposit	26
" " after boiling	18
Appearance	Turbid yellow.

The lime treatment is very difficult to work. The clarification is slow. The sludge is abundant, and shortly after a putrid fermentation sets up in it which becomes more and more active as the temperature rises. The abundance of sludge is the great difficulty

in this method of treatment. It reaches about 7,000 cubic metres per day in the case of the Espierre and an encumbrance of sludge accumulates too liquid to be passed into the filter press and compressed. Lime therefore should not be used unless it is accompanied with other reagents.

Acid Process.—Let us examine the application of a process of purifying Espierre water on a basis similar to that used at the wool factory of Messrs. Holden. Hydrochloric acid is poured into the collector, the fatty acids are set at liberty and a greasy magma floats on the surface. It is collected, hot-pressed, and yields a fat with a cake as residue which unfortunately is usually of little value.

The extraction of the grease by this means is very incomplete. A yield of about 60 per cent. is obtained. With bisulphide of carbon the yield is much higher, but this treatment necessitates many precautions and a special plant. Lately, however, a practical apparatus has been devised to extract the fat with gasoline. We will calculate the cost of dealing with Espierre water containing 1·08 kilo. of fat per cubic metre, which is the average found by analysing the water for seven consecutive days.

To treat 1·08 kilo. of fat in the 1 cubic metre of Espierre water we estimate that 0·300 kilo. of commercial hydrochloric acid of 22° B. is needed. Putting the cost of this acid at 4 francs the 100 kilogrammes and obtaining a yield of 60 per cent. of the fatty matter, to recover 0·648 kilo. of fat per cubic metre an expenditure of 0·12 fr. for hydrochloric acid is necessary.

This fat may be estimated as worth 25 francs the 100 kilogrammes, so that the yield of 648 grammes is worth 0·16 fr. The cost of the lime used in neutralisation must be added, which may be estimated at 2 centimes per cubic metre of water.

To sum up, the 648 grammes of fat worth 16 centimes is obtained at an expense of 12 centimes + 2 centimes for reagents = 14 centimes for reagents. Two centimes only remain to cover the establishment charges, wages, cost of fuel, etc., which is altogether insufficient, and with this treatment therefore the balance is on the wrong side.

Hydrochloric acid, more and more in demand for commercial usés, tends to rise in price, and its application in this process will therefore become less practical constantly.

Sulphuric acid, the price of which has a tendency to fall, may be substituted for it.

P. Gaillet's Process.—This process can be used to purify Espierre water on a basin situated on the collector from whence the water runs into a cistern provided with mechanical stirrers into

which milk-of-lime is poured continuously. The liquid runs into a tank from whence the first decantation is operated and the liquid sludge is drained at the bottom and collected in four reservoirs, 10 metres in diameter by 10 metres in height.

The drained sludge may be pressed in special filter presses in order to furnish cakes. This process eliminates the fatty matters, the soluble sulphides and three-quarters of the organic substances present, and the final residue of the treatment yields chloride of lime.

The action without heat of hydrochloric acid on peroxide of iron made from pyrites yields an acid peroxide of iron of 30° B. acting very well on greasy waters, and if heat be used a saturated peroxide of from 35° to 40° B. is obtained.

M. Gaillet recommends the employment of this 40° B. peroxide, which, with hydrochloric acid at 4 francs the 100 kilogrammes, costs 4·60 francs the 100 kilogrammes, all charges included.

Combined with lime the cost of this applied to the Espierre water is:—

200 cubic centimetres of perchloride of iron of 40° B.	0·0126
3 kilogrammes of lime	0·0300
	0·0426

If the establishment charges are taken into account, depreciation, interest on capital, cost of maintenance, wages, fuel, reagents, etc., the expense may be put at 0·072 fr. per cubic metre of the Espierre water purified.

Legrand's Process.—In this process the reagent is ferrous chloride. As compared with ferric chloride there is no advantage in employing it. Ferrous chloride is an expensive salt as it must be made from pure non-oxidised iron. It is not an ordinary commercial article and the user is compelled to make it for himself. As for its action it is less energetic than ferric chloride, the use of which has been recommended by Dr. Kaene, P. Gaillet and Gunning.

Chloride of Manganese Process.—Like ferric chloride, chloride of manganese may be used in treating Espierre water with lime as a neutraliser. By this treatment P. Gaillet has eliminated the major part of the organic matter. The chloride of manganese used is a by-product in chlorine manufacture, but Velden's recovery process makes this salt more and more difficult to procure.

Howatson's Process.—As already mentioned Howatson's process applied to Espierre water depends on the action of two products known as ferozone and polarite, analyses of which we have already given. To begin with the water to be purified is

given a first treatment with lime in order to facilitate the further processes by precipitating the major part of the solid bodies. Next the water is mixed gradually with ferozone, largely composed of ferrous and ferric sulphates and sulphate of alumina. The reagent is prepared daily in a special tank. It runs out of this from a regulating cock which distributes it in proportion to the quantity and nature of the water to be purified in a decanting tank. After decanting the water is filtered and leaves behind all the matters in suspension.

The water is finally dealt with in a polarite filter, the filtering body being an oxidising agent consisting of oxides of magnetic iron, calcium, magnesium, silicon and aluminium. This oxidises the organic matter.

According to the researches of A. Langumier the trials made of this process with the Espierre water have given the following results :—

	Espierre water.	Ditto purified.	Percentage of total elimination.
Residue at 100° C.	4·840	1·760	63·6
Colour of residue	black	white	
Loss at red heat	3·180	5·70	82·1
Burnt oxygen (acid solution)	1·360	1·69	87·6
Ammoniacal nitrogen in NH_3	23·38	10·40	55·5
Albuminoid nitrogen in NH_3	35·36	2·50	93·2
Alkalinity (CaO)	251	45	82·2
Total lime (CaO)	352	95	73·0
Sulphuric acid (SO_3)	72	338	—
Oxide of iron and alumina	300	20	92·3
Chloride of sodium	187	64	12·3
Hydrotimetric degree	75	41	—
„ „ after boiling	75	33	—
Appearance of the water	muddy black	limpid and colourless	

The residues are collected in a decanting tank and the filters are easily cleaned with a current of water.

Houzeau's Process.—From the liquids used in washing lignites Houzeau obtains a product consisting of a mixture of ferrous and ferric sulphates of sulphate of alumina. This reagent acts energetically on Espierre water which is then treated with lime. The drawback of this process is that sulphate of lime is produced, and it has been sought to remedy this, as under the influence of reducing agents such as the organic matter present it forms sulphuretted hydrogen. The reagent therefore has been treated with the view of converting the sulphates into chlorides.

An analysis of the resultant product shows that its composition per litre is :—

	Grammes.
Sulphate of alumina	199'50
Ferric sulphate	10
Free sulphuric acid	4
Ferric chloride	156
Ferrous chloride	75
Insoluble clayey matters	22'60
Water	756
	<hr/> 1223'10

This product still contains a notable quantity of sulphuric acid and the drawback still exists. It requires from 9 to 10 kilogrammes of this reagent to purify 1 cubic metre of Espierre water. Estimating its cost at 1 franc per 100 kilogrammes, the cost of treating a cubic metre of the water is therefore 9 to 10 centimes, without counting other expenses, lime, wages, etc.

Ferrous Sulphate Process.—Purification with ferrous sulphate combined with lime, which has been highly recommended, gives fairly good results. The major part of the organic matter is eliminated and the soluble sulphides are fixed as insoluble sulphide of iron. Not only, however, is there sulphate of lime in solution, but as the precipitation of the ferrous sulphate by the lime is incomplete, salts of iron still remain in solution, and this is an objection. It is true that it may be said that these salts serve to neutralise the soluble sulphides, but it is rare that one or the other are not in excess and in either case this is a drawback to the process.

Boblique's Process.—To begin with, Boblique's process consisted in employing magnesia to obtain, in combination with the phosphates and magnesia in the water, a compound containing these three bases of great value as a fertiliser. The principle was recommended by Schloesing. On the same principle Boblique made experiments with ferruginous phosphate of soda obtained by his special process which consists in fusing Ardennes nodules with iron. Phosphate of iron is thus obtained which is fired to a red heat with sulphate of soda and charcoal. The cooled mass is left for some days in the open air. It is then moistened with water and gives fine crystals of phosphate of soda.

Later still M. Boblique obtained the phosphate more economically by the action of soda on redondite, which at the same time produces alumina as a profitable by-product. Lately M. Boblique has been experimenting on the Espierre water, but he prefers to remain silent as to the results.

A. and P. Busine's Process.—Applied to the Espierre water this process depends on the action of ferric sulphate. Trials were made at Grimonpont on a daily flow of 20,000 cubic metres of water for five weeks. The ferric sulphate introduced is converted into per-

oxide of iron by the salts of the alkalies and alkaline earths always present in polluted waters, and this precipitates, carrying with it all matters in suspension, the fats, the albuminoid substances, the colouring matters and the soluble sulphides which are fixed by the iron and transformed into insoluble sulphide of iron. The major part of the organic matter in solution and the majority of the microbes are carried down by the precipitate. We have already given some data on the process.

Comparative experiments with the lime process on the Espierre water gave the following results:—

	Untreated Es- pierre water. gr.	Treated with 4 kilos. slaked lime per cubic metre. gr.	Treated with 1 kilo. ferric sul- phate per cubic metre. gr.	Untreated Es- pierre water. gr.	Treated with 1.5 kilo. slaked lime per cubic metre. gr.	Treated with 0.4 kilos. ferric sul- phate per cubic metre. gr.
Dry residue per litre . . .	5.75	3.90	2.10	3.20	1.65	1.06
Mineral residue	1.95	2.90	1.80	0.72	0.99	0.91
Fats	2.08	—	—	1.10	—	—
Organic matters in solution (taken as oxalic acid) . . .	1.35	1.20	0.22	—	0.86	0.12
Alkalinity (CaO)	—	0.80	Neutral	—	0.26	Neutral
Weight of dry precipitate per litre	—	0.96	4.29	—	3.03	1.90

The water runs off clear, colourless and odourless, and is neutral or only slightly acid. The sludge deposited after the ferric sulphate treatment, after being spread over the soil and dried, has the following composition:—

Water	20.90
Mineral residue	30.63
Fats	30.00
Nitrogenous organic matters	18.00
	<hr/> 99.53

The fats are extracted with bisulphide of carbon. They are composed of the fatty matters from wool, soap and household fats. After this treatment a powder remains which contains 3 per cent. of nitrogen. The fats may be distilled with superheated steam. Products are obtained in this way which can be used in soap and candle-making or as lubricants. To deal with the Espierre water an average of 1 kilogramme of ferric sulphate must be used per cubic metre. This reagent is prepared with roasted pyrites, an abundant by-product in many industries, by treating the pyrites with sulphuric acid of 66° B. After obtaining a thick syrup the

whole is heated for several hours at from 100° to 150° C., and in this way a dry powdery mass is obtained, which, taken up with water, gives ferric sulphate solution.

Solution of the Question of the Purification of Espierre Water : Application of Delattre's Process.—The international problem of purifying the waters of the Espierre, which is of great interest to the French and Belgian Governments, and to the towns of Roubaix and Tourcoing, began to be considered an insolvable problem. After many years and long series of experiments the interested towns of Roubaix and Tourcoing have decided to adopt the process of M. J. Delattre, as a result of most conclusive trials.

An agreement between the towns of Roubaix and Tourcoing was entered into in 1899, by which Delattre agreed to purify 100,000 cubic metres of water per day and to put down a plant at his Grimonpont works in order to obtain this result.

The two towns of Roubaix and Tourcoing agreed to find 270,000 francs per annum, and M. Delattre will be allowed an annual subsidy of 365,000 francs for the undertaking. This subsidy will cease to be granted as soon as it is proved that by treating the residuary waters with a view of obtaining vitriol a sufficiently remunerative result is obtained.

We have already described minutely in a paragraph relative to the purification of soapy waters at the works producing them the process of purifying the effluent of the wool-works at Dorignies les Douai by sulphuric acid. Delattre intends to apply this process on a large scale in purifying the Espierre water. A slight modification, however, will be introduced in the recovery of the fats. At the Grimonpont works this will be effected in one operation instead of two.

The two processes, pressure and extraction, will be advantageously replaced by a single treatment aiming at extracting the fats with benzine with a subsequent recovery of the benzine from the liquid sludge. The suintine fats, the sludge cakes and the vitriol will give three residuary products which will yield a large profit. The Franco-Belgian question of the purification of the Espierre waters, which has been brought before the Chamber of Deputies, and which, outside the question of its high technical importance, is deeply interesting from the point of view of the public health, has thus been resolved.

(C.) UTILISATION OF THE RESIDUE FROM THE PURIFICATION OF SOAPY WATERS AND EXTRACTION OF THE FATS.

The fats extracted from soapy residuary waters can be utilised in candle and soap-making and in the manufacture of lubricants.

At the works of M. Souffrice at Saint-Denis the fats extracted from residuary waters and from the scum of the same are very advantageously treated. It is difficult to use the fats from the effluent of wool-works or from the Espierre water in soap-making because of the presence of cerotic acid. Nevertheless after purification they may be used in soap-making, and this is facilitated by mixing them with fresh fat. A soap known as *savon de bronze*, for instance, is made by mixing the recovered suintine with tallow and resin. At Holden's works the cerotic acid is isolated from the other fatty acid and the oleic and stearic acids are saponified in a pressure kier.

Trials with Rohard's process show that melted suint sometimes retains as much as 100 times its volume of sulphuretted hydrogen. This fat undergoes a modification of its constitution, and moreover the carbonate of soda will be decomposed instantaneously, and this allows the fat to be saponified in less than half an hour with a cold solution of carbonate of soda. Outside the question of the value of the fats extracted, the residue, in the form of sludge cakes, can be used in agriculture, and are of value according to their richness in nitrogenous matter.

In the extraction of the fats, bisulphide of carbon may very advantageously be replaced by gasolene. Working with the exhausting apparatus of Donard and Boulet, gasolene is used without danger. The essence is distilled by steam in a closed vessel, then condensed, and after extracting the fat very thoroughly it is recovered almost without loss and may be used again.

This apparatus is shown in fig. 123, and consists of twin-boilers A and A' and two extractors B and B'.

Two large double pipes E and E' connect each extractor with the boiler below it. The extractors B and B' are charged with the matter to be exhausted, the boiler A contains the gasolene, water and oil from a previous operation.

The taps F, H, J are turned on, and after shutting the taps F', H', J' the steam jet S is turned on. The essence distils and rises in the tube E, then on turning on the tap U cold water circulates in the flat coil T, and the essence condenses.

The taps F, H, J being open, and F', H', J' shut, steam is turned on by the jet S'. The essence distils, rises in the pipe, and is condensed on the coil T by turning into it cold water by means of the tap U. The condensed essence falls in a hot rain over the matter, and extracting the fats carry them away with it. After re-cooling in the coil G, in the boiler A, the essence is recovered from the fat by turning steam from the jet V into the coil T.

The boiler B and the extractor A are cleared out, and the spent material is generally used as manure. Then the work is carried on as before on the matter to be exhausted of fat in the extractor B'. The recovery of the benzine leaves only a slight loss, put at about '25 per cent. of the benzine for every 100 kilogrammes of matter treated.

A recent improvement in the apparatus of Donard and Boulet

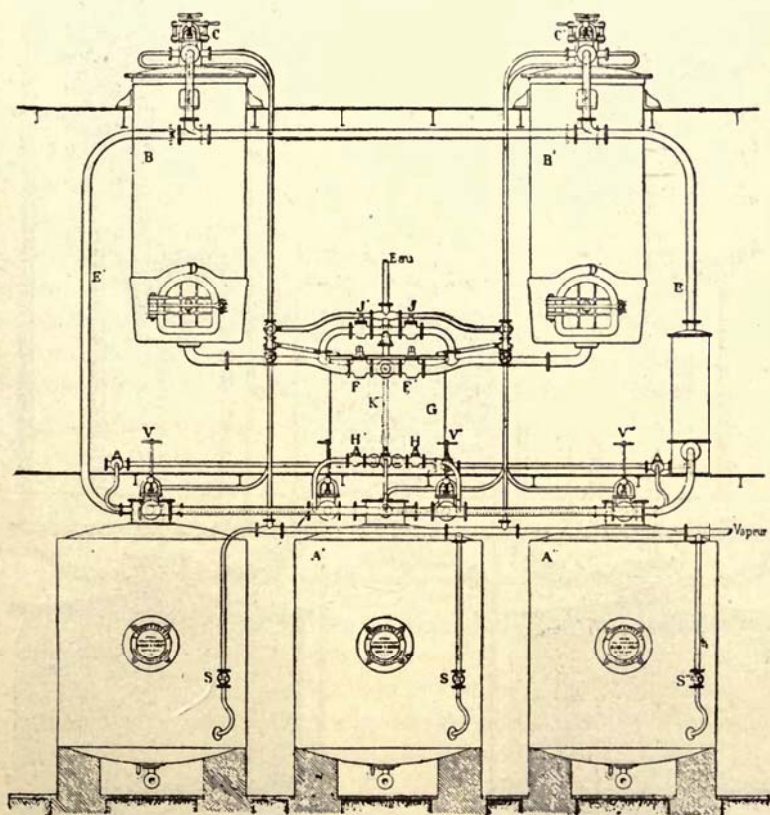


FIG. 122.—Donard and Boulet's fat extractor.

is shown in fig. 122. It consists in using three boilers, which allows the product of the exhaustion to be turned into the middle one, and in this way the fats are extracted by a continuous process which doubles the working capacity of the apparatus. It follows, therefore, that the size of the apparatus may be diminished.

In the process of purification by lime, this reagent may be recovered from the calcined sludge and used again. The calcination of the sludge from divers sources yields an illuminating gas

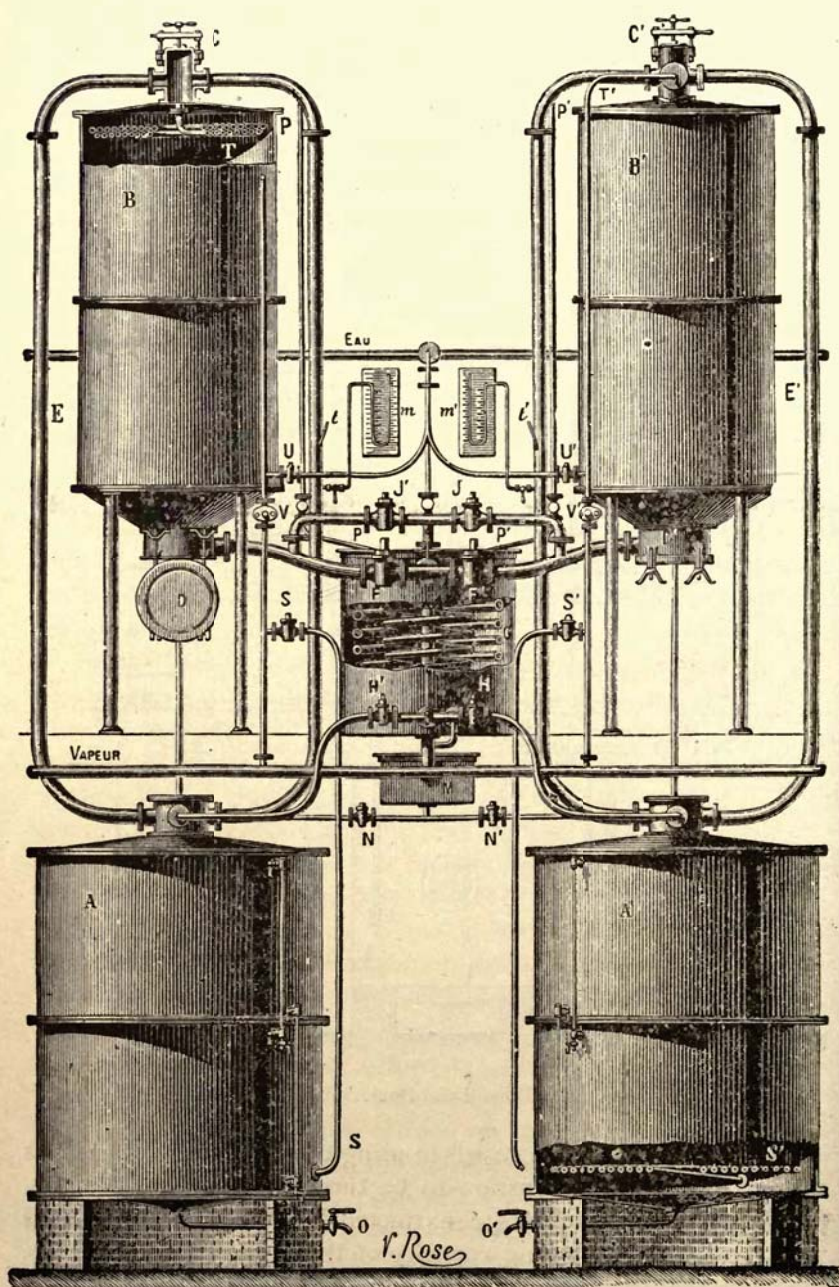


FIG. 123.—Donard and Boulet's fat extractor.

with a lighting power superior to that furnished by the Paris Gas Company.

M. Durand Claye calculated, at the Clichy Laboratory, the illuminating power of gas extracted from the stagnant sewer waters of the Clichy collector. According to his analysis, the composition of the gas obtained was :—

Hydrogen	72.88
Carbonic acid	13.30
Oxide of carbon	2.54
Sulphuretted hydrogen	6.70
Nitrogen and other matters	4.58
	<hr/>
	100.00

The specific gravity of this gas was 0.92. It had a good lighting power and its composition proves it to be very similar to coal gas. It will be seen that the sludge from residuary waters can be turned to profit, particularly those from woollen factories and from the Espierre water. Experiments have been made at the gas-works at Tourcoing by M. Barrois, the director, on the limy sludge from the Espierre. According to the analysis of M. Garreau, a professor at the Lille University, this sludge contains :—

Organic matter precipitated on settling	12.81
" " " chemically	16.27
Precipitable mineral matters	23.46
Sludge dried by evaporation	47.46
	<hr/>
	100.00

The mineral matters in this sludge were oxide of iron, sand, chalk and alumina. A ton of this sludge, dried, gave 200 cubic metres of gas, with a lighting power of 1.36 as compared with the Paris gas, the latter being taken as the unit. In addition to lighting gas, ammoniacal products and tar are obtained in the distillation.

Finally, a lightly phosphated powder remains in the retorts which may be used as a fertiliser and sells at 2 centimes the kilogramme. This powder contains phosphates, potash, a little carbonate of soda and lime. After extracting the utilisable matters, the fats, etc., the residue is usually employed as manure. It is dried in ordinary stoves, or better still in a rotary apparatus drying solid matter in a vacuum, as for instance that of Donard and Boulet, which allows the process to be carried on rapidly and economically.

This apparatus consists of a horizontal cylinder A in bearings G on hollow axles giving access by the stuffing-box D to the steam for heating purposes, and for the purpose of clearing out after work. The steam is sent into a vertical circular chamber H formed by the left side of the cylinder and provided with cogs E to

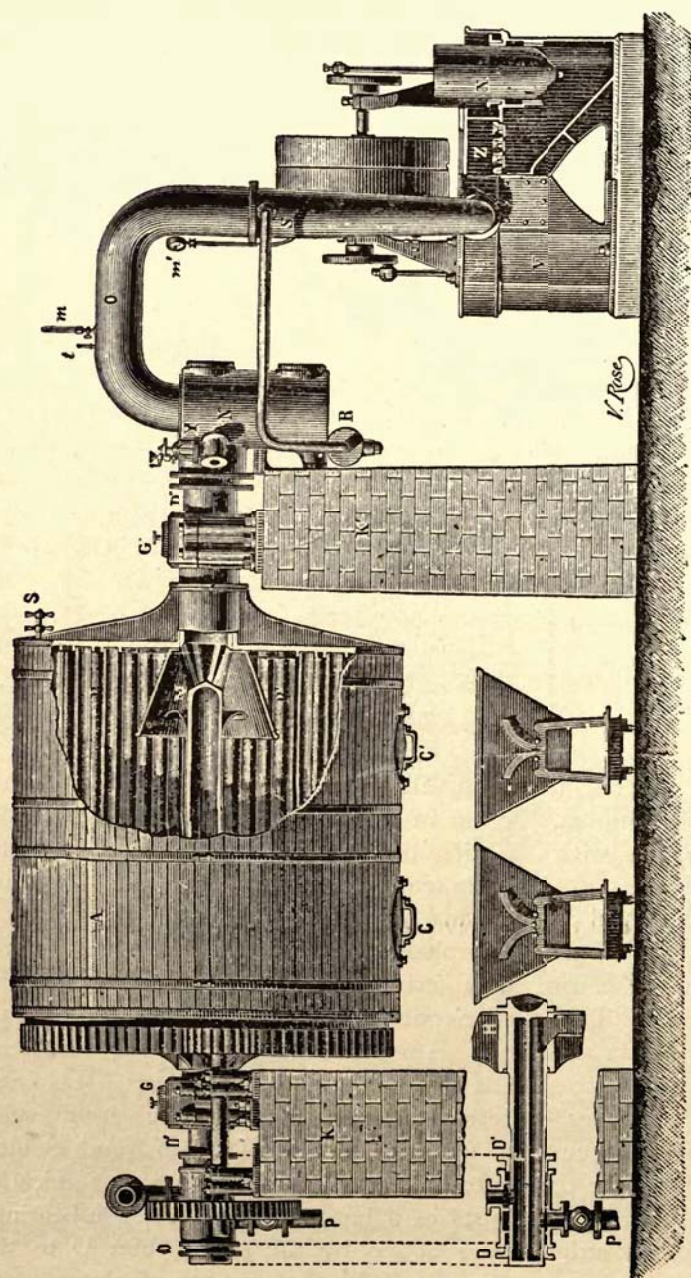


FIG. 124.—Donard and Boulet's vacuum drying apparatus.

rotate it. A series of horizontal tubes, B, inserted through this side of the cylinder and shut at the other end, provide a large heating surface, estimated at about 50 square metres. At the other end of the cylinder a pipe puts the hollow axle in communication with a double effect vacuum pump. The vapour from the treated matters is carried out by the stuffing-box D", and the matters are put in at the manhole C.

In the course of the fourth part of this work, relative to residuary waters, we had the occasion to examine the utilisation of certain residuary products, and in particular the substances recovered from the waters of woollen factories. We noted that the process of Mauméné and Rogelet by calcination of these residues obtained from 70 to 80 per cent. of pure carbonates and lighting gas with a strong illuminating power.

The use of oil of acetone in Switzerland for denaturising spirits of wine,¹ suggested to A. and P. Buisine the idea of manufacturing this product on a large scale in order to allow its applications to be increased.

Acetone oil is a mixture of ordinary acetone, methyl acetone, methyl propylcetone and other higher cetones. To obtain acetone oil, the wash liquors of wool in suint are allowed to ferment for a few days in tanks. Carbonate of ammonia and volatile fatty acids such as acetic, propionic and butyric acids are thus formed. The ammonia is driven off by boiling the liquid which is then soured with sulphuric acid, and heated with a jet of steam to obtain the volatile acids. These acids are saturated with lime and after evaporation distilled to dryness. After several rectifications the distillation product gives 60 per cent. of methyl acetone boiling at 81° C. A litre of fermented liquor yields 20 grammes of volatile acid.

One cubic metre of scour liquors from the wool factory, marking 11° B., gives 15 litres of acetone oil. Carbonate of potash is obtained without any difficulty from the residues of the distillation.

¹ That is to say methylated spirits.—TR.

PART V.

ANALYSIS.

USEFUL hints as to the troubles which may result from the use of particular waters for industrial purposes, and as to the remedies which may be efficaciously applied, can be gathered by the determination of the substances contained in the water. Water should therefore be tested qualitatively for all the different substances which it may contain, and particular attention should be paid to those bodies which may have a good or bad influence according as to whether they are contained in the water in greater or smaller proportion.

The analysis may be made by the hydrotimetric (volumetric) method, which is easy to use, as little apparatus is necessary and the operations are simple. Hydrotimetric analysis is used particularly to test for certain salts, such as those of the alkaline earth; and in order to complete the information which the manufacturer should have concerning the water he uses, we will describe in a third chapter the methods of analysis by which he can ascertain the proportion of the principal bodies contained in the water.

Sometimes in analysing water, the results furnished by the hydrotimetric method are checked by testing the water for each particular substance in the manner about to be described.

The Use of Distilled Water in Analysis.—It is necessary in analysing by any method, to make use of chemically pure water. It will be understood that if reagents be prepared with impure water or one that is not absolutely chemically pure, the impurities of this water will be discovered in the subsequent tests and mislead the analyst. In the same way the result of a quantitative analysis will be misleading, and in hydrotimetric analysis the figures for the water will be put too high.

We will show, therefore, the especial precautions to be taken in order to obtain chemically pure water by distillation. The water distilling apparatus, made on Egrot's system, may be used in the laboratory and in distilleries where the purity of water is an impor-

tant factor in the dilution of alcohol. The Egrot apparatus is especially used in the manufacture of mirrors.

The water to be distilled is put into a copper boiler lined with pure tin. A steam coil transforms the water into steam, which

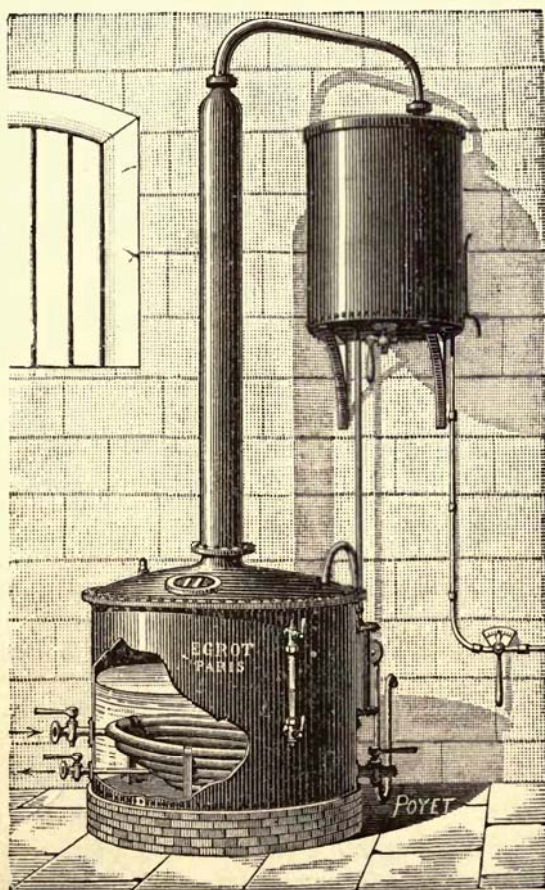


FIG. 125.—Egrot's still.

rises into a pipe and is condensed in the distilled water cistern. Neither impurities nor uncondensed water can pass over.

This apparatus, producing from 25 to 1,000 litres of distilled water per hour according to size, acts automatically. The level of the water in the boiler is kept constant by a supply which is used to cool the steam and therefore is hot when it reaches the boiler.

CHAPTER XXV.

QUALITATIVE ANALYSIS OF SUBSTANCES IN SOLUTION IN WATER.

THE substances most frequently found in water are :—

Sulphuric, carbonic, hydrochloric, sulphurous, silicic, nitric and nitrous acids.

Potash, soda, lime, magnesia and ammonia.

Organic matters and divers matters in suspension.

The acids are usually combined with the bases, forming salts which are generally in solution in the water. In addition to the substances enumerated: iron and zinc, then a group of metals, the salts of which are poisonous, copper, lead and arsenic are also sometimes found in water.

The presence of these poisonous salts renders the water unfit for certain manufactures, and in particular for the preparation of beverages, such as beer, cider and mineral waters, and in ice-making. All the above substances which may be contained in water should be tested for by qualitative analysis.

I. QUALITATIVE TESTS FOR THE ACIDS.

Sulphates.—To detect the presence of sulphates in water, a little of the water is put into a test tube, and a few drops of hydrochloric acid are added. Then a solution of chloride of barium is added drop by drop. If the liquor becomes turbid and a white precipitate forms, the water contains sulphates in solution.

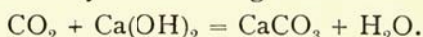
The white precipitate is sulphate of barium, formed by the following reaction :—



The more abundant it is, the more sulphate the water contains, and this gives an approximate idea of the richness of the water in sulphates.

Sulphate of barium is insoluble in acids, consequently when an excess of hydrochloric acid is added, if it is really sulphate of barium the precipitate should remain undissolved.

Carbonates and Carbonic Acid.—If the water contains bicarbonate or free carbonic acid, on the addition of a little lime water a white precipitate is formed. This white precipitate of carbonate of calcium is formed by the following reaction:—



On adding an excess of carbonic acid, or on pouring some seltzer water into the test tube containing the precipitate, it disappears, as it is soluble in an excess of carbonic acid. The precipitate is also soluble in hydrochloric acid.

When water contains carbonate of calcium, the addition of a little tincture of logwood produces a reddish-violet colour. This colour is lighter or darker according as the water contains more or less carbonate.

Chlorides.—A little of the water to be examined is put into a test tube and a few drops of nitrate of silver are added. If a white precipitate is produced when ammonia is added until the solution is quite alkaline, the precipitate formed is chloride of silver:—



The formation of the chloride of silver of course shows that chlorides are present.

Nitrates.—A test for nitrates in water can be made with sulphate of diphenylamine. This reagent is prepared by dissolving one-tenth of a gramme of diphenylamine in ten cubic centimetres of pure concentrated sulphuric acid, free from nitrous fumes. The test for nitrates in the water is made in the following manner. About a dozen drops of the reagent are put into a porcelain dish, and over this the water to be tested is allowed to fall drop by drop. Care must be taken to avoid an excess of the water, which would cause the coloration to disappear. As a rule the maximum amount of water added is half the volume of the reagent. If the water contains nitrates a very distinct blue coloration is produced. By this test one milligramme of nitrate in a litre of water can be detected.

In testing for nitrates brucine may also be used. This test will detect from 1 to 2 milligrammes of nitric acid in a litre of water by the pink coloration formed.

In using brucine 5 or 6 drops of the water to be tested are put into a porcelain dish, and then the same bulk of brucine solution, and finally about 15 drops of sulphuric acid, drop by drop. If a red coloration is produced the water contains nitrates.

The solution of brucine is prepared by dissolving 1 centigramme of brucine in 30 cubic centimetres of distilled water.

Nitrites.—When a water contains nitrites it proves to begin with that it is badly aerated. The presence of nitrites in water may be discovered by the aid of a solution of metaphenylene-diamine prepared as follows :—

Five centigrammes of metaphenylene-diamine are dissolved in 10 cubic centimetres of distilled water, to which a few drops of pure sulphuric or hydrochloric acid have been added. This solution should be prepared immediately before use as it keeps badly.

In testing for nitrites about 20 cubic centimetres of the water are taken and half a cubic centimetre of the reagent is added. The presence of nitrites is shown by a reddish yellow coloration. The quicker this appears, and the darker it is, the more nitrites there are in the water. This reaction allows the presence of 1 milligramme of an alkaline nitrite to be detected in a litre of water, and this small amount gives a very appreciable yellowish colour. In this reaction nitrous acid is produced and the metaphenylene-diamine is transformed into Bismarck brown, or tri-amido-azobenzene. The presence of nitrites may also be tested for with sulphanilic acid. In this test 10 cubic centimetres of the water are put into a test tube and a drop of very pure dilute sulphuric acid is added, then a drop of a saturated solution of sulphate of naphthylamine.

If the water contains nitrites, a coloration is produced turning from pink to ruby red. The coloration forms with more or less rapidity according to the proportion of nitrites present.

Water containing 1 milligramme of nitrite per litre gives a very apparent pink coloration. Tromsdorff's process, which is very much used, detects the presence of nitrites in water by a blue coloration which is more or less intense according to the proportion of nitrites present.

About 20 cubic centimetres of the water to be examined are put into a test tube, and 2 cubic centimetres of Tromsdorff's reagent with from 4 to 5 cubic centimetres of dilute sulphuric acid are added.

If the water contains nitrites there is a blue coloration in the liquid owing to the formation of iodide of starch.

Tromsdorff's reagent is prepared with :—

Chloride of zinc	20 grammes.
Starch	5 "
Distilled water	100 cubic centimetres.

The whole is boiled together for six hours, adding distilled water from time to time to replace the evaporated water.

After cooling, 2 grammes of iodide of zinc are added and the whole is brought up to 1 litre. The reagent is left to settle for

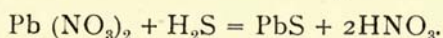
twenty-four hours, then decanted and kept in a bottle of yellow glass in a dark place.

Sulphocyanides.—Waters are sometimes polluted by the infiltrations from gas-works. These waters contain sulphocyanides, and the presence of these very poisonous bodies makes the water totally unfit for use in several manufactures, and especially in the preparation of beverages, such as cider, beer and mineral waters, and of course in the making of ice.

To test for sulphocyanides in a water supposed to contain them, the water is concentrated by boiling, then filtered, and a few drops of hydrochloric acid are added and a little perchloride of iron solution. If sulphocyanides are present, a red coloration will appear, more or less intense according to the proportion of the sulphocyanides present.

Sulphides.—The presence of sulphuretted hydrogen, free or combined, can be detected in water with nitrate of lead.

If a brown coloration is formed on adding a few drops of nitrate of lead solution to the water it contains sulphides:—



The free sulphuretted hydrogen also makes its presence known by the characteristic odour of stale eggs which it emits.

By making the following test it can be ascertained whether the water contains free sulphuretted hydrogen or sulphuretted hydrogen combined, that is to say a sulphide. A flask is half filled with the water to be tested. The flask is then stoppered with a cork with a hole cut through it. Over the hole is placed a strip of paper steeped first in a solution of acetate of lead and next in a solution of carbonate of ammonia. After having shaken the flask, if the paper does not turn brown the water contains no free sulphuretted hydrogen. A few drops of a solution of nitrate of lead are added to it. If there is a brown precipitate the water contains a sulphide. Nitro-prussiate of soda is also a test for sulphides. With a solution of this, the water takes a violet coloration, which disappears gradually. Free sulphuretted hydrogen does not give this coloration with nitro-prussiate of soda.

Phosphates.—To test for phosphoric acid, 25 cubic centimetres of the water to be tested are put into a test tube and acidulated with nitric acid, then the volume of the water is reduced to a half by boiling. It is then filtered. Into another test tube 2 centimetres of this boiled-down water are treated with from 6 to 7 cubic centimetres of a solution of molybdate of ammonia. The solution in the test tube is raised to a temperature of from 35 to 40° C., and if

a yellow precipitate then falls down it contains phosphates in solution. The precipitate formed is phospho-molybdate of ammonia and is more or less rapid in formation according to the quantity of phosphates present.

Silicates or Silicic Acid.—The test for these is made by evaporating 500 cubic centimetres of the water to dryness in a porcelain capsule, first acidulating it with hydrochloric acid.

To the residue thus obtained a few drops of hydrochloric acid are added, then a little water, and it is filtered and the precipitate retained by the filter paper is well washed with distilled water.

The precipitate is then calcined and if silica is present in the water a white powder is thus obtained. This may be dissolved completely in hydrofluoric acid by evaporating it in the acid several times over.

2. QUALITATIVE TESTS FOR THE BASES.

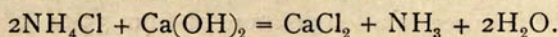
The presence of lime may be detected in water with oxalate of ammonia. About 50 cubic centimetres of the water are put into a test tube and 2 or 3 drops of ammonia, and then 2 or 3 cubic centimetres of a 10 per cent. solution of chloride of ammonia, and finally a few cubic centimetres of a 10 per cent. solution of oxalate of ammonia.

The whole is allowed to settle, and if a white precipitate, insoluble in acetic and oxalic acid, but soluble in hydrochloric and nitric acid, is formed, the water contains salts of lime, and the precipitate is oxalate of calcium.

Magnesia.—To ascertain if a water contains salts of magnesia, the test is made as in the case of lime already described. If a precipitate of oxalate of calcium is formed the solution is filtered and the test for magnesia is made on the filtrate. To the filtrate a few drops of phosphate of soda are added. The solution is stirred up quickly with a glass rod, and allowed to settle for twelve hours or so. If a crystalline white precipitate forms, this proves the presence of magnesia. The precipitate is a phosphate of magnesia.

Ammonia.—To test for ammonia free or combined about 50 cubic centimetres of the water are put into a porcelain capsule, acidulated with a few drops of hydrochloric acid, then almost completely evaporated. This is then poured into a test tube, and about 1 gramme of pure lime is added. A piece of red litmus paper moistened with distilled water is then put loosely in the mouth of the test tube.

The test tube is then carefully warmed. If the water contains ammonia or ammoniacal salts the litmus turns blue :—



The characteristic odour of ammonia, moreover, is given off.

A test for ammonia may also be made with Nessler's reagent.

About 5 cubic centimetres of this reagent are put into 50 cubic centimetres of the water to be tested, and the whole is shaken up.

If the water contains ammonia, a reddish coloration is produced, depending as to its intensity upon the amount of ammonia in the water. Nessler's reagent is prepared by dissolving 25 grammes of iodide of potassium in 25 cubic centimetres of hot water, then a hot saturated solution of bichloride of mercury is made and added to the iodide until the red precipitate of iodide of mercury thus obtained no longer dissolves. The liquid is then filtered while still hot. A solution of 75 grammes of caustic potash in 100 cubic centimetres of distilled water is added to it, and the whole is brought up to 500 cubic centimetres with distilled water, finally a little more of the solution of bichloride of mercury is added. It is allowed to settle, the clear liquid is decanted and Nessler's reagent thus obtained is ready for use. This reagent must be kept in the dark in a well-stoppered bottle.

Soda and Potash.—To test for the presence of the salts of the alkaline metals, sodium or potassium, 50 cubic centimetres of the water to be tested are put into the test tube and a solution of baryta is added in excess. The carbonate of lime in solution in the water is precipitated, and also all the metallic salts, with the exception of the salts of the alkalies and of the alkaline earths. The liquid is then filtered, and the sulphate of calcium, chloride of calcium together with the excess of baryta in the filtrate, is precipitated with carbonate of ammonia. The liquid is filtered, evaporated to dryness, and the residue calcined in order to drive off the salts of ammonia.

The test for the salts of sodium and potassium is made on this calcined residue. It is taken up with distilled water and the salts of potassium and sodium being all soluble in water are dissolved. The liquid is then divided into two portions. The one is tested for sodium, the other for potassium.

Sodium.—If the water contains a salt of sodium, on adding acid pyro-antimoniate of potassium (bi-meta-antimoniate of potassium) to one of the portions of the water, a crystalline white precipitate is formed which however takes some time to appear.

Potassium.—To the other portion of the liquid, concentrated as much as possible, chloride of platinum is added. If a yellowish precipitate is obtained the water contains a salt of potassium. This yellow precipitate is a double chloride of platinum and potassium. The presence of potassium may also be shown by adding to the

water a very concentrated solution of sulphate of alumina. If a crystalline white precipitate is obtained, potassium is present and the precipitate is alum, that is the double sulphate of aluminium and potassium.

On adding acid tartrate of soda to the water a crystalline white precipitate of cream of tartar, that is acid tartrate of potassium, shows the presence of potassium. The formation of the precipitate is facilitated by shaking the test tube.

3. QUALITATIVE TESTS FOR THE METALS.

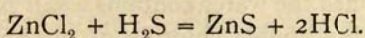
Iron.—To detect the presence of iron in water, 20 cubic centimetres of the water to be tested are put into a test tube, a few drops of nitric acid are added, and the liquid is concentrated by boiling. After it has completely cooled, a few drops of a solution of sulpho-cyanide of ammonium are added. If the liquid turns red the water contains iron. If in place of the sulphocyanide of potassium ferrocyanide of potassium is added, a blue coloration is obtained if the water contains a salt of iron. The red and blue colorations are the more intense as the water contains more iron.

Lead.—The presence of lead or of a salt of the metal is detected in water by filling a series of test tubes with the water to be tested and adding the following reagents. On the addition of sulphuretted hydrogen the presence of lead is shown by a black precipitate insoluble in hydrosulphate of ammonia.

Hydrosulphate of ammonia gives a black precipitate insoluble in an excess of the reagent. Iodide of potassium gives a yellow precipitate soluble in an excess of iodide of potassium or in potash. Chromate of potash gives a yellow precipitate soluble in potash and insoluble in dilute nitric acid.

Copper.—Copper shows its presence by the following reactions. Sulphuretted hydrogen produces a black precipitate. Ferrocyanide of potassium gives a reddish-brown precipitate insoluble in hydrochloric acid. This test is a very delicate one. Ammonia gives a blue coloration. In testing for copper the water should be concentrated by boiling to commence with.

Zinc.—As in searching for copper, the water should first be concentrated by evaporation. A few drops of hydrochloric acid are added. A current of sulphuretted hydrogen is passed through, then a little ammonia is added, and if zinc is present a white precipitate of the sulphide forms:—



With hydrosulphate of ammonia the same white precipitate

of sulphide of zinc is obtained if ammonia is first added to the water until it smells strongly of it. The sulphide of zinc obtained is soluble in hydrochloric acid, and insoluble in an excess of hydro-sulphate of ammonia. If the water is concentrated, on adding potash or ammonia a white precipitate, soluble in an excess of the reagent, shows the presence of zinc.

Arsenic.—A little nitric acid is added to the water to be tested, and it is evaporated to dryness. The residue thus obtained is taken up with sulphuric acid and then calcined in order to drive off the nitric acid.

After cooling, the residue is taken up with distilled water and put into a Marsh apparatus, that is to say simply a flask containing chemically pure granulated zinc with a tube fitted into the cork to

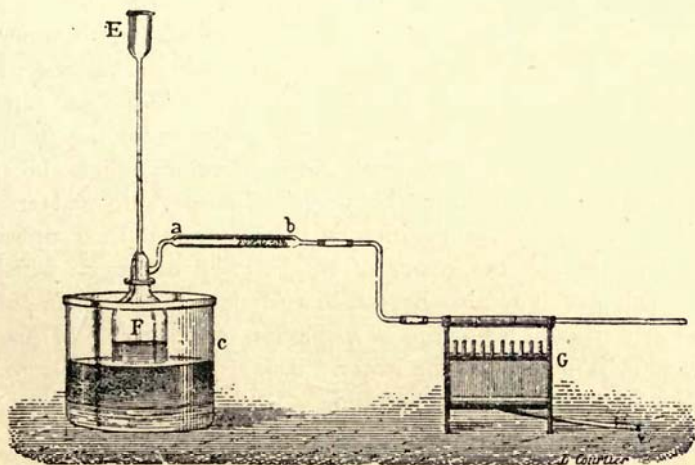


FIG. 126.—Marsh test for arsenic.

allow sulphuric acid to be added, and an arrangement as shown in fig. 126 to lead off the hydrogen evolved. The hydrogen gas is lighted after it has been allowed to flow for a few minutes in order to clear the air out of the apparatus. If there is arsenic in the water, it combines with the hydrogen and arsenuretted hydrogen is evolved.

If the flame of a spirit lamp be held to the tube say at *a* the metallic arsenic is freed from the gas and deposits on the cool part at *b*. This deposit on treatment with nitric acid, then with acetate of silver, gives a brick-red precipitate of arseniate of silver.

The gas flame from the Marsh apparatus is livid if there is arsenic in the water. If a porcelain dish be held against it, the flame thus burning with less oxygen, a black mirror of metallic

arsenic is left upon it. If arsenic is present when the gas is bubbled through a solution of a salt of silver or copper, a black precipitate is produced.

4. TEST FOR ORGANIC MATTERS.

A water containing organic matter reduces chloride of gold, and metallic gold is precipitated as a brown powder. To make this test the water is boiled for a short time, with a few drops of a solution of chloride of gold. The presence of organic matters is detected by a brown coloration. Organic matter may also be detected with permanganate of potassium. When a solution of this is added to the water, drop by drop, if the pink tint produced disappears, organic matter is present. The decolouring action however is variable, according to the nature of the organic matters. Certain substances, such as gum, urea and sugar, act in a very incomplete manner on the permanganate, and on the other hand certain bodies which are not organic substances, such as sulphuretted hydrogen, nitrites, ferric salts, etc., also have a decolouring effect upon the permanganate. The use of this reagent alone, therefore, might be misleading, and other tests must be made. The organic matters are often in a state of decomposition in the water and their presence is then indicated by the odour of sulphuretted hydrogen which it emits. This gas may also be put in evidence by the black colour which forms when a few drops of a solution of protoxide of lead in caustic soda is added to the water. This coloration is due to the formation of a precipitate of sulphide of lead.

CHAPTER XXVI.

HYDROTIMETRIC ANALYSIS.

HYDROTIMETRIC analysis allows the water to be tested rapidly, and shows first its number or degree, that is to say the place it occupies in the volumetric scale of waters, secondly its hardness, that is to say the proportion of earthy matters which it contains.

The soap test also gives information as to the suitability of a water for manufacturing use or for household purposes, such as cooking.

Clarke's soap test is based on the fact that the hardness of a water is proportional to the mineral salts which it contains, and the quantity of these present may be determined by the amount of soap solution which must be added to the water before a lather can be produced. Boutron and Boudet, by developing this principle, have invented a rapid method of hydrotimetric analysis. This method is based on the fundamental fact of the production of a lather by soap in pure water, and on the obstacle which is put in the way of the production of this lather by the transformation of the soap used into insoluble compounds. If a few drops of a solution of soap in alcohol are poured into a flask containing distilled water and the flask is shaken, a persistent lather is at once obtained. If the experiment is repeated with a water containing salts of lime or magnesia, the lather is only produced when the action of these salts has been neutralised, and for this a quantity of tincture of soap must be used in proportion to the amount of the salts present. It will be seen that this furnishes a method of analysis.

This method allows the quantity of the salts of lime and magnesia contained in the water to be ascertained, that is to say the total hardness or the hydrotimetric degree. The permanent hardness of a water may also be ascertained by finding the hydrotimetric degree after boiling the water to be examined. Finally, the temporary hardness of a water is the degree obtained by calculating the difference of the numbers indicating the total hardness and the permanent hardness of the water.

In determining the permanent hardness, after having precipitated the carbonate of calcium, and driving off the carbonic acid gas by boiling, on cooling it must not be forgotten that the water must be brought to its first level by the addition of distilled water before determining the hydrotimetric number.

1. SOLUTIONS AND APPARATUS.

The following solutions are used in hydrotimetric analysis :—

1. A standard solution of soap.
2. A solution of chloride of calcium.
3. A solution of oxalate of ammonium.

The Standard Soap Solution.—This is prepared by dissolving :—

	Grammes.
White Marseilles soap	100
In 90° alcohol	1,600

The spirits of wine are boiled to dissolve the soap, filtered to separate out any foreign matter, and 1,000 grammes of distilled water are added to the filtrate. This should give 2,700 grammes of liquor, with a volumetric number very near to that aimed at. It is preferable to use in the place of the Marseilles soap a medicinal preparation known as amygdaline soap. This immediately furnishes a liquor with the desired volumetric number, 22. The numerous and variable impurities found in Marseilles soap have often led to inaccuracies in analytical results. M. Courtonne suggests that the analyst should manufacture his own soap from the following recipe :—

Boil in a flask—

	Cubic centimetres.
Olive oil or oil of sweet almonds	30
Caustic soda of 36° B.	10
Alcohol	10

After a few minutes the soap is formed and is dissolved by adding 900 cubic centimetres of alcohol of 60°.

The flask is shaken up a few minutes, the contents filtered, and after cooling the solution is brought up exactly to 1 litre with 60° alcohol. If the work has been properly done the number of this liquor should be exactly 22.

Solution of Chloride of Calcium.—This solution is prepared by dissolving one-quarter gramme of chloride of calcium in 1 litre of distilled water. It is preferable to prepare solutions containing equivalent quantities of the chloride or nitrate of barium. Errors are thus avoided that may arise through the excessive deliquescence of the chloride of calcium.

A solution is made containing either '59 gramme of nitrate of

barium, $\text{Ba}(\text{NO}_3)_2$, per litre, or .55 gramme of chloride of barium, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, per litre of distilled water.

Solution of Oxalate of Ammonia.—A solution of oxalate of ammonia is prepared by dissolving 1 gramme of oxalate of ammonia in 60 cubic centimetres of distilled water.

Hydrotimetric Burette.—The liquor is tested and the different numbers of the water are determined by the aid of an apparatus known as a volumetric burette. This burette is graduated so that from the point marked 0 in fig. 127 to the mark 22 it contains two and four-tenths cubic centimetres divided into 23 equal parts. The divisions of the burette in tenths of a centimetre are equal from top to bottom.

The division between the top mark and that immediately below indicates the quantity of standard soap solution necessary to produce a persistent lather with 40 cubic centimetres of distilled water.

Zero is marked below the first division, and each division represents one hydrotimetric degree, and the number 22 is marked against the twenty-third division, counting from the top mark.

Test Bottle.—The different tests are made in a bottle with an emery stopper and of a capacity of from 60 to 80 cubic centimetres, gauged by a circular mark at the point at which the contents are 40 cubic centimetres.

Verification of the Standard Soap Solution.—To ensure exactness the standard soap solution should be of such a strength that when the burette is filled to the circular mark zero it is necessary to pour out the solution down to the mark 22 into 40 cubic centimetres of the chloride of calcium solution to obtain a persistent lather. To make this test 40 cubic centimetres of one of the solutions prepared as already described with chloride of barium, nitrate of barium, or chloride of calcium, are poured into the flask with the emery stopper to the 40 cubic centimetre mark. Then the burette is filled up to the top circular mark with the soap solution to be verified. The liquor in the burette down to the division 22 is then

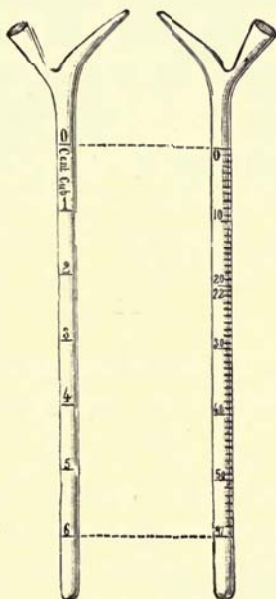


FIG. 127.—Hydrotimetric burette.

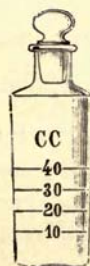


FIG. 128.—Test bottle.

poured into the flask, which is then shaken, and if there is a persistent lather for about five minutes the soap solution is exact and is said to be normal. If the soap liquor indicates a lower degree than 22, water is added until the wished-for degree is obtained. To diminish the strength of the liquor by 1° about one twenty-third of its weight in water must be added. The quantity of water to be added can be calculated in the following way. If n is the number of divisions read on the burette to obtain the persistent lather with the soap solution to be proved, the following equation is obtained :—

$$\frac{n + 1}{23} = \frac{1000}{x}$$

from whence :—

$$n = \frac{23000}{n + 1}$$

To correct the solution the quantity of water added must be equal to $x - 1,000$ cubic centimetres for each litre of soap solution.

The soap solution thus corrected should pass the test as described above. Water may however be tested with a soap solution which is not normal. If for instance it is noted that instead of 22 the soap liquor gives a number p , and if in titrating water to be tested it is found that it requires a number q of this soap solution, the real degree may be deducted according to this formula :—

$$x = \frac{22}{p} (q + 1) - 1$$

x gives the real number.

With the normal soap solution, taking into account that 22 of the liquor are neutralised by 1 centigramme of chloride of sodium, 40 grammes of chloride of calcium containing one-quarter of a gramme of CaCl_2 , it may be deduced that 1° of the burette corresponds to $\frac{0.01}{22} = 0.00045$ of this calcium chloride.

Consequently each degree of the soap solution being neutralised by 40 cubic centimetres of chloride of calcium solution containing one-quarter gramme per litre represents :—

$$\frac{0.01 \text{ gr} \times 25}{22} = 0.0114 \text{ of chloride of calcium per litre.}$$

The burette is graduated in such a way that in operating with 40 cubic centimetres of a normal solution of chloride of calcium, 22° of the normal soap solution must be put in to obtain a persistent lather. Taking into account the proportion of the soap neutralised it will be seen that each degree of the burette corresponds to 0.1 gramme of neutralised soap per litre. (The exact figure is 0.106 gramme.) The graduation of the burette and the composition of the

soap solution allow, therefore, in operating on 40 cubic centimetres of a solution containing any weight of chloride of calcium, the exact weight of the calcium and the proportion of soap that it has neutralised to be ascertained by the degree at which the persistent lather is obtained. It is easy to understand that by a simple sum in proportion the corresponding weight to a degree of the burette can be worked out for all the solutions of mineral salts.

The salts of calcium, magnesium and barium are insoluble in the presence of the fatty acids of the soap and their quantification can be calculated exactly in the same manner as for chloride of calcium. This allows the different mineral salts contained in water to be exactly quantified.

2. OPERATIONS.

Determination of the Total Hydrotimetric Degree, or Total Hardness of the Water.—Before the actual test a preliminary trial should be made. For this 20 to 25 cubic centimetres of the water to be tested are put into a beaker and about 1 cubic centimetre of the soap solution is added.

After having shaken the mixture for a few seconds, its appearance is noted. If there are no clots in the water, and it takes simply an opaline tint, it is in excellent condition for testing, and this may be at once proceeded with. If, on the other hand, clots form in the water it shows that it is too heavily charged with the salts of calcium and magnesium, and in this case it is necessary in order to obtain good results in the test to dilute the water so as to diminish the excess of these salts of the alkaline earths and to give the water a number inferior to 30 hydrotimetric degrees.

This is done by adding to the water a volume of distilled water equal to one, two or three times that of the water to be tested, in order to reach a lower number than 30 degrees. Of course the dilution must be taken into account, and the result obtained as hydrotimetric number must be multiplied one, two or three times according to the volume of distilled water added to the water to be analysed.

It must be ascertained that the distilled water employed is perfectly pure, and the number of divisions of the normal soap solution which have to be poured out to obtain the persistent lather must be noted. If in obtaining this result with distilled water it is necessary to pour out more than 1°, this must be taken into account.

In the same way the soap solution must be verified with one of the normal solutions of chloride of barium, nitrate of barium, or chloride of calcium, as under certain influences the volumetric number of this liquor may vary, and therefore falsify the result.

Quantification of the Carbonic Acid, Salts of Lime, and Salts of Magnesia in Water.—To quantify the carbonic acid, the salts of lime and the salts of magnesia contained in a water, four operations must be carried out.

1. Take the total hydrotimetric degree of the water in its natural state.
2. Take the degree of this water after having precipitated the lime which it contains with oxalate of ammonia.
3. Take the degree after having boiled it in order to drive off the carbonic acid and separate out the carbonate of lime.
4. Finally, take the degree of the water after boiling it and precipitating with oxalate of ammonia the salts of lime which have not been separated out by boiling.

These different operations necessitate :—

1. A solution of oxalate of ammonia. This is prepared by adding 1 gramme of oxalate of ammonia to 60 grammes of distilled water.
2. A glass flask marked round the neck at a point which will indicate the volume of the contents as 100 cubic centimetres.

Method of Operation.—1. This operation has been described already.

2. When the hydrotimetric degree of the water in its natural state is ascertained, a fresh lot of the water is taken and 50 cubic centimetres of it are put into a beaker, and 2 cubic centimetres of the solution of oxalate of ammonium are added. After having stirred up the liquid well with a glass rod it is left to settle for half an hour, and the salts of lime are precipitated in the form of oxalate of lime and fall to the bottom. The liquid is filtered and the water is thus freed from all the salts of lime. Forty cubic centimetres of it are taken and the volumetric degree determined.

3. Next the flask is filled with water up to the circular mark, and boiled for about half an hour to separate out the carbonate of lime. The boiling must be carefully managed in order to avoid any loss of the liquid which would falsify the results of the analysis. The water is allowed to cool completely and the flask is filled to the circular mark again with distilled water to replace that which has evaporated. A cork is then put in the flask and it is shaken up well and finally filtered to get rid of the precipitated substances. The volumetric degree of this water, boiled and filtered, is ascertained by taking 40 cubic centimetres of it and using the soap solution as already directed.

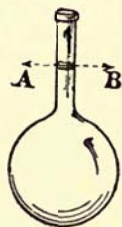


FIG. 129.—Flask gauge for hydrometric analysis.

Finally the salts of lime which have not been precipitated in the state of carbonate of lime are separated out. In order to do this 50 cubic centimetres of the boiled water are taken after making good the loss due to evaporation with distilled water. These 50 cubic centimetres of the water are put into a test tube or beaker. Two cubic centimetres of oxalate of ammonium are added and the liquid is stirred up well with a glass rod.

Finally the liquor thus prepared is allowed to settle for half an hour or so, filtered, and 40 cubic centimetres are put into the flask and the hydrotimetric degree is ascertained.

3. CALCULATIONS AND FORMULÆ.

Calculation of the Results Obtained.—Use the first four letters of the Greek alphabet, α , β , γ , δ , to signify the volumetric numbers corresponding to the figures found in operating on:—

- (a) The water directly.
- (b) The water treated with oxalate of ammonia.
- (c) The water boiled.
- (d) The water boiled, treated with oxalate of ammonia.

A correction must be made in the result c obtained with boiled water. The carbonate of lime is slightly soluble and is not completely precipitated. Boutron and Boudet estimate that .03 gramme of the calcium carbonate remain in solution when 1 litre of the water is boiled.

To correct the results, therefore, 3 volumetric degrees must be deducted from the number obtained with the boiled water, so that taking γ as the number found the correction is made by calculating the formula $\gamma - 3$.

Therefore:—

α represents the sum of the reactions on the soap caused by the carbonic acid, the carbonate of calcium, the salts of lime and the salts of magnesia in the water analysed:—

$$(1) \quad \alpha = \text{CO}_2 + \text{CaCO}_3 + \text{any salts of calcium} \\ + \text{any salts of magnesium.}$$

β represents the salts of magnesium and the carbonic acid which remain in the water after the lime is separated out with oxalate of ammonium.

$$(2) \quad \alpha - \beta = \text{the salts of lime.}$$

γ , making allowance for the correction $c - 3$, represents the salts of magnesium and the salts of calcium other than the carbonate.

$$(3) \quad \alpha - (\gamma - 3) = \text{CaCO}_3 + \text{CO}_2,$$

or:—

$$\alpha - \gamma + 3 = \text{CaCO}_3 + \text{CO}_2.$$

δ represents the salts of magnesium contained in the water, as by boiling the carbonic acid has been eliminated and the carbonate of calcium (almost), and the oxalate of ammonium has separated out the salts of calcium.

$$(4) \quad \delta = \text{salts of magnesium.}$$

Thus we have four equations by which the value of the unknown contents of the water can be calculated. The carbonic acid is calculated by deducting the volumetric degrees of the salts of magnesium and calcium contained in the water from the volumetric degree of the water in its natural state, that is to say the difference between the equation (1) and the equations (2) and (4).

Thus for carbonic acid:—

$$(5) \quad a - [(a - \beta) + \delta] = \text{CO}_2,$$

or:—

$$\beta - \delta = \text{CO}_2.$$

As we know, on the one hand, the volumetric degrees corresponding to the carbonic acid, and on the other the degrees corresponding to the sum of the action exercised by the carbonic acid and the carbonate of calcium by ascertaining the difference between these degrees, we shall have the degree corresponding to the carbonate of calcium, that is to say the difference between the equations (3) and (5).

Thus:—

$$(6) \quad a - \gamma + 3 - (\beta - \delta) = \text{CaCO}_3,$$

or:—

$$a - \gamma + 3 - \beta + \delta = \text{CaCO}_3.$$

Knowing now the volumetric degrees corresponding, on the one hand, to the totality of the salts of calcium, and on the other hand to the carbonate of calcium, we can calculate the degrees corresponding to the sulphate of calcium and to the salts of calcium other than the carbonate by taking the difference of these degrees, that is to say by deducting the equation (6) from the equation (2).

Thus:—

$$(7) \quad a - \beta - a + \gamma - 3 + \beta - \delta = \text{CaSO}_4,$$

or salts other than the carbonate;

or:—

$$\gamma - \delta = \text{CaSO}_4,$$

or salts other than the carbonate.

Formulæ.—The degrees ascertained for the tested water being represented by a, β, γ, δ , for the four different tests with the soap solution, the following formulæ allow the numbers of the degrees corresponding to the different salts to be ascertained:—

Carbonic acid	$= \beta - \delta$
Carbonate of lime	$= a - \gamma + 3 - \beta + \delta$
Sulphate of lime, or salts other than the carbonate	$= \gamma - \delta$
Salts of magnesia	$= \delta$

By the aid of the table below it is easy, by using their formulæ, to transform the degrees found into weight in the case of the salts, and into volume in the case of the carbonic acid.

To do this it is merely necessary to multiply the degree found for each substance by the weight or volume of the substance in the following table.

Table of Equivalents in Weight of 1 Hydrotimetric Degree per Litre of Water.

	Gram.
Lime	'0057
Chloride of calcium	'0114
Carbonate of calcium	'0103
Sulphate of calcium	'0140
Magnesia	'0042
Chloride of magnesia	'0090
Carbonate of magnesia	'0088
Sulphate of magnesia	'0125
Chloride of sodium	'0120
Sulphate of sodium	'0146
Sulphuric acid	'0082
Chlorine	'0075
Soap (50 per cent. solution)	'1061
	Litre.
Carbonic acid	'005

If the figures found in this table are used with the preceding formulæ, and, for instance, the water contains lime in the form of carbonate and of sulphate and magnesia as a sulphate the formulæ become :—

Carbonic acid	$= (\beta - \delta)$	Litre. '005
Carbonate of lime	$= (a - \gamma + 3 - \beta + \delta)$	Gram. '0103
Sulphate of lime	$= (\gamma - \delta)$	'0140
Sulphate of magnesia	$= \delta \times$	'0125

Because of the small proportion of free carbonic acid in soft waters and of the small difference in the proportional numbers of the different salts in the water, sulphates of lime and of magnesia, and carbonate of lime it results that the hydrotimetric degree of a water represents very nearly the weight in centigrammes of the mineral salts contained in 1 litre of the water. If for instance a is found to be the hydrotimetric degree of a tested water we can say at once that the weight of the mineral salts that it contains per

litre is very nearly the one hundredth part of the number a , that is to say $0.0a$.

Hydrotimetric Analysis with any Graduated Burette and any Strength of Soap Solution.—The processes of volumetric analysis which have already been described do not necessitate the employment of the hydrotimetric burette.

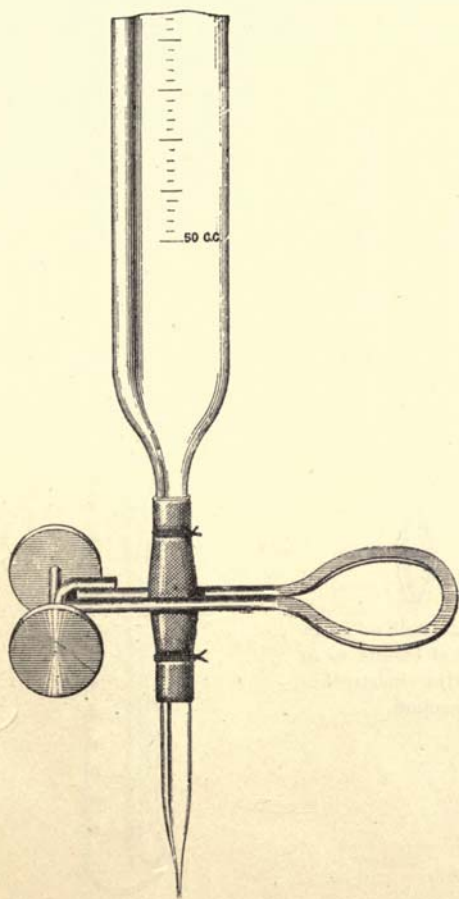


FIG. 130.—Mohr's burette.

Very correct results may be obtained in volumetric analysis by using an ordinary burette graduated in tenths of a cubic centimetre such as is found in all chemical laboratories, the burette of Mohr or that of Gay-Lussac for instance. Moreover the soap liquor need not be the standard solution and any strength of soap solution may be used.

If the number of cubic centimetres of the soap solution necessary to obtain a persistent lather in distilled water be expressed by ϵ , and the number of cubic centimetres necessary to produce the persistent lather in the water to be analysed be expressed by θ ,

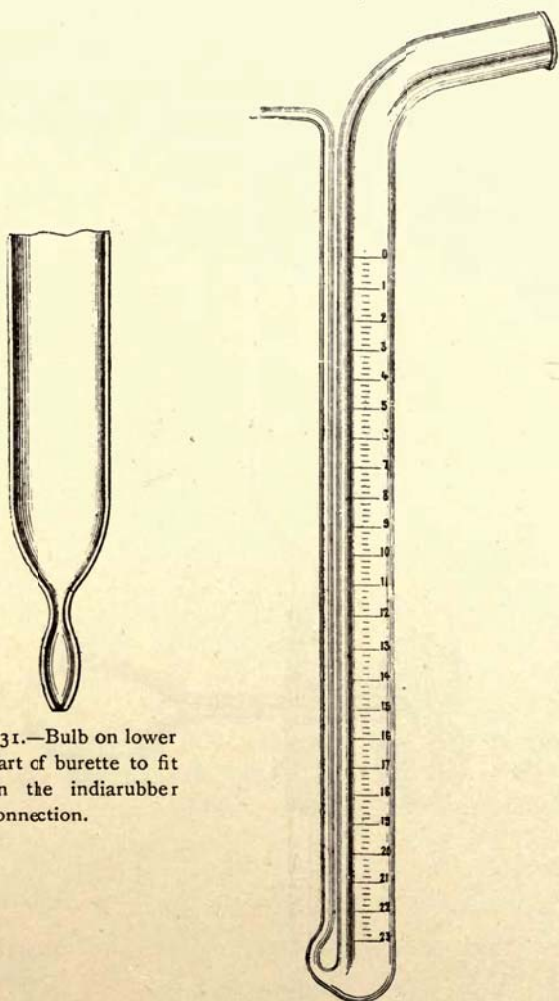


FIG. 131.—Bulb on lower part of burette to fit on the indiarubber connection.

FIG. 132.—Gay-Lussac's burette.

by expressing by x the corresponding degree found by the aid of any burette, we obtain the following formula:—

$$x = \frac{22}{\frac{230}{24} \epsilon - 1} \left(\frac{230}{24} \theta - 1 \right) - 1;$$

from whence:—

$$x = \frac{115 (22\theta - \epsilon) - 252}{115 - \epsilon - 12}.$$

Let us suppose that instead of using a non-standard soap solution we employ a normal solution, that is to say a liquor of such a strength that the number $\epsilon = 22^\circ$. The above formula is then simplified.

By expressing by θ' the number of cubic centimetres of normal soap solution necessary to obtain a persistent lather in the tested water, and by x' the number of hydrotimetric degrees corresponding to the number of cubic centimetres of the normal soap solution poured out, we obtain the formula :—

$$x' = \frac{230}{24} \theta' - 1 ;$$

from whence :—

$$x' = 9.5833 \theta' - 1.$$

CHAPTER XXVII.

QUANTIFICATION OF SUBSTANCES IN SOLUTION IN WATER.

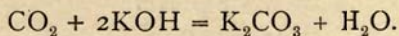
I. GASES.

Quantification of Gases Dissolved in Water.—This is done by boiling the water and so eliminating the gas. The carbonic acid gas is absorbed by potash. A test flask is completely filled, and then stoppered with a cork through which passes a bent glass tube leading into a mercury trough. Over the bent end of the tube in the mercury is put a graduated test tube. After having filled this graduated tube with mercury, the water in the flask is brought to the boil.

During this operation a small quantity of water passes into the graduated tube, but this is of no consequence. The tube gradually fills with gas, and at the end of ten minutes or so when it is noted that the flow of gas is stopped, the flask is taken off the gas and allowed to cool to the exterior temperature. The water in the graduated tube then returns to the flask. The water must be boiled up a second time and even a third, in order to be certain that all the gas contained in the water has been driven into the graduated tube.

The gas is then dried by passing it over a little coke impregnated with sulphuric acid, then the volume V is read, which represents the total volume of the gases contained in the water: oxygen, carbonic-acid gas and nitrogen.

A solution of potash is then run into the graduated test tube with a pipette, ending in a bent tube, and the carbonic acid is absorbed:—



The volume of gases, V' , read on the graduated tube, represents oxygen and nitrogen.

The oxygen is then absorbed by pyrogallic acid, and the reading of the volume of gas, V'' , represents the nitrogen contained in the water.

The amount of oxygen is ascertained by making the deduction $V - V''$.

V = the volume of gases contained in the water.

V'' = the volume of nitrogen.

$V - V''$ = the volume of oxygen.

These volumes should be corrected to 0° C., and to 760 pressure.

The volume of the flask and of the tube, leading into the mercury trough, is measured by filling them with water and by weighing the contents in a tared glass.

Quantification of Oxygen by Mohr's Process.—This process depends upon the absorption of oxygen by a solution of the double sulphate of iron and ammonia known as Mohr's salt:—

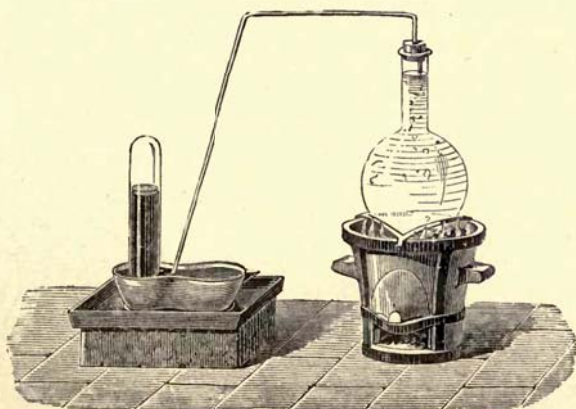
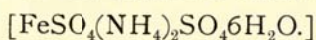


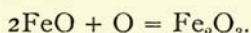
FIG. 133.—Quantification of gas contained in water.

Two solutions are prepared:—

1. A solution containing 39.2 gr. (molecular weight) of the double sulphate of iron and ammonia per litre of distilled water.
2. A standard solution of permanganate of potassium corresponding volume by volume to the titrated solution of the double sulphate of iron and ammonium. This solution contains 3.2 gr. of permanganate of potassium corresponding to the theoretical formula KMnO_4 . A flask stoppered with a caoutchouc stopper pierced with two holes is used. Through one of the holes is led a tube to supply a current of carbonic-acid gas in order to have no contact with the air.

Next 100 cubic centimetres of the water to be analysed and 10 cubic centimetres of the standard solution of the double sulphate of iron and ammonium are put in, and a little caustic potash solution

is added to make sure that the solution is alkaline. The flask is well shaken in order to mix the liquors well. A precipitate of ferrous oxide falls down, and is transformed into ferric oxide by the oxygen contained in the water. It is allowed to settle for ten minutes or so :—



The precipitate of oxide of iron formed is then dissolved in sulphuric acid. The iron which has not been peroxidised is then quantified with the titrated solution of permanganate of potash.

A graduated burette is filled with this permanganate solution and it is poured into the liquid until it takes a pink tint. At this point the number of cubic centimetres poured out is noted. If n is this number, it represents the quantity of permanganate of potassium necessary to oxidise the iron which has not been oxidised by the oxygen in the water.

Now the solutions of permanganate of potash and of the double sulphate of iron and ammonium have been titrated so that they neutralise each other, volume by volume, that is to say that a volume of the one corresponds to the same volume of the other, and consequently 1 cubic centimetre of permanganate of potassium oxidises 1 cubic centimetre of this solution of the double sulphate of iron and ammonium. To begin with, 10 cubic centimetres of sulphate were put into the flask, and to oxidise this completely 10 cubic centimetres of permanganate of potash were required, but as we have used only n cubic centimetres to obtain the oxidation of the double sulphate, it is evident that the difference $10 - n$ has been peroxidised by the oxygen in the water. This oxidation must now be calculated in oxygen gas.

The solution of permanganate of potassium has been prepared, so that 1 cubic centimetre of it is equivalent to 0.0008 gr. of oxygen. If we represent by x the weight of oxygen sought, contained in the 100 cubic centimetres of water, n being the number of cubic centimetres of double sulphate of iron and ammonium put into the flask, we have the formula :—

$$x = (10 - n) 0.0008.$$

We can calculate the oxygen contained in the water in volume if we call V the volume of the oxygen contained in 100 cubic centimetres of the water to be analysed, and if we note that 1 cubic centimetre of oxygen gas at 0°C. , and 760 pressure, weighs 0.00143, by the formula :—

$$V = \frac{(10 - n) 0.0008}{0.00143}$$

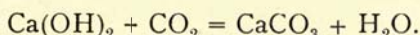
and per litre :—

$$= \frac{(10 - n) 0.0008}{0.00143}$$

2. ACIDS.

Quantification of the Free Carbonic Acid and Half-combined Carbonic Acid (not in a State of Simple Carbonate).—Pettenkofer's method depends upon titrating with oxalic acid an excess of a determined quantity of barium or calcium introduced into the water to be analysed in order to precipitate its free carbonic acid.

With a graduated pipette 100 cubic centimetres of the water to be analysed are put into a flask, 3 cubic centimetres of a concentrated solution of chloride of calcium or of barium are added, and 2 cubic centimetres of a saturated solution of hydrochlorate of ammonia; and finally 45 cubic centimetres of a solution of lime or baryta, this making in all 150 cubic centimetres. The flask is then corked, shaken well, and allowed to settle for twelve hours. The free or half-combined carbonic acid is precipitated by the lime in the state of carbonate of calcium :—



The carbonate of calcium deposits at the bottom of the flask, 50 cubic centimetres of the clear supernatant liquor containing the excess of lime are drawn off gently with a graduated pipette, and this excess is quantified with a titrated solution of oxalic acid.

The oxalic acid solution should contain 2.8636 gr. of oxalic acid per litre of distilled water, and 1 cubic centimetre of it should correspond to 1 milligramme of carbonic acid. As for the solution of lime or of baryta employed (in this case lime) it is titrated to begin with with 45 cubic centimetres of the oxalic acid solution by way of trial.

To titrate the excess of lime in the flask a rapid trial on the 50 cubic centimetres of liquid taken out with the pipette is first made. Then a more precise trial is made with a second 50 cubic centimetres extracted in the same way.

If n' is the number of cubic centimetres of oxalic acid found in testing 50 cubic centimetres of the liquor, the number of cubic centimetres of oxalic acid for the 150 cubic centimetres of liquid contained in the flask will be $3n'$.

If n is the number necessary to neutralise the 45 cubic centimetres of lime water in the preliminary trial, the difference $n - 3n'$ of oxalic acid corresponds to the lime precipitated by the carbonic acid. Each cubic centimetre of oxalic acid corresponds to 1 milli-

gramme of carbonic acid, and if we represent by x the weight of carbonic acid in the 100 cubic centimetres of water, we shall get the formula :—

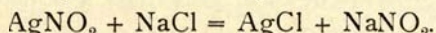
$$x = n - 3n,$$

and per litre :—

$$x = (n - 3n) 10.$$

Quantification of the Nitrites.—The quantification of the nitrites may be done either with metaphenylene-diamine or with Tromsdorff's reagent. The reactions obtained with nitrous acid have already been indicated in the part of this work treating of qualitative analysis.

According to the intensity of the tints obtained, judging by comparison with known standards, the proportion of the nitrites contained in the water is determined. A solution of an alkaline nitrite is prepared in such a way that 1 cubic centimetre corresponds exactly to the one-hundredth part of a milligramme of nitrous anhydride N_2O_3 , which is the standard solution. This standard solution is obtained by taking 0.406 gr. of pure crystallised nitrite of silver, dissolving it in distilled water, and adding a solution of chloride of sodium in excess. The silver is precipitated as the chloride. It is allowed to deposit and nitrite of sodium is obtained by double decomposition :—



The clear liquid is decanted and put into a flask graduated with 1 litre mark. The precipitate of chloride of silver is washed on a filter and the filtrate is added to the contents of the flask. The solution is brought up to 1 litre with distilled water, and in this way a standard solution of nitrite of sodium is obtained of which 1 cubic centimetre corresponds exactly to 0.0001 gr. A more dilute titrated solution may be used by taking 100 cubic centimetres of the solution thus obtained and bringing it up to 1 litre with distilled water in another graduated flask. This will then contain 0.00001 gr. of nitrous acid N_2O_3 per litre.

A standard solution may also be prepared by simply taking nitrite of potassium and titrating the solution with permanganate of potassium which transforms the nitrous oxide into nitric oxide :—



Titred solution of permanganate of potassium is poured into a known quantity of nitrite of potassium solution, until the pink tint given by the permanganate remains. The standard solution of nitrite of potassium is prepared with a small quantity of nitrite of potassium, and when its degree of strength is known it is diluted

with distilled water to the extent necessary to obtain a solution containing 0.0001 or 0.00001 gr. of nitrous acid per litre.

With Metaphenylene-Diamine.—To test with metaphenylene-diamine colorimetric glasses are used. These are glass tubes which allow the coloration to be noticed under equal bulk of liquor. Fifty cubic centimetres of the water to be examined are put into a colorimetric tube and to this is added 1 cubic centimetre of a solution of sulphuric acid obtained by mixing 1 part of sulphuric acid of 60° B. with 5 parts of distilled water. The mixture is stirred with a glass rod, and under the influence of the nitrous acid in the water a yellow coloration is produced, its intensity depending upon the amount of nitrous acid present.

Standard solutions are prepared with titrated nitrite of sodium.

For this purpose several colorimetric tubes are taken and numbered 1, 2, 3, 4, 5, and so on. In each of these is put 1 cubic centimetre of the solution of metaphenylene-diamine, 1 cubic centimetre of sulphuric acid, and 50 cubic centimetres of distilled water. In No. 1 is put 0.1 cubic centimetre of the titrated solution of nitrite of potassium, in No. 2 0.2 cubic centimetre, and so on. The depths of tint are noted, and the one among these standards corresponding to that of the water under examination is sought for.

Suppose, for instance, that the tint of No. 4 is identical with the coloration obtained with the water under examination. If No. 4 has been obtained with the titrated solution containing 0.0001 gr. of nitrous acid per cubic centimetre, this proves that in the 50 cubic centimetres of the water there are 0.0004 of nitrous anhydride, and per litre :—

$$0.0004 \text{ gr.} \times 20 = 0.008 \text{ gr. of } \text{N}_2\text{O}_3.$$

If n is the number of cubic centimetres of the solution of nitrite of potassium used in the standard corresponding to the tint noted in the water under examination, t the number corresponding to the amount of nitrous acid in the nitrite of potassium solution, by representing by x the weight of nitrous acid contained in 50 cubic centimetres of the water under examination, we get the equation :—

$$x = t \times n,$$

and per litre :—

$$X = t \times n \times 20.$$

With Tromsdorff's Reagent.—The quantification of the nitrous acid with Tromsdorff's reagent is done in a similar way to the metaphenylene-diamine test. In this method blue tints are obtained by the action of the nitrous acid, which causes the formation of iodide of starch. This blue tint is all the more intense as the

liquor contains more nitrites. The analysis is made with a series of colorimetric glasses. Into one of them 50 cubic centimetres of the water to be analysed are put, and 1 cubic centimetre of sulphuric acid at 60° B. together with 2 cubic centimetres of Tromsdorff's reagent are added. For the preparation of the reagent refer to the part of this work treating of qualitative analysis.

A blue coloration forms which is compared with the standards prepared as follows :—

In 5 colorimetric glasses numbered 1, 2, 3, 4, 5, the corresponding number of cubic centimetres of a titrated solution of nitrate of potassium or of sodium is introduced, that is to say 1 cubic centimetre is put into No. 1 glass, 2 cubic centimetres into No. 2, and so on. Each glass is brought up to 50 cubic centimetres with distilled water, then into each is put 1 cubic centimetre of hydrochloric acid of 60° B. and 2 cubic centimetres of Tromsdorff's reagent. The tints of the standards are compared as before with that of the water under examination.

If n be the number of cubic centimetres in the standard corresponding with the tint obtained in the analysed water, and t the amount of nitrous acid in the titrated solution of nitrite of potassium, by representing the weight of the nitrous acid contained in 50 c.c. of the water analysed as x , we obtain the formula :—

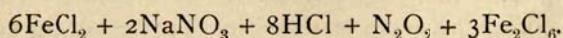
$$x = n \times t,$$

and per litre :—

$$X = n \times t \times 20.$$

Nitrates.—The quantification of nitrates can be effected by evaporating 1 or 2 litres of the water with 1 gramme of caustic soda down to 20 cubic centimetres, and then analysing the nitric acid by Schloesing's process.

This process depends upon the reduction of the nitrates to nitrogen dioxide with protochloride of iron in an aqueous solution and in the presence of hydrochloric acid. The reaction is as follows :—



By calculating according to the molecular weights it will be seen that to have a titrated solution of nitrate of sodium which gives off, per 5 cubic centimetres, 100 cubic centimetres of nitrogen dioxide gas, it is necessary that the solution should contain 76 grammes of nitrate of sodium per litre. A titrated solution is therefore prepared containing 76 grammes of nitrate of sodium per litre. In commencing the analysis 40 cubic centimetres of a solution of a ferrous salt prepared by treating 200 grammes of iron in 200

cubic centimetres of water acidulated with an excess of hydrochloric acid, and bringing this up to a litre with distilled water, are put into a flask. The arrangement of the apparatus is shown in fig. 134. About 40 cubic centimetres of pure hydrochloric acid are poured into the funnel and allowed to run into the flask. After having boiled the liquor for a few minutes to expel all the air, a graduated tube is filled completely with water and put in the hydraulic trough over the end of the bent tube B.

The liquid is again brought to the boil and the residue of the evaporation of the water to be analysed is put into the funnel and allowed to run drop by drop into the flask. The reaction quickly takes place, and nitrogen dioxide bubbles into the graduated tube. The funnel is washed with 10 cubic centimetres of pure hydro-

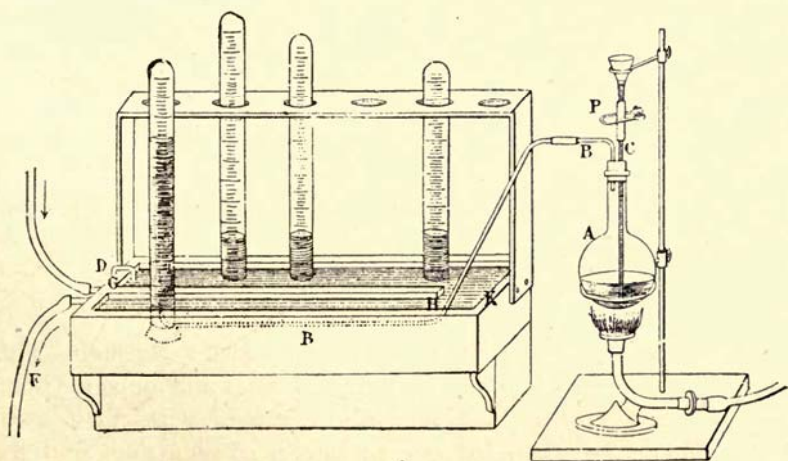


FIG. 134.—Quantification of nitrites by Schloesing's method.

chloric acid and this is allowed to run into the flask, continuing the boiling. In a short time no more gas is given off, and the level of the water in the graduated tube remains constant. This graduated tube is then placed on one side in the hydraulic trough to be used later in the comparative analysis.

Another trial is made with the titrated solution of nitrate of sodium, the graduated tube put on one side is replaced by another full of water and put over the end of the glass tube and the liquor is brought to the boil. Five cubic centimetres of the titrated solution of nitrate of sodium are put into the funnel and allowed to run drop by drop into the flask. The gas is given off and finally the funnel is washed with about 10 cubic centimetres of hydrochloric acid. The operation is made exactly as before, and stopped when the gas ceases to be given off. The graduated tube is then put side

by side with the one used in analysing the water, and the volume of gas in the two tubes is compared.

Let V be the volume of nitric dioxide, obtained with the analysed water, B' the volume of nitrogen dioxide obtained with the titrated solution. Now B corresponds exactly to 0.33 gr. of nitrate of sodium.

If we represent the corresponding quantity of nitrate of sodium contained in the water to be analysed by x , that is to say corresponding to the volume B of nitric dioxide, we shall obtain the equation :—

$$\frac{V}{V'} = \frac{x}{0.33};$$

from whence :—

$$x = \frac{V \times 0.33}{V'}.$$

From this may be easily calculated the contents in pure nitric acid HNO_3 by multiplying the result obtained by 0.7411, which is given by the calculation.

By representing by X the weight of nitric acid contained in 1 litre of the water, if p represents the quantity used in analysis in litres :—

$$X = \frac{V \times 0.33 \times 0.7411}{V' \times p}.$$

Quantification of the Nitrates by Tromsdorff's Method.—This method is convenient in the majority of cases and depends upon the decoloration of an indigo solution titrated with nitric acid. Two solutions are prepared, one of nitrate of potassium and the other of sulphate of indigo. The solution of nitrate of potassium is got by putting 1.8724 gr. of pure nitrate of potassium into 1 litre of water, and thus a solution is obtained of which 1 cubic centimetre corresponds to 0.001 gr. of nitric anhydride per litre.

To prepare the titrated solution of indigo, 6 parts of fuming sulphuric acid are put into a beaker and 1 part of indigotine in powder is added gradually with constant stirring.

After allowing it to settle a little the solution is put into 240 parts of distilled water. The liquid obtained is filtered and then diluted with water. A solution is thus obtained of such a strength that from 6 to 8 cubic centimetres of it correspond to 0.001 gr. of nitric anhydride.

To do this 5 cubic centimetres of the titrated solution of the nitrate of potassium are put into a porcelain capsule, distilled water is added, and the whole is brought up to a temperature of from 110°

to 120° C. Into this the solution of sulphate of indigo is added drop by drop by means of a graduated burette, and the addition is stopped the moment that the liquid takes a light bluish-green tint. The number of cubic centimetres of the sulphate of indigo solution used is then noted.

Another trial is made by operating in the same way on 5 cubic centimetres of the titrated solution of nitrate of potassium, by pouring in at once n divisions of indigo, then continuing to pour gradually until a greenish tint is obtained. The number n' of divisions is then noted, n' thus corresponds to 5 cubic centimetres of nitrate of potassium, that is to say to 0.005 gr. of nitric anhydride N_2O_5 and 0.001 gr. of nitric anhydride corresponding to $\frac{n'}{5}$ of sulphate of indigo solution.

From this we can easily deduce the quantity of water to be added to have a solution of sulphate of indigo 6 to 8 cubic centimetres of which will correspond to 0.001 gr. of nitric anhydride, that is to say to 1 cubic centimetre of a titrated solution of nitrate of potassium.

In quantifying the nitrates 25 cubic centimetres of the water to be analysed is put into a porcelain capsule. Twenty-five cubic centimetres of pure concentrated sulphuric acid are added and the mixture is raised from 110° to 120° C. The sulphate of indigo solution is poured in rapidly with a graduated burette, until the greenish coloration is obtained, and the number of cubic centimetres δ of the solution used is noted.

This trial is made with a fresh 25 cubic centimetres of water, but δ cubic centimetres of the titrated solution of sulphate of indigo are put in, and the pouring out of the solution is continued until the coloration is obtained. The number δ' of cubic centimetres of sulphate of indigo used is noted.

If the titrated solution of sulphate of indigo is such that 1 cubic centimetre = $\frac{0.001 \text{ gr.}}{n}$ of nitric anhydride, n being the number of cubic centimetres of titrated sulphate of indigo, corresponding to 0.001 of anhydride; if, moreover, δ is the number of cubic centimetres of the nitrate of potassium solution used, by representing the weight of anhydride contained in 25 cubic centimetres of the water by x , we obtain:—

$$x = \frac{0.001 \text{ gr.}}{n} \times \delta',$$

and per litre of water:—

$$X = \frac{0.001 \text{ gr.}}{n} \times \delta' \times 40.$$

With this method the results obtained are less than the true figures when the water contains organic matters, as these matters are easily oxidisable and the nitric acid consequently acts upon them. A more exact analysis may be made by quantifying to begin with the organic matters contained in the water.

When once the quantity of permanganate of potassium necessary to destroy the organic matter is known, we can take 100 cubic centimetres of the water to be analysed and add to it the necessary quantity of permanganate to destroy the organic matter, and then bring the volume up to 150 cubic centimetres.

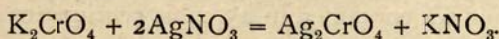
The analysis is made as before on 25 cubic centimetres of this water. The proportion of nitric anhydride contained in 25 cubic centimetres of this water is calculated by multiplying by $\frac{3}{2}$ the weight of nitric anhydride obtained in the preceding formula.

Quantification of the Chlorides.—The quantitative analysis of the chlorine can be done either by the volumetric method or by gravimetric analysis.

Volumetric Method.—This method depends upon the following principle. If we pour a solution of nitrate of silver into a solution of an alkaline chloride, on adding chromate of potash a precipitate of chromate of silver forms, which dissolves in the alkaline chloride until all the chlorine has been precipitated in the state of chloride of silver. To use this principle in analysis, therefore, we take with a graduated pipette 50 or 100 or more cubic centimetres of water according as the quantity of chlorine contained in the water is more or less, the qualitative analysis having already indicated this.

The water is put into a beaker and 2 or 3 drops of the solution of neutral chromate of potassium, which serves as indicator, are added. A graduated burette is filled with a solution of nitrate of silver, prepared so that 1 cubic centimetre of the solution contains 0.001 gr. of chlorine, which is obtained by dissolving 4.79 gr. of nitrate of silver in a litre of distilled water.

The solution of nitrate of silver is poured drop by drop from the burette, and the addition is stopped when on stirring a red colour appears and remains, by reason of the formation of insoluble chromate of silver :—



The number of cubic centimetres used to obtain this reaction is then noted. If n be this number, and N be the number of cubic centimetres of water, the weight x of chlorine contained in these N cubic centimetres of water will be given by the formula :—

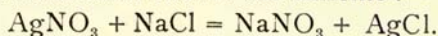
$$x = 0.001 \times n,$$

and per litre :—

$$X = 0.001 \times n \frac{1000}{N}.$$

Gravimetric Method.—This method depends upon the fact that a determined weight of chlorine corresponds to a determined weight of silver.

If a solution of nitrate of silver is added to a solution of alkaline chloride, a white precipitate of chloride of silver is formed, the weight of which determines that of the chlorine :—



A quantity of the water, 50, 100, or more cubic centimetres, according to the proportion of the chlorine which it contains, is taken with a graduated pipette.

This is put into a beaker, then acidulated with nitric acid. A solution of nitrate of silver is then added until no fresh precipitate is formed by the addition of the nitrate. The contents of the beaker are filtered and the precipitate on the filter paper is washed until the wash waters are no longer precipitated by a solution of chloride of sodium. The precipitate is then dried and weighed.

Let n be the number of cubic centimetres of water tested, p be the weight of chloride of silver found.

The weight x of chlorine contained in these n cubic centimetres will be given by the formula :—

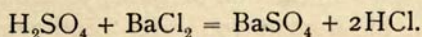
$$x = p \times 0.2474,$$

and per litre :—

$$X = \frac{247.4 p}{N}.$$

Quantification of the Sulphates.—This analysis depends upon the precipitation of sulphuric acid by chloride of barium in the state of sulphate of barium. An exactly determined weight of sulphuric acid corresponds to an exactly determined weight of sulphate of barium.

According to the proportion of sulphuric acid which may be contained in the water, 50, 100, or more cubic centimetres of it are taken with a graduated pipette. This is put into a flask of Bohemian glass, acidulated with hydrochloric acid and brought to the boil. Then a hot solution of chloride of barium is added, and the whole is boiled up for about a quarter of an hour, the following reaction occurring :—



The precipitate of sulphate of barium formed, ordinarily difficult to separate, easily deposits by this method. It must be ascertained

that a fresh addition of chloride of barium produces no precipitation, then the contents of the flask are filtered, and the precipitate is washed and calcined.

Let n be the number of cubic centimetres of water tested, and p be the weight of sulphate of barium found, the weight x of sulphuric acid SO_3 contained in the n cubic centimetres of water will be given by the formula :—

$$x = p \times 0.3433,$$

and per litre :—

$$X = \frac{3.433 p}{N}.$$

To avoid the water spurting out of the flask for want of air, it is necessary to use a little glass bulb made by drawing out a glass tube in the blowpipe flame and soldering one of its extremities. By putting this into the liquid a quiet boil is obtained, as it supplies a little air.

3. BASES.

Quantification of Organic Nitrogen or Albuminoid Ammonia.—

Waters contain ammonia free or in combination and there may be ammonia arising from the different organic matters contained in the water. The method of Wanklyn and Chapman to quantify this organic nitrogen or albuminoid ammonia depends upon its transformation into ammonia by boiling it in the presence of a solution of permanganate of potassium with an excess of alkali.

Five hundred cubic centimetres of the water to be analysed are put into a glass retort and 15 cubic centimetres of a saturated solution of carbonate of soda are added. The liquid is distilled and the operation stopped when 200 cubic centimetres of the distilled product have been obtained. These 200 cubic centimetres contain all the free or combined ammonia of the water. The 300 cubic centimetres remaining in the retort are operated upon to quantify the albuminoid ammonia.

Fifty cubic centimetres of a solution of alkaline permanganate of potassium obtained by dissolving 200 grammes of solid caustic potash and 8 grammes of permanganate of potassium crystals in 1 litre of distilled water are added to the contents of the retort.

The distillation is continued and the distillate is collected in two colorimetric glasses. In the first of these, 50 cubic centimetres are collected, and in the second 100 cubic centimetres. These 150 cubic centimetres contain all the albuminoid nitrogen, that is to say transformable into ammonia. The operator may be assured of

this by distilling a fresh 50 cubic centimetres of the liquid which will contain less than one-hundredth part of a milligramme of ammonia.

The two portions of liquid contained in the two colorimetric glasses are then examined by comparison with a standard solution of chloride of ammonium containing 3.150 gr. of the salt per litre, 1 cubic centimetre of this solution corresponding to 0.001 gr. of ammonia. In order that equal bulks of liquid should be examined, 100 cubic centimetres of liquid are operated upon in all the trials. To the first portion of the distillate 50 cubic centimetres of distilled water are therefore added.

The standards are now prepared. Five colorimetric glasses are taken, and 1, 2, 3, 4, 5 cubic centimetres are added to them respectively. Then they are brought up with distilled water so that they each contain 50 cubic centimetres of liquid.

Finally in the two glasses containing the distillation products and in each of the five standards are put five cubic centimetres of Nessler's reagent. The contents of each glass is stirred up with a glass rod and the coloration noted. Let us suppose that the colorations corresponding to the first portion of the distillate are similar to the type containing θ cubic centimetres of solution of chloride of ammonium, and for the second portion θ' cubic centimetres.

The sum $\theta + \theta'$ represents the total chloride of ammonium used to give these two colorations.

Therefore this solution of chloride of ammonium is such that 1 cubic centimetre corresponds to 0.0001 gr. of ammonia, and consequently if the weight of the organic nitrogen or albuminoid ammonia contained in the 150 cubic centimetres of the distilled product is expressed by x , we obtain the formula :—

$$x = (\theta + \theta') 0.0001 \text{ gr.,}$$

and per litre :—

$$X = (\theta + \theta') 0.0002 \text{ gr.}$$

Quantification of the Ammonia.—The ammonia in a free state or in combination in the waters may be quantified by distillation in Schloesing's apparatus.

This apparatus consists of a glass retort B in connection with a serpentine coil of glass tubing S which runs into a tube of glass R through which a current of cold water can be kept flowing as a refrigerant. Fifty cubic centimetres of the water to be analysed are put into the retort and 3 to 4 grammes of pure calcined magnesia are added. The retort is then connected with the serpentine

coil. Heat is applied and at the end of a few minutes the ammonia is given off. Ten cubic centimetres of a titrated solution of sulphuric acid are put into a flask *b*, and the end of the tube connected with the serpentine is put into the acid.

The ammonia neutralises sulphuric acid as it comes off, and the water is kept boiling for about an hour and a half.

To quantify the ammonia contained in the water, therefore, the

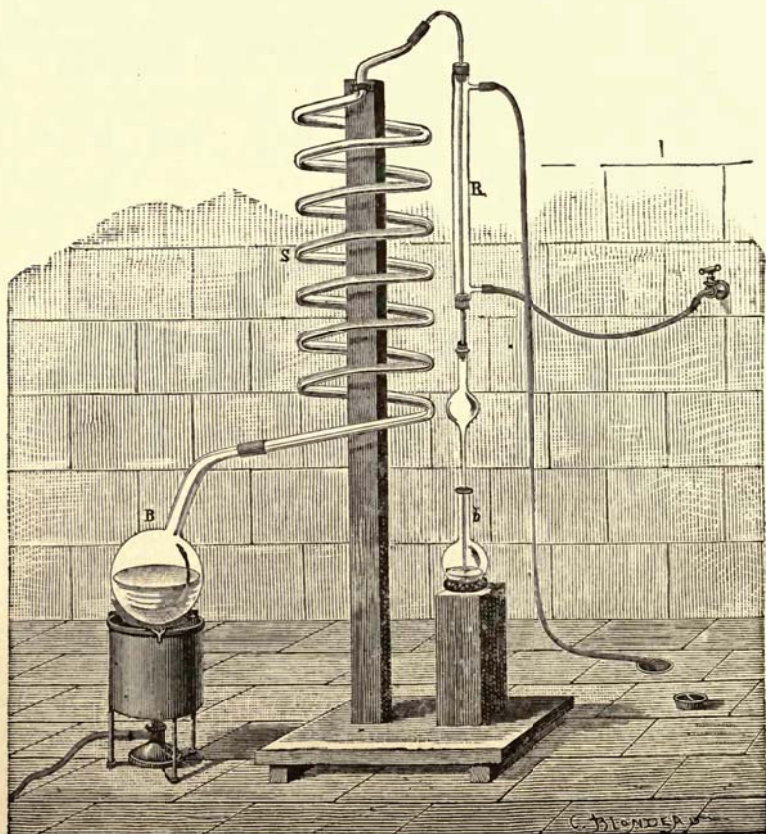


FIG. 135.—Schloesing's apparatus for quantifying ammonia.

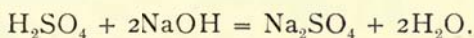
quantity of ammonia absorbed by the sulphuric acid must be ascertained. To do this tincture of litmus is used as an indicator, and this is reddened by the presence of the sulphuric acid in excess in the flask. In determining the proportion of this acid in excess, *that is to say the acid not neutralised by the ammonia*, we learn, by difference, the quantity of sulphuric acid which has absorbed all the ammonia, and thus the proportion of ammonia in the water.

All that has to be done, therefore, is to titrate the sulphuric

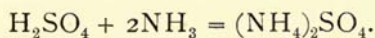
acid. This is done by using a titrated solution of soda, neutralising volume by volume of it with the titrated solution of sulphuric acid employed in such a way that 1 cubic centimetre of soda solution corresponds exactly to 1 cubic centimetre of the solution of sulphuric acid.

The graduated burette is filled with the titrated solution of soda, and this is poured drop by drop into the flask containing the sulphuric acid and the ammonia which has been distilled over.

When the tincture of litmus turns blue, this shows that enough soda has been added, and that the excess of acid is completely neutralised :—



The operation is then stopped and a number δ of cubic centimetres of titrated soda poured out is noted. This number corresponds exactly to δ cubic centimetres of titrated sulphuric acid, and consequently the number of cubic centimetres of sulphuric acid neutralised by the ammonia is $10 - \delta$:—



To obtain these results with precision, the sulphuric acid solution should be very dilute.

If 1 cubic centimetre of this solution of sulphuric acid corresponds to a weight θ of ammonia determined beforehand, we get, represented by x , the weight of ammonia contained in the 500 cubic centimetres of water :—

$$x = (10 - \delta) \theta,$$

and per litre :—

$$X = (10 - \delta) 2 \theta.$$

Colorimetric Method with Nessler's Reagent.—This method depends on the red coloration with Nessler's reagent, the tint of which is more or less intense in proportion to the quantity of ammonia in the water. By comparing the tints with standards containing known quantities of ammonia the proportion of ammonia contained in a water may be ascertained.

A solution containing 0.317 gr. of hydrochlorate of ammonia per litre is prepared, and as 0.317 gr. of sal ammoniac correspond exactly to 0.10 gr. of ammonia, 1 cubic centimetre of this titrated solution of chloride of ammonia corresponds to 0.0001 gr. of ammonia. The quantification of ammonia contained in the water by Nessler's reagent can be done with the distillation product obtained with Schloesing's apparatus or with the water directly.

If the water itself is quantified it is preferable to begin by

precipitating the salts of lime and magnesia in order to obtain a clear coloration with Nessler's reagent.

This preliminary precipitation can be done by adding a few drops of a 30 per cent. solution of caustic soda and carbonate of sodium to 100 cubic centimetres of the water, and then filtering. The filtrate of course is operated upon, and for this purpose 50 cubic centimetres of it are put into a colorimetric glass. The standards are prepared by putting 1, 2, 3, 4, 5 cubic centimetres of a titrated solution of chloride of ammonium into as many glasses and filling them up with distilled water so as to have in each a bulk of 50 cubic centimetres of liquid. Into the water to be tested and into each of the standards 5 cubic centimetres of Nessler's reagent are added, and the liquids are stirred up with a glass rod.

The tint obtained is noted in the water under analysis, and the standard corresponding with it is sought for by comparison.

Let us suppose that this is the standard containing n cubic centimetres of the titrated solution of chloride of ammonium, 1 cubic centimetre of this solution corresponding to 0.0001 gr. of ammonia. Then if x represents the weight of ammonia contained in the 50 cubic centimetres of water to be analysed, we have:—

$$x = n \times 0.0001,$$

and per litre:—

$$X = 0.0004 \, n.$$

Quantification of the Silica, Lime and Magnesia.—Into a porcelain capsule 500 cubic centimetres of the water to be analysed are put and evaporated to dryness.

Silica.—The residue obtained is taken up with hydrochloric acid to dissolve the soluble salts of calcium and magnesium, and the silica remains behind as it is insoluble.

The capsule is filled up with distilled water and the contents are filtered, the silica remaining on the filtre paper is washed with water acidulated with hydrochloric acid and then with distilled water. After having dried the precipitate it is calcined in a tared capsule and weighed. If p is the weight of the tared capsule, P that of the capsule containing the calcined precipitate, the difference of the weight is represented by silica, and if this weight is put as x we obtain:—

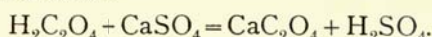
$$x = P - p,$$

and per litre of water:—

$$X = (P - p) 2.$$

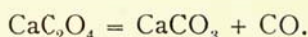
Lime.—The filtrate contains the lime and the magnesia. To quantify the lime we commence by neutralising the hydrochloric

acid in excess with ammonia, adding ammonia until the filtrate is slightly alkaline, and finally we add oxalate of ammonia to precipitate the salts of lime:—



The precipitate is then filtered and washed with hot water.

It is then dried and calcined in a tared capsule, until it is at a dull red heat. The oxalate of calcium is decomposed into carbonate of calcium, and the result is calculated as the carbonate.



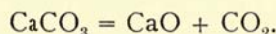
If p is the weight of the capsule before the calcination and P that of the capsule after calcination, the weight x of calcium will be furnished by the formula :—

$$x = (P - p) 0.4001,$$

and per litre :—

$$X = P - p 0.8002.$$

By continuing the calcination of the oxalate of calcium to a cherry red heat, the carbonate of calcium is converted into quicklime :—



This quicklime being very hygroscopic should be weighed as soon as it is cool, in order that it shall not take any moisture from the air.

If p' expresses the weight of the capsule before the calcination, P' the weight of the capsule after calcination, the weight x' of the calcium contained in the 500 cubic centimetres of water will be given by the formula :—

$$x' = (P' - p') 0.7143,$$

and per litre :—

$$X' = (P' - p') 2 \times 0.7143.$$

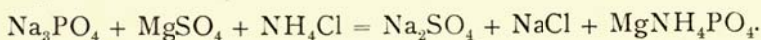
If it is desired to express the results in oxide of calcium, the formulæ become :—

$$x = (P - p) 0.5600,$$

$$x' = (P' - p') 0.5600.$$

Magnesia.—The filtrate now contains only the salts of magnesia. It is evaporated to dryness in a porcelain capsule and the residue is calcined to drive off the ammonia. This residue is treated with hydrochloric acid, and a little nitrate of ammonia should be added in order to retain the iron and alumina that the water may contain in solution. The magnesia is quantified in the state of double phosphate of ammonia and magnesia, and for this purpose phos-

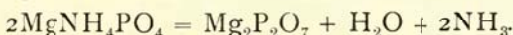
phate of soda is added and ammonia in excess. After thorough stirring it is allowed to settle for twelve hours, and the phosphate precipitates according to the following reaction:—



It is then filtered and the precipitate is washed in water to which a little ammonia has been added, then dried and calcined in a tared capsule.

By calcination the double phosphate with the formula MgNH_4PO_4 is transformed into the pyrophosphate with the formula $\text{Mg}_2\text{P}_2\text{O}_7$, a well-defined body.

This change is shown in the reactions:—



If p is the weight of the capsule before calcination, and P that of the capsule after calcination, the weight of the magnesia MgO contained in the 500 cubic centimetres of water will be given by the formula:—

$$x = (P - p) 0.3602,$$

and per litre:—

$$X = (P - p) 0.7204.$$

The magnesium in the magnesia is calculated by the formula:—

$$x = (P - p) 0.2161.$$

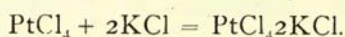
Quantification of the Soda and Potash.—After having quantified the lime and magnesia, phosphate of ammonia and magnesia remain in the liquor. It is filtered and the precipitate is washed. The filtrate contains the salts of potassium and sodium, with a certain amount of phosphoric acid which must be eliminated. The phosphoric acid is got rid of either by precipitation by the salts of lead or by lime. To separate it out with lime the liquid is first concentrated by evaporation and then milk-of-lime is added in sufficient quantity to precipitate all the phosphoric acid. It is allowed to settle for some time. As the lime is of course in excess it is got rid of by adding a little solution of carbonate or oxalate of ammonia. The lime is deposited in the form of a precipitate, which is filtered and washed. The wash waters are collected in a capsule with the filtrate and evaporated to dryness. The evaporated residue contains the soluble salts of potassium, sodium and ammonium.

By calcining the residue in a porcelain capsule the salts of ammonia are driven off. The residue is taken up with water acidulated with hydrochloric acid. Salts of potassium and sodium which remain in the capsule are in a state of chloride.

The residue is dissolved by the water acidulated with hydro-

chloric acid and the solution obtained is put into a flask graduated at 100 cubic centimetres, and the level is kept up to this mark with distilled water. After having mixed the liquid well it is divided into two equal parts. The one is tested for potash, the other for soda.

Potassium.—Half the liquid, that is to say 50 cubic centimetres, is put into a capsule, chloride of platinum is added and the liquid is concentrated by evaporation in the water bath. By the action of the chloride of platinum on the chloride of potassium a precipitate of a double chloride of platinum and potassium is obtained :—



When the liquid is sufficiently concentrated and the chloride of platinum is well in excess, the evaporation is stopped, and after complete cooling, 80° alcohol is added.

The precipitate is then collected on a tared filter, washed with the alcohol, dried in an oven at 100° C., and finally weighed. If p is the weight of the precipitate, representing by x the weight of the potassium contained in the 50 cubic centimetres, we obtain :—

$$x = 0.1601 p,$$

and per litre :—

$$X = 0.3202 p.$$

Sodium.—The second portion of the liquid is put into a tared capsule. Two cubic centimetres of pure hydrochloric acid are added, and evaporated to dryness. The residue is then slightly calcined, and a mixture of chloride of sodium and chloride of potassium is obtained. This residue is weighed. If p' is the weight of the tared capsule, P' the weight of the capsule with the residue, the difference :—

$$P' - p' = \text{weight of NaCl} + \text{KCl}.$$

Knowing the weight of potassium contained in the water by the preceding analysis, if we call the weight of the potassium τ we can calculate this weight of potassium in chloride of potassium.

Representing by π the weight of the chloride of potassium found we obtain :—

$$\pi = \tau \times 1.9103.$$

Knowing $P'p'$, the weight of the sum of the chloride of potassium and of sodium, and π the weight of chloride of potassium, we obtain for the weight x' contained in 50 cubic centimetres of liquid, that is to say 500 cubic centimetres of the water to be analysed :—

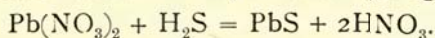
$$x' = P' - p' - \pi,$$

and per litre :—

$$X' = (P' - p' - \pi) 2.$$

4. METALS.

Quantification of the Lead.—A litre of the water to be analysed is evaporated to dryness, and after cooling the residue a few drops of nitric acid are added, and it is again evaporated to dryness. The residue is then calcined to get rid of the organic matters of the water. The residue of the calcination is taken up with water acidulated with nitric acid. The salts of lead which may be in the water are dissolved and may be quantified by colorimetric analysis by means of the characteristic reaction of sulphuretted hydrogen.



This method was adopted by Dr. Smith in the inquiry into the action of the waters of the Dee and the Don on leaden pipes.

The sulphuretted hydrogen may of course be replaced by hydro-sulphate of ammonia. In operating in this method the calcined residue taken up with water acidulated with nitric acid is put into a colorimetric glass. The volume is brought up to 50 cubic centimetres, then the standards are prepared by putting 1, 2, 3, 4, 5 cubic centimetres of a titrated solution of nitrate of lead into 5 glasses in the usual manner. One cubic centimetre of the lead solution corresponds to 0·0001 gr. of metallic lead. One cubic centimetre of sulphuretted hydrogen, or from 2 to 3 drops of hydro-sulphate of ammonia, is poured into each glass. After having noted the tint, that in the trial glass is compared with the standards in the usual manner.

If, for instance, the water has a tint corresponding to the standard contained in 0·0001 of lead, if we represent by x the weight of lead contained in the litre of water taken for examination, we obtain :—

$$x = 0\cdot0001 \text{ gr.}$$

Quantification of Copper.—The copper can also be quantified by the colorimetric method, which allows mere traces of it to be estimated. To commence with, 250 or 500 cubic centimetres of the water are evaporated to dryness, then taken up with water acidulated with a few drops of nitric acid, and filtered. The filtrate is put into a colorimetric glass and this is filled up to 50 cubic centimetres with distilled water. Then 2 cubic centimetres of ammonia are added. This addition of ammonia produces a blue coloration, more or less intense according to the amount of copper in the water. The tint is compared as usual with a series of standards containing known proportions of copper.

These standards are prepared by putting into a series of colori-

metric glasses 1, 2, 3, 4 and 5 cubic centimetres of a solution containing 0.0001 gr. of nitrate of copper per litre, filling them up to 50 cubic centimetres of distilled water and adding 2 cubic centimetres of ammonia.

If p is the water evaporated to dryness, q the weight of copper corresponding to the standard of the same tint as the water under examination, and X the weight of copper per litre of water, we obtain :—

$$X = \frac{1000 q}{p}.$$

Quantification of Iron.—The iron may be quantified by the gravimetric method. It is evaporated to dryness with a few drops of nitric acid taken up with water acidulated with hydrochloric acid, and precipitated in the state of sesquioxide of iron with ammonia, the amount of ammonia used determining the quantity of the iron sought for. The colorimetric method, however, is quicker to operate and allows smaller quantities of iron to be quantified.

A measured quantity of the water to be examined is evaporated to dryness with a little nitric acid added. The residue is taken up with water acidulated with nitric acid and put into a colorimetric glass. The standards are prepared as in the case of copper in colorimetric glasses with a titrated solution of nitrate of iron containing 0.0001 gr. per litre, and putting into the glasses respectively 1, 2, 3, 4 and 5 cubic centimetres. The solution in each is brought up to 50 cubic centimetres with distilled water, then to each is added 2 cubic centimetres of a 10 per cent. solution of sulphocyanide of ammonium. Red colorations are produced, the tint deepening as more iron is present, and the tints are compared in the usual way.

If the standard corresponding in tint with that of the water contains a weight q of iron, and p is the measured quantity of water examined, by representing by X the weight of iron per litre of water, we get :—

$$X = \frac{1000 q}{p}.$$

5. QUANTIFICATION OF THE ORGANIC MATTER.

The quantitative analysis of the organic matter with permanganate of potassium depends on the property of this salt of reducing the organic matter. It thereby loses its colour, and the quantity of organic matter present may be deducted from the quantity of permanganate added to the water necessary to obtain a persistent pink coloration. Only approximate results can be

obtained, as the organic matters act very unequally on the permanganate, and moreover certain inorganic matters have the same discolouring effect.

The nitrites for instance reduce the permanganate, and this may frequently occur, as the compounds of nitrogen are frequently found in waters. On the other hand, urea and analogous compounds have no reducing effect on the permanganate. As a rule, the indications obtained by this process underestimate the quantities of organic matters. The titrated solution of permanganate of potassium should be prepared in such a way that 1 cubic centimetre is equivalent to 0·0001 gr. of oxygen or 0·000788 gr. of oxalic acid.

This solution is prepared with a standard solution used in laboratories, which contains exactly 3·162 gr. of permanganate of potassium per litre. One cubic centimetre of this is equivalent to 0·0008 gr. of oxygen, or 0·0063 gr. of oxalic acid. By taking 125 cubic centimetres of this standard solution, and filling up with distilled water so as to obtain 1 litre of liquid, we obtain the proposed solution. The permanganate of potassium solution may be titrated in the manner we have described in explaining the quantification of oxygen by Mohr's process. For this purpose a solution containing exactly 39·2 gr. of the double sulphate of iron and of ammonium or Mohr's salt per litre is used.

Instead of the double sulphate iron may be used in the form of pianoforte wire, taking into account the fact that 100 of pianoforte wire corresponds to 99·7 of pure iron, and that 0·56 gr. of pure iron corresponds to 0·008 gr. of oxygen, that is to say to 1 cubic centimetre of normal oxalic acid, or 0·63 gr. of true oxalic acid.

The strength of the permanganate of potassium may be gauged by the quantity of iron necessary to reduce it, and when this is known we are able to prepare the proposed solution. Together with this solution of permanganate of potassium we prepare another solution of oxalic acid, capable of neutralising it volume by volume, so that 1 cubic centimetre of the solution of oxalic acid corresponds exactly to 1 cubic centimetre of the titrated solution of permanganate of potassium.

To prepare this solution, 0·788 of pure oxalic acid is added to 1 litre of distilled water. The solution thus prepared should neutralise the titrated solution of permanganate of potassium, volume by volume. If it does not, the quantity of oxalic acid to be added to enable it to do so must be calculated.

For the purposes of the analysis, 200 cubic centimetres of the water are put into a flask, and 5 cubic centimetres of pure 10 per cent. caustic soda, together with 10 cubic centimetres of the per-

manganate solution, are added. The solutions are boiled together for ten minutes or so, and the liquid is allowed to cool down to 50° C., then 5 cubic centimetres of diluted sulphuric acid are added. This is prepared by adding 1 part of water to 1 part of concentrated sulphuric acid. Finally, 10 cubic centimetres of the titrated solution of oxalic acid are put in.

The organic matters contained in the water, like the oxalic acid, exercise their reductive action. The permanganate of potassium poured in is discoloured, and there is an excess of oxalic acid which must be calculated. The amount of the excess of oxalic acid is ascertained by pouring the titrated solution of permanganate of potassium into the liquid from a graduated burette.

The number of cubic centimetres poured out which corresponds to the excess of oxalic acid is noted, and as the excess results from the reductive action exercised by the organic matters in the water on the 10 cubic centimetres of solution put in to begin with, we can make the following calculation:—

If n is the number of cubic centimetres of permanganate of potassium necessary to obtain the persistent pink tint, this number n corresponds to n cubic centimetres of oxalic acid, that is to say to $n \times 0.000788$ gr. of oxalic acid. The results of the quantification of organic matters are often indicated in oxalic acid. Sometimes these results are expressed in the organic matters themselves, it being granted that the weight of permanganate of potassium found in the analysis is five times that of the organic matters contained in the water under examination.



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