and 1892, on the mortality from typhoid fever in the French army, demonstrated in the clearest manner that a conspicuous diminution in the number of deaths had followed the substitution of spring or filtered water for the water of rivers or wells which had been previously used. A striking instance of the connection between typhoid and water occurred in the barracks of Melun. In 1889, the deaths from this disease had been 122; after the introduction of the Pasteur-Chamberland filter, the mortality of subsequent years fell to fifteen, six, two, seven, and seven. In one case the attacks were absolutely confined to soldiers lodged in the better rooms of the barracks, who, contrary to strict orders, had made use of water from troughs fed from the Seine, on account of the filters being frozen. The other battalions, who had drunk nothing but the regimental tea, had not a single case. Similar and quite as conclusive examples occur throughout the report in reference to typhoid and cholera, and still more striking results to the same effect are given in the report for 1894.

CHAPTER X.

SOFTENING OF WATER.

Among the gases dissolved by water from the atmosphere, carbonic acid, being the most soluble (at ordinary temperatures water dissolves its own volume of this gas), occurs in the largest proportion. Although the carbonates of lime and magnesia are almost insoluble in water, in presence of carbonic acid they dissolve to an appreciable extent, forming the unstable bicarbonates. As rainwater and other natural waters contain free carbonic acid, they exert a solvent action upon any carbonates present in the soil or rocks with which they come in contact, and thus most natural waters contain these bicarbonates in solution. Such waters are said to be *hard*, and, as a rule, the hardness is due to lime salts. Formations containing magnesium carbonate, such as the new Red Sandstone and the Permian, usually yield waters in which the hardness is due to magnesium bicarbonate.

The word *hardness*, implying the hard or harsh feeling to the hands in washing, is thus used in a purely technical and commercial sense. In very hard waters the curds which are formed before a permanent lather is produced by the soap are often considerable, whereas in distilled, or a very soft water, a lather will be obtained almost immediately, and little or no precipitate will be formed in the water. Natural fats are converted into soaps by heating with soda or potash. This process effects the decomposition of the fat into the potash or soda soap, or salt of the fatty acids which exist in the fat in combination with glycerine. The hard soaps contain soda, whilst soft soap contains potash; when dissolved in water they both yield a solution of the well-known soapy feel, frothing and forming a lather on shaking. The other metallic salts of these fatty acids are insoluble in water, so that when a soap solution comes into contact with a hard water it is decomposed, white curdy precipitates of lime or magnesia soaps are produced, and at the same time the solution ceases to have a soapy feel, and loses the property of lathering.

When a water containing earthy bicarbonates in solution is boiled, an escape of gas will be noticed, and gradually a white precipitate will be thrown down, with a corresponding loss of hardness. The white precipitate produced consists of the carbonates of lime and magnesia formed by the decomposition of the bicarbonates, and as this change takes place on boiling, when the hardness of a water is due solely to presence of these salts, it is said to be *temporary*. On the other hand, the sulphates, chlorides, and nitrates of lime and magnesia are soluble in water, even in the absence of carbonic acid, and are not precipitated

on boiling. They, therefore, constitute what is known as *permanent* hardness, or hardness after boiling.

For purposes of comparison, both forms of hardness are recorded in terms of the amount of dissolved carbonate of lime that would decompose and precipitate the same amount of soap. A measured volume of the water, usually fifty cubic centimetres, is taken, and "Clark's soap-test" (a definite amount of soap dissolved in proof spirit) is added from a burette until a permanent lather is produced. Each cubic centimetre of soap solution used represents one grain per gallon of *total hardness* estimated as carbonate of lime. Another measured quantity of the water is then boiled for about half-an-hour, until the bicarbonates are decomposed, filtered, if necessary, and the soap test again added from the burette until a permanent lather remains. This second reading gives the *permanent hardness* in terms of carbonate of lime, and the difference between the two values is the *temporary hardness*.

Hardness is usually recorded in degrees, *i.e.*, grains of carbonate of lime per gallon, equivalent to the soap-destroying power of the water under examination. From this number the parts per 100,000 can be obtained by multiplying by ten and dividing by seven. Since a perfectly pure water requires a small amount of soap before it produces a lather, some analysts are accustomed to deduct one degree from the reading to correct for this consumption. It is, however, best not to do this, as the figure required is the actual soap-consuming power of the water. Hardness determinations by different analysts often show slight discrepancies, owing to the above correction and to variations in the time of boiling and other causes.

Statistics from a number of towns show that the hardness of the water supply does not produce any perceptible effect upon the mortality, notwithstanding the fact that it is commonly held that hard waters tend to induce gout and calculous disorders. It is, however, certain that a change of water produces frequently as much effect as a change of air, and that persons who are habituated to a soft drinking water experience slight derangements of the digestive system on partaking of hard water for a few days.

For industrial and general domestic uses, a hard water has very serious disadvantages. The waste of soap alone is generally stated to amount to twelve pounds per 10,000 gallons of water for every degree of hardness. From the author's experiments, and from calculation, the quantity is probably rather less than the above, but may be safely estimated as from nine to ten pounds per 10,000 gallons for every degree. Not only does a hard water cause this serious waste, but the curd produced occasions a greasy deposit in sinks, pipes, and utensils, and forms one of the difficulties in dealing with sewage. When soda is added in washing to overcome the hardness, the fabrics are more or less injured, and insoluble earthy soaps are left in the

fibre. For most industrial purposes a soft water is indispensable, and, with the exception of London, all great manufacturing centres have soft supplies. The woollen trade of Bradford would be seriously affected if that town had a hard water supplied to it; and (as already mentioned) Glasgow is estimated to save £36,000 annually in the matter of soap since using Loch Katrine water.

In cooking, a hard water is objectionable, as a deposit of lime salts is formed upon the surfaces of tea-leaves, meat, vegetables, &c., which hinders their extraction or hardens their tissues. It has been asserted that "ten ounces of tea made with soft water is as strong as eighteen ounces brewed with hard water;" and M. Soyer, in his evidence before a Royal Commission, proved that in the making of soup more meat is required with a hard water, and the operation takes a longer time. Vegetables have their colour darkened by the action of the carbonate of lime. For these reasons, it is a common practice to add a little bicarbonate of soda to the water in culinary operations. In baking, the dough rises better, and bread is lighter in colour, when soft water is used.

Brewers and distillers find a soft water very desirable, as, when the water has a high temporary hardness, the refrigerators become coated with a non-conducting scale of carbonate of lime mixed with organic matter, which is often very thick and difficult to remove. The presence of a large quantity of carbonate of lime makes the water alkaline, and so hinders the fermentation and favours the growth of unhealthy organisms. Permanent hardness, on the other hand, seems a condition for the brewing of light-coloured ales, and Burton has gained its reputation from the sulphate of lime which is present in the water of the Trent and wells in the neighbourhood. So much is this the case that, in other localities, sulphate of lime, as gypsum, is added by the brewer when the water supply is deficient in this ingredient.

The fouling or furring of steam boilers is due to the deposit of earthy salts which is formed on boiling and evaporation. The reactions which take place in water heated to a high temperature under pressure are different to those which obtain in water boiling in an open vessel. The carbonic acid is less easily disengaged, and consequently the carbonate of lime is deposited more slowly. The incrustation given by waters whose hardness is mainly temporary, such as those of the Chalk, the Thames, and most other rivers, takes the form of warty, detached plates, or cauliflower-like masses, which are fairly friable, and do not adhere very strongly to the iron. Such boiler deposits, therefore, do not present any serious difficulties beyond the trouble and expense of cleaning the boiler from time to time. At the same time, careless removal of the scale by workmen may cause damage to the boiler-plates, and in most cases it is more economical to soften the water before use.

"Selenitic" waters, or those heavily charged with sulphate of lime, and magnesian waters containing magnesium chloride and sulphate, deposit a crust which is very hard and crystalline. When chloride of magnesium is present, the heat causes this salt to be decomposed, and hydrochloric acid is produced, which is given off with the steam in small quantities, and causes corrosive effects which may be of a serious character. Magnesium hydrate is at the same time deposited in the crust, according to the equation :—

$$MgCl_2+2H_2O = Mg(OH)_2+2HCl.$$

This decomposition is retarded in the presence of alkaline chlorides, like common salt, so that sea water, although it contains a large quantity of magnesium chloride, may be evaporated nearly to dryness without any evolution of hydrochloric acid, and even at the high temperature of boilers the decomposition is very limited. The addition of salt to such waters has therefore been suggested as a remedy for this pitting action, but in most cases it would be better to use a softening process before the water enters the boiler. The magnesium hydrate, which is invariably found in crusts from magnesian waters, owes its origin mainly to the decomposition of the magnesian salt by the carbonate of lime previously deposited, the carbonic acid escaping, as shown by the equations :—

$$\begin{aligned} CaCO_3+MgCl_2 &= CaCl_2+MgCO_3. \\ CaCO_3+MgSO_4 &= CaSO_4+MgCO_3. \\ MgCO_3+H_2O &= Mg(OH)_2+CO_2. \end{aligned}$$

Vivian Lewes points out that this explains the almost entire absence of calcium carbonate from marine crusts, and also that ferric chloride is not found in the water, which would be the case if corrosion or pitting were due to hydrochloric acid. At the same time, it is quite possible for both actions to occur, and some corrosion may take place before the calcium carbonate has time to take up the hydrochloric acid, the iron being afterwards precipitated. It will be noticed, that all the incrustations from marine boilers contain a considerable quantity of iron (Table B in Appendix).

Calcium chloride and nitrate, and also magnesium nitrate, although present in most hard waters, are so soluble in water that they are never precipitated, and are consequently not found in boiler crusts. Some soluble salts, like sodium chloride, form slightly soluble double salts with the magnesium chloride and sulphate, and are therefore occasionally met with in deposits. Magnesium sulphate is very soluble in water, but, in presence of calcium chloride and carbonate, reacts with them, and thus eventually is found as magnesium hydrate in the crust. Calcium sulphate is, as already mentioned, the most objectionable constituent of waters for use in steam boilers, as it yields a hard, crystalline scale, which is exceedingly difficult to remove. When first deposited it is hydrated in the form of gypsum, $CaSO_4 2H_2O$, but slowly changes into anhydrite, $CaSO_4$, which is still

denser and more insoluble. At a temperature of 150° C. (300° F.), calcium sulphate is practically insoluble in either salt or fresh water, and is therefore completely deposited under such conditions. If the water be heated under pressure above this temperature before entering the boiler the salts are deposited outside the boiler, but the difficulty is only transferred to the tubes of the heater, so that in this case also a softening process is to be recommended.

Waters impregnated with sewage often have a considerable quantity of oily or fatty substances, with soda salts and ammonia, present in them. The last-named acts upon copper, and any dissolved copper will be subsequently deposited upon the iron of the boiler and cause local corrosion, or "pitting," by galvanic action. The scale under such circumstances often shows green spots, and such waters should be treated chemically before use. Moss or peaty waters are often valuable for boilers on account of their softness, and because the mud is easily *blown*. But if they contain much of the organic humus acids, they must be neutralised with lime before using, or the action upon the iron will be considerable.

Lefévre proved that the rapid pustular corrosion of steam-boilers used with some river waters was due to solid organic particles, which, by oxidation, developed pectic acid. He prevented this action with success by adding either alum or, better, ferric chloride, in quantities determined by experiment, followed by lime, to the feed-water. The purified water was easily decanted, and no longer acted on iron, and when ferric chloride was used deposited hardly any scale. In tidal rivers the proportion of admixed sea water is greatest at high tide, and as at low tide the water is generally too dirty for use in boilers, such a supply must be chosen with regard to these conditions. As a rule, however, the water of the lower part of a tidal river is quite unfit for use. Pit waters, especially from shale and coal, frequently contain acid sulphates of iron and alumina, which are most injurious to boiler-plates. Those that are not acid can be used with some advantage, as the coal-dust gives a scale which is much looser, and where such water is used on an old boiler it sometimes detaches the existing scale. Surface waters, on account of their hardness, are generally unfit for use in boilers. Some years ago, two 30 h.p. boilers, supplied from a well in Lambeth, gave such a deposit that nearly a ton of incrustation had to be removed monthly by cleaning and chipping.

An idea of the composition of boiler-crusts is given in the table (Table B, Appendix). Collet estimates the amount as follows:—" Condensing engines, when large and of very high steam economy, require about two gallons per hour per indicated h.p. for boilers, and generally twice as much for condenser water; small and inferior, but yet 'high class,' three to five; low class, in bad condition, six to fifteen gallons per hour. Three gallons is the average, equal to

3,000 gallons per day of ten hours for 100 h.p. If the water has fifteen degrees of total hardness, the deposit per working day will weigh six and a half pounds, or over a ton per annum, of which the larger portion will remain as scale, equal to thirty-five cubic feet of soft, or seventeen of hard scale." The order in which the deposition usually takes place is:—(1) Carbonate of lime; (2) sulphate of lime; (3) oxide of iron; (4) silica, alumina, and organic matter, with magnesium hydrate; (5) common salt.

These coatings are very bad conductors of heat. Rankine states that the resistance to heat of carbonate of lime is eighteen times, and that of sulphate of lime fifteen times, that of iron. The consequent waste of heat in urging the fire for steam-raising in a foul boiler is enormous. It is estimated that one-sixth of an inch of scale necessitates the use of 16 per cent. more fuel; quarter of an inch, 50 per cent.; and half an inch, 150 per cent. additional coal. These figures are probably in excess of the truth, but the loss is still very large. In addition to this, there is the damage to the boiler-plates by overheating, and a certainty of explosion if the coating should crack suddenly, and the water be admitted to the nearly red-hot iron. The scale evidently prevents a proper internal examination of the boiler. Chipping off the crust injures the boiler, and may start the rivets.

" Blowing off " for a short time at frequent intervals is always necessary, as only the deposit near the cocks is blown out. The cocks themselves are often worn out by the friction with the scale. When the whole boiler has to be blown, it should be cooled first by the very gradual injection of cold water, or any loose deposit will cake together as the water runs off. The loss of time, heat, and water, in frequent blowing off is very great. In marine boilers using salt water the neglect to blow out is often the cause of collapsed furnace crowns, the density of the water gradually increasing until it reaches the saturation point, when solid sodium and magnesium chlorides separate on the plates, even though there may be a copious supply of water; then the same non-conduction and overheating occur as in the case with lime deposits. For this reason, condenser water (which is the spent steam condensed and used again, amounting practically to distilled water, and therefore perfectly soft) is returned to the boiler to dilute the salt water. Approximately, one ton of water per 100 h.p. per twenty-four hours is required to make up the condenser water to the right amount.

C. E. Stromeyer, at the Institute of Naval Architects (May, 1896), proposed to control the composition of water in boilers by chemical testing. At intervals a sample is withdrawn and tested by nitrate of silver, caustic soda, or carbonate of soda, to determine the salts it has acquired by concentration. The feed of condenser, distilled, or softened water is regulated in proportion. In all cases where condensed exhaust steam is used as feed-water, the boiler should never be blown out without first using the scum-cocks freely, so as to remove as much as possible of the grease and scum.

A large number of patents have been taken out for the prevention of boiler incrustations. Some of these are mechanical, introducing twigs, fibres, wires, chains, balls, or brushes to entangle the deposit, like the familiar marble in the kettle. One of the most modern, which appears to have a wonderful power of aggregating the sediment to itself, is in the form of a metal centre with radiating wires. Electricity has, of course, been invoked, the boiler being made the negative terminal, and suspended plates or chains the positive, in the hope that the hydrogen gas generated by galvanic action would protect the boiler from oxidation, hinder a crust from forming, or render it loose and friable if deposited, but the result has not answered the expectations. Spent tan, peat, moss, wheat bran, potato-pulp, chestnuts, peas (patent 3,395, 1883), and other solid materials acting mechanically, undoubtedly render the crust looser, but they clog the boiler, promote priming, and furnish so much more solid matter to remove. Treacle (patent 4,717, 1877) and glycerine (patent 4,236, 1881) are worse than useless.

Tallow and fat-oils are to be condemned, not only because they form greasy lime or magnesia soaps, which agglomerate into hard concretions, but because by the heat they are decomposed into glycerine and fatty acids, which are known to act vigorously upon iron plates. The scale where tallow is used has been found to contain 12 to 26 per cent. of iron from the plates. A sediment from a condensed steam tank where tallow was used as a lubricator contained 50 per cent. of ferric oxide, 41 of fatty matter, and nearly 1 per cent. of copper oxide from the fittings. This shows that the fatty acids, rising with the steam, penetrate the cylinder and pumps. In a great many cases considerable injury has been caused to a boiler by the presence of copper in the feed-water. For these reasons "cylinder oils" are used that consist mainly of mineral or hydrocarbon oils, not acid, and not decomposed by superheated steam. The main part of the fatty matter which always accumulates in boilers fed partially by condenser water is drawn off at intervals by the scum-cocks.

Paraffin oil, which is extensively used in America, causes the deposit to be thrown down in a pulverised form by incrusting the particles with a very thin oily coating. Such a deposit is easily blown, while in a singular manner the oil sinks into the scale already formed, and causes it to split up and be removed with facility. Indeed, it has been actually mentioned as a drawback that it so thoroughly cleanses the joints that it sometimes causes a boiler to leak. Its use is unattended by priming or frothing. But its action is only temporary, as it passes off with the steam and requires constant renewal. It should be free from solid paraffins, or "hard scale," or it will form concretions like tallow. It is recommended to be first introduced when the boiler is empty, to make an oily coating over the plates; afterwards it is added with the water, sometimes by an automatic arrangement. In buying a crude product, a careful test should be made for acidity by shaking up with distilled water and testing the water with litmus paper, since some sulphuric acid is often left behind from the purification of the raw petroleum; if any acid be found, the sample should be rejected, or the acid may be neutralised with soda.

"Soda-tar," from paraffin refining, containing caustic soda and carbonate of soda, is a well-known anti-incrustator.

Chemical incrustation-preventers have been numerously patented and advertised, and no doubt many of them yield a large profit to their manufacturers. The majority are, however, useless, and many injurious. Tannin, as contained in extracts of various barks, gives a loose and friable tannate of lime, but it attacks iron dangerously, and has no effect on the permanent hardness of waters. If tannate of soda be used, its virtue is little greater than the soda it contains, while its expense and the ease with which it decomposes are fatal defects. Any acid preparation designed to dissolve the scale will attack the iron of the boiler-plates also. Ammonium chloride has also this objection, as by dissociation with the heated steam it generates ammonia gas and hydrochloric acid, $NH_4Cl = NH_3 + HCl$, both of which originate serious local mischief to metal parts, either iron, copper, or brass.

Caustic soda and sodium carbonate are the most inoffensive members of the class, but if in excess they cause foaming and wet steam, especially in locomotives, and are apt to corrode the fittings, particularly asbestos packing. They are sold at very large profits to manufacturers, and are known under numerous fancy names. Sometimes they are coloured with litmus powder or aniline dyes. The scale from soda crystals is often very hard and difficult to remove. Borax and boric acid (3,721, 1878) have nothing to recommend them. The triple sodium phosphate, Na_3PO_4, is said to have given good results; the product, phosphate of lime and magnesia, has been proposed to be sold as manure. "Baudet's patent" is sodium hyposulphite, glycerine, and rainwater. Sulphite of soda ("Morgan's compound") has also been recommended, while in Germany barium chloride has been used to turn the calcium sulphate into the soluble calcium chloride, leaving a pulverulent precipitate of barium sulphate:—

$$CaSO_4 + BaCl_2 = BaSO_4 + CaCl_2.$$

Sodium Fluoride.—Doremus gives the following prescription for preventing scale: "Determine the lime and magnesia in the water; multiply the CaO by $1\frac{1}{2}$ and the MgO by 2. The sum gives the amount of sodium fluoride required to throw down the lime and magnesia. It is only necessary to add one-fourth of this quantity, as the fluorides formed do not adhere, but form nuclei for the other hardening salts to deposit in a pulverulent form. Sodium fluoride is now manufactured for the purpose at a reasonable rate by the American Fluoride Company, New York. Two ounces per 1,000 gallons is the average quantity added to the feed."

Any chemical reagent is better added outside the boiler before the water enters. Even if used in the feed-heater it chokes up the tubes, and requires continual removal. In any case, an analysis of a compound, and of the water for which it is proposed to be used, should be obtained, and chemical advice sought, or heavy expense and injury to the boiler may ensue. Many large firms expend as much as £150 a year on incrustation-preventers, which amount would go a long way towards the cost of the far more preferable preliminary softening.

In the case of works or factories where large quantities of water are used, as the lowest price charged for town's water is generally far in excess of the cost of pumping, it will pay to sink a well, unless a spring or river is near. The saving in large establishments often amounts to more than £1,000 a year. But the water, if hard, must be previously softened. To show the importance of procuring analysis of the waters, we may mention that considerable changes in the composition sometimes occur owing to atmospheric conditions, to fresh strata being tapped, or to new factories being established on a stream. Clear water may be obtained at great cost from a well or other source, and may be unfit for use on account of its hardness, whereas turbid water from a neighbouring stream may, by simple filtration or deposition, furnish a suitable supply at a much cheaper rate.

Methods for softening Water.—It has already been mentioned (p. 192) that temporary hardness can be removed by boiling, but this method is costly, and causes a loss of water. Boiling is said to cost not less than 1*s.* per 1,000 gallons, while lime costs about a farthing. Professor Clark, about 1840, patented his well-known process of adding lime water, so as to combine with the carbonic acid which kept the earthy carbonates in solution, with the result that both portions of carbonate of lime were precipitated.

$$\overset{\text{Calcium Bicarbonate.}}{CaCO_3,CO_2}+\overset{\text{Slaked Lime.}}{Ca(OH)_2}=2CaCO_3+H_2O.$$

Thus only the permanent hardness was left, plus about two grains per gallon of carbonate of lime in solution. The precipitate was allowed to deposit in reservoirs or tanks, and the clear water drawn off, but the area required by these tanks was considerable, their sediment settled slowly, the finer particles were apt to remain suspended and render the water milky, and the carbonic acid of the air also re-dissolved some of the earthy carbonates.

The Porter-Clark modification mixes the lime with the water by paddles, and then passes it through filter presses of cloth, saving much time and space, and ensuring a clear product. The quicklime is preferably slaked first; a good quality should be employed (Buxton lime is reputed the purest), as far as possible free from stones and clinkers. The best generally is "stone lime" from limestone. Grey and shell lime from chalk often contains a large quantity of clay and stones. It should be almost entirely soluble in hydrochloric acid without much effervescence (which would show carbonate from under-burning or exposure to the air), and not more than 4 or 5 per cent. should be insoluble in water. It should also give no smell of sulphur compounds, and should be kept away from air.

Lime water can be tested by blowing through it, when it should give a heavy turbidity, or by nitrate of silver. Its strength is determined from time to time by standard acid. As it has to be used in definite proportion, the excess of lime must be allowed to settle: the clear lime-water, containing about sixty to seventy grains of CaO per gallon, being agitated with the water. After the deposition of the main part of the precipitate, the still turbid liquid passes on to the filters. The process is made continuous by running the lime solution into the water as it passes through a mixing chamber. To ascertain the proper proportions, the lime-cock is at first turned on until the lime is in excess, as shown by withdrawing a sample of the softened water, and testing it with nitrate of silver, when a grey-brown precipitate of silver hydroxid is obtained. The cock is now turned off until a sample shows no brown, but only a white precipitate: the proportions are now correct. An automatic arrangement, worked by steam or water, maintains the supply of lime water at the right amount, increasing or diminishing it as the water flows more rapidly or more slowly. Further tests must be made from time to time, as waters change somewhat in composition from day to day.

An intermittent system without filtration consists of two lime-water tanks, in which the lime-water is prepared one day and used the next, and three softening tanks, of which two are for use on alternate days, and the third is for reserve while cleaning out, &c. The lime is run into one of the softening tanks and the hard water pumped in; next day the carbonate of lime has deposited, and the clear water is run off for use. For a moderate-sized town requiring 250,000 gallons a day, the two lime water tanks should hold 40,000 gallons each, and the three softening tanks 300,000 gallons each, or a total of 980,000 gallons.

The objections to this system are (1) the imperfect mixing of the solution with the hard water; (2) the cost of construction of the tanks, and the large area of ground required; (3) the heavy working expenses.

Clark's process removes only the temporary hardness. Lime does not affect calcium sulphate; with magnesium salts, it indeed precipitates magnesia, but it leaves lime salts instead, so does not reduce the permanent hardness; although, under certain circumstances, it precipitates the bicarbonate of magnesia. Waters permanently hard, therefore, require additional treatment with an alkaline mixture, which will vary in composition and amount according to the character of the water.

Caustic Soda, NaOH, is usually purchased in the crude form as "soda-ash," containing sodium hydrate, carbonate, sulphate, sulphide, thiosulphate, and insoluble impurities. Only the hydrate and carbonate are useful, and the proportion of these should be known. The sulphide is exceedingly detrimental. Therefore, soda for softening should always be bought by analysis. It is sold in drums. On opening it rapidly deliquesces, cakes together, and absorbs carbonic acid; therefore, it is better to dissolve a whole drum in the proper quantity of water in a well-covered iron tank (not painted inside), and to siphon off portions for use. The solution greedily absorbs carbonic acid from the air, and powerfully attacks the hands or clothing. The strength may be approximately ascertained by its specific gravity, but more accurately by standard acid. The solid soda should contain not less than 80 per cent. of sodium hydrate.

Sodium carbonate.—The ordinary crystals have the formula $Na_2CO_3,10H_2O$, and contain only 37 per cent. of the anhydrous carbonate, with 63 per cent. of water of crystallisation. They are called "soda crystals," "Scotch soda," "washing soda," or simply soda. Brunner, Mond & Co.'s concentrated crystal soda is a sesquicarbonate, containing 70 per cent. of Na_2CO_3, in the form of small crystals readily soluble in water, and presents the great advantage of less weight and bulk, and therefore less freight than "soda crystals." The so-called "carbonate of soda" of the shops is *bicarbonate*, $NaHCO_3$, and is useless for softening.

The use of these three agents, lime, soda, and sodium carbonate, is often wrongly and imperfectly stated, and the solutions added by guesswork, hence the frequent failures in attempts at commercial softening. The total and permanent hardness of the water, and the strength of the reagents must first be known; these require simple operations in volumetric analysis by soap-test and by standard acid solutions. If the water be fairly constant in composition, and a sufficient stock of the solutions be made, the determinations need not be frequently repeated. But the softened effluent must be occasionally tested with nitrate of silver, or by the taste, to see that there is no excess of the chemicals, as such an occurrence would be

injurious for many purposes. It is better in most cases not to carry the precipitation to its final limit, but to leave the softened water with about three to five grains of hardness. Sometimes a partial softening is easily and cheaply effected, where to go further would be costly. The following are the equations on which the calculations are based, taking calcium sulphate as the representative of permanent, and calcium carbonate of temporary hardness.

$$(a)\ CaSO_4+2NaOH=Ca(OH)_2+Na_2SO_4.$$
$$(b)\ Ca(OH)_2+CaCO_3CO_2=2CaCO_3+H_2O.$$

As these reactions happen almost simultaneously, the two equations may be combined thus:—

$$(c)\ CaSO_4+CaCO_3CO_2+2NaOH=2CaCO_3+Na_2SO_4+H_2O.$$

The remainder of the temporary hardness will be removed in the usual way by lime:—

$$(d)\ CaCO_3CO_2+Ca(OH)_2=2CaCO_3+H_2O.$$

The result may be summarised thus:—

RULE I.—*For a water in which the temporary hardness exceeds the permanent, caustic soda must be added equivalent to the permanent hardness, and lime equivalent to the temporary hardness minus the permanent hardness.*

In waters of great permanent hardness due to lime salts, carbonate of soda must be used instead of caustic:—

$$(e)\ CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

If it be necessary to remove also the temporary hardness, lime must be added *subsequently*, as in equation (*d*) above. We should then have:—

RULE II.—*For a water in which the permanent hardness, due to sulphate of lime, exceeds the temporary hardness, carbonate of soda must first be added in proportion to the permanent hardness, and then, if necessary, lime equivalent to the temporary hardness.*

Every degree of hardness, reckoned as carbonate of lime, whether as grains per gallon, or as parts per 100,000, is equivalent to 0·8 grains, or parts, of NaOH, to 0·56 of CaO or 0·74 of $Ca(OH)_2$, to 1·06 of the anhydrous Na_2CO_3, or to 2·86 of the crystallised $Na_2CO_3,10H_2O$.

For magnesian waters the case is different, and here it will be useful to correct a prevalent mis-statement. It is usually asserted that calcium and magnesium bicarbonates are precipitated on boiling. But magnesium carbonate is much more soluble than is commonly supposed; it is only partially thrown down on boiling, the main part remaining in solution *as a part of the permanent hardness.* On the other hand, magnesium chloride, if present in any considerable amount, is liable to be decomposed by the boiling, hydrochloric acid escaping, and a basic chloride of magnesium depositing. This portion of the magnesium salts would therefore figure in the soap-test as *temporary hardness.* Magnesium chloride also reacts with the precipitated calcium carbonate, as mentioned in speaking of steam-boilers (p. 199), yielding dissolved

calcium chloride, and at first basic magnesium carbonate, and then, finally, insoluble magnesium hydrate. Magnesium sulphate can also interchange with sodium chloride, forming sodium sulphate and magnesium chloride, which then may undergo the above changes, although the presence of alkaline chlorides, by forming double salts, renders it more stable.

Lime decomposes magnesium salts, throwing down magnesia, and leaving a sulphate, chloride, or nitrate of calcium as the case may be. In neither case is the hardness reduced; in that of the sulphate it is rendered still more objectionable. The chlorides and nitrates of calcium, however, give no fur in steam boilers, as they are so soluble. It follows that, in waters containing much chloride or nitrate of magnesium, lime effects a great improvement if they are intended for steam boilers; those containing magnesium sulphate, on the other hand, are deteriorated; while the relation to soap is little affected by lime. For an improvement in this direction caustic soda must be employed, but the separation of the magnesium hydrate is never complete. As to the proportion to be used, the soap-test is not a satisfactory guide; a chemical analysis must be made, and eighty parts of NaOH used for every forty parts of MgO, the lime salts being dealt with, if necessary, by the other reagents, as above described. The process is more difficult, but a considerable improvement may be effected.

S. E. Davis, of Manchester (English patent 5,655, April, 1887), has proposed to use crystallised tribasic phosphate of soda, Na_3PO_4, which is now an article of commerce, for softening waters, especially for removing magnesia, under the name of "Tripsa." 2·5 grains per gallon for every degree of hardness (Clark's) is recommended. The precipitation of the magnesium phosphate is somewhat slow, but the product is reported to have some value as manure. Sodium fluoride has been proposed by Professor Doremus, of New York, as it precipitates both lime and magnesia. He has patented the use of a double phosphate and fluoride, $Na_3PO_4, NaF, 12H_2O$, which has the advantage of crystallising in large octahedra, like alum, of a definite composition and permanent in the air, whereas the phosphate Na_3PO_4 itself readily becomes damp and alters. The precipitate has a similar constitution to apatite. In waters which are not potable through the purgative action and bitter taste of magnesium salts, such as occur in the Permian and other formations (see Table D in Appendix), lime, by substituting calcium for magnesium, would probably in great part remove the objection, while in this case, if soda were used, the sulphate of sodium formed would be little less objectionable than the sulphate of magnesium. Chloride of magnesium with soda would of course form common salt.

The calculation of the amount of reagents required will be simplified by the following scheme, which gives the weight in grains of the reagents required to be added per gallon:—

A.—When Temporary Hardness is more than Permanent.

$\frac{8}{10}$ of the Permanent Hardness = Soda, NaOH, in grains per gallon.

And $\frac{56}{100}$ (Temporary Hardness *minus* Permanent Hardness) = Quicklime, CaO, in grains per gallon.

Or $\frac{74}{100}$ (Temporary Hardness *minus* Permanent Hardness) = Slaked Lime, $Ca(OH)_2$, in grains per gallon.

B.—When Permanent Hardness exceeds Temporary.

$\frac{106}{100}$ of the Permanent Hardness = Anhydrous sodium carbonate, Na_2CO_3.
Or $\frac{151}{100}$ " " " = "Brunner-Mond's concentrated crystallised soda."
Or $\frac{286}{100}$ " " " = "Soda crystals," $Na_2CO_3, 10H_2O$
Afterwards $\frac{56}{100}$ " Temporary " = Quicklime, CaO.
Or $\frac{74}{100}$ " " " = Slaked lime, $Ca(OH)_2$.

The amount is given as quicklime, not because it is added in that form, but because it is easier to calculate the strength of lime and lime water as CaO.

C.—For Magnesian Waters.

$\frac{56}{40}$ of the MgO found by analysis gives the weight of Quicklime, CaO, required for softening one gallon.

And $\frac{80}{40}$, or twice the MgO = Soda, NaOH.

The lime salts can be afterwards treated, if necessary, according to A or B above. It must be understood that in the use of soda little reduction of the total solid matter is effected, as the corresponding sodium salts are left in solution. Also that, as it is not advisable to push the softening to its lowest limits, the above theoretical quantities of reagents should be reduced by from $\frac{1}{10}$ to $\frac{1}{5}$.

By the softening process a water is rendered clear, its colour is usually diminished, and a large proportion of the organic matter, and sometimes all the bacteria, are entangled and removed. Some people object to soft water owing to its flat taste, but the palate soon gets habituated to its use.

In the Sixth Report of the Rivers Commission, Dr. E. Frankland urged that the water companies ought to use Clark's process for softening their waters "before they were allowed to raise fresh capital."

In the case of clean water, the lime precipitate produced by softening can be used for commercial purposes, or can be re-burned to quicklime, but in dirty waters it is very much discoloured, and is usually thrown away.

Softening apparatus.—These are made in many distinct patterns, which aim at improving the process in different ways:—

1. *To economise space.*—Several forms consist of divided iron tanks, with cisterns affixed above for the regulated supply of water and chemicals. The mixture passes down one side, partially settles, and passes upwards on the other through filters of various construction, the cleared and softened water emerging through a pipe at the top. Some types are designed on a small scale for softening a domestic supply. The softening solutions are generally soda or carbonate of soda; the powders contain lime, and are often sold at a large profit.

Many of these contrivances are exceedingly ingenious, but also particularly liable to get out of order. The regulating, and withdrawal of sludge, are delicate operations, and on the whole, except in remote neighbourhoods, where no other course is possible, private softening on a small scale by a machine cannot be recommended. It would probably be better to have a large iron cistern of known capacity, to add the chemicals definitely in known strength, to stir thoroughly, allow to subside, and dip out or siphon off the clear water as wanted.

In kitchen boilers, however, the use of a hard water occasions continual trouble and expense, and great danger of explosion. If rainwater apparatus cannot be obtained, or a softer local supply, some form of automatic softener will become necessary.

2. *To insure the proper proportions and mixing of the reagents.*—At the locomotive sheds of the London and North-Western Railway, at Camden Town, 7,000 gallons per hour of chalk well-water from Watford is continuously reduced from seventeen or eighteen degrees of hardness to four degrees, under a pressure of sixty pounds per inch (Porter-Clark process). The lime is churned in a horizontal cylinder, all the mixing and delivery being accomplished by a water-motor worked by the pressure of the water itself, therefore adjusting its

rate of supply to the current of water. Filter presses separate the sediment.

The Porter-Clark process is specially adapted for waters of high temporary hardness, like those of London. At Duncan's sugar refinery, Victoria Docks, it was found that the pipes were becoming rapidly choked by carbonate of lime, owing to the removal of carbonic acid by the vacuum in the sugar evaporation. Hence that process was adopted, and worked successfully. They found that "if the proportion of lime was too little there was great difficulty in filtration, but by arranging the lime valve so as always to have a slight excess, the difficulty was removed; the filtration was also much easier if the water was warmed (the deposit becomes crystalline). The slight excess of lime in the boilers did not cause any trouble. The water lost its yellow colour and became blue."

The following illustrations show different forms of the plant used for working the Porter-Clark process:—

Fig. 40 is an apparatus that treats continuously 1,200 gallons per hour. The square tank on the right contains the lime water, which is transferred to the central softening cylinder by a small feed-pump. On the left is the filter press.

A smaller apparatus for softening and filtering 350 gallons per twelve hours, and working under pressure from the main without any motive power, is shown in Fig. 41. The softened water passes upwards to the cisterns of the house.

Fig. 42 is a form of "Industrial" purifier for use where motive power is not available. The pair of upper tanks contain lime water and other solutions for working twenty-four hours daily. The hard water and the solutions are introduced at the bottom of the lower tank, and the mixing is completed by causing the liquid to issue in a very thin stream over the edge of a trough fixed internally round the top of the lower vessel. The materials have to be carried up, and there is a corresponding inconvenience and loss of time as compared with working with a motor on the ground level.

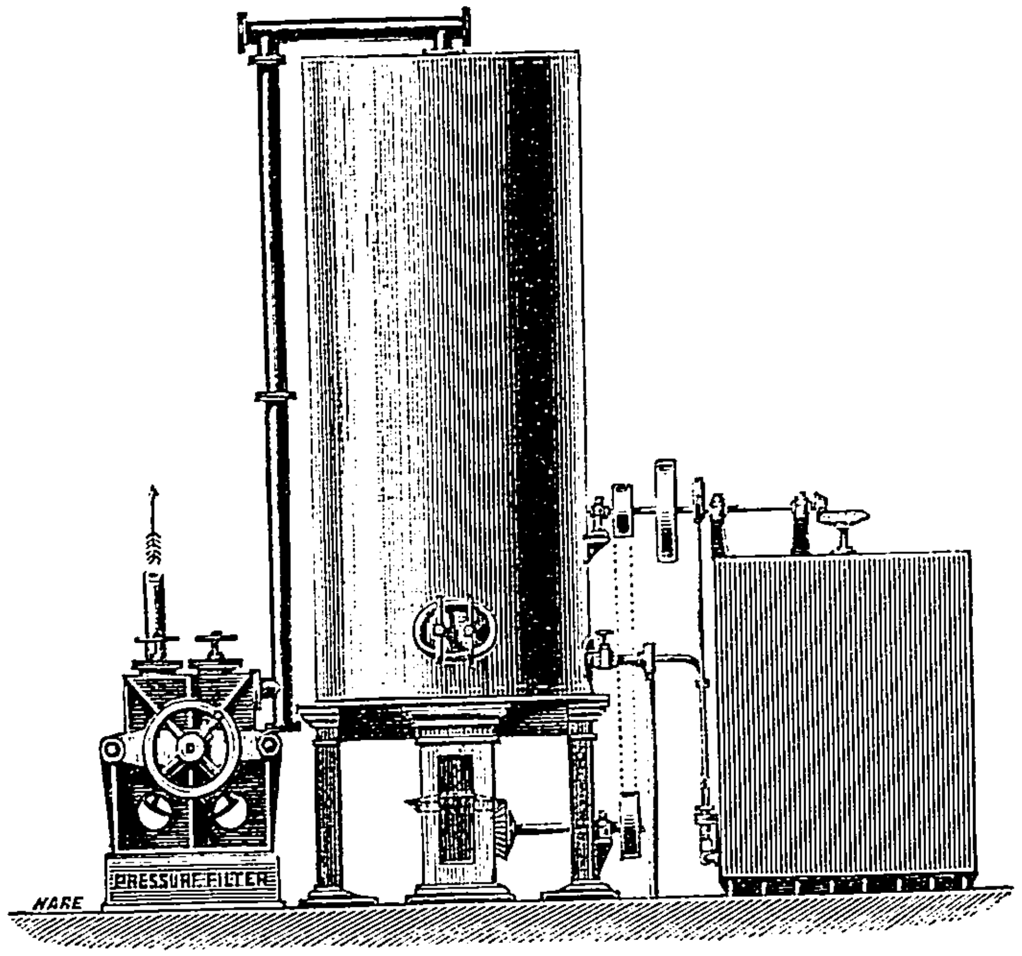

FIG. 40. Porter-Clark Water-softening and Filtering Plant (1,200 gallons per hour).

Fig. 43 is a recent apparatus intended to reduce the cost of cleansing the filters daily. The longer tank consists of a mixing chamber and a filtering compartment. The water passes through a series of pendent filtering mats and cloths into perforated pipes and then into a main pipe connected with a suction-pump.

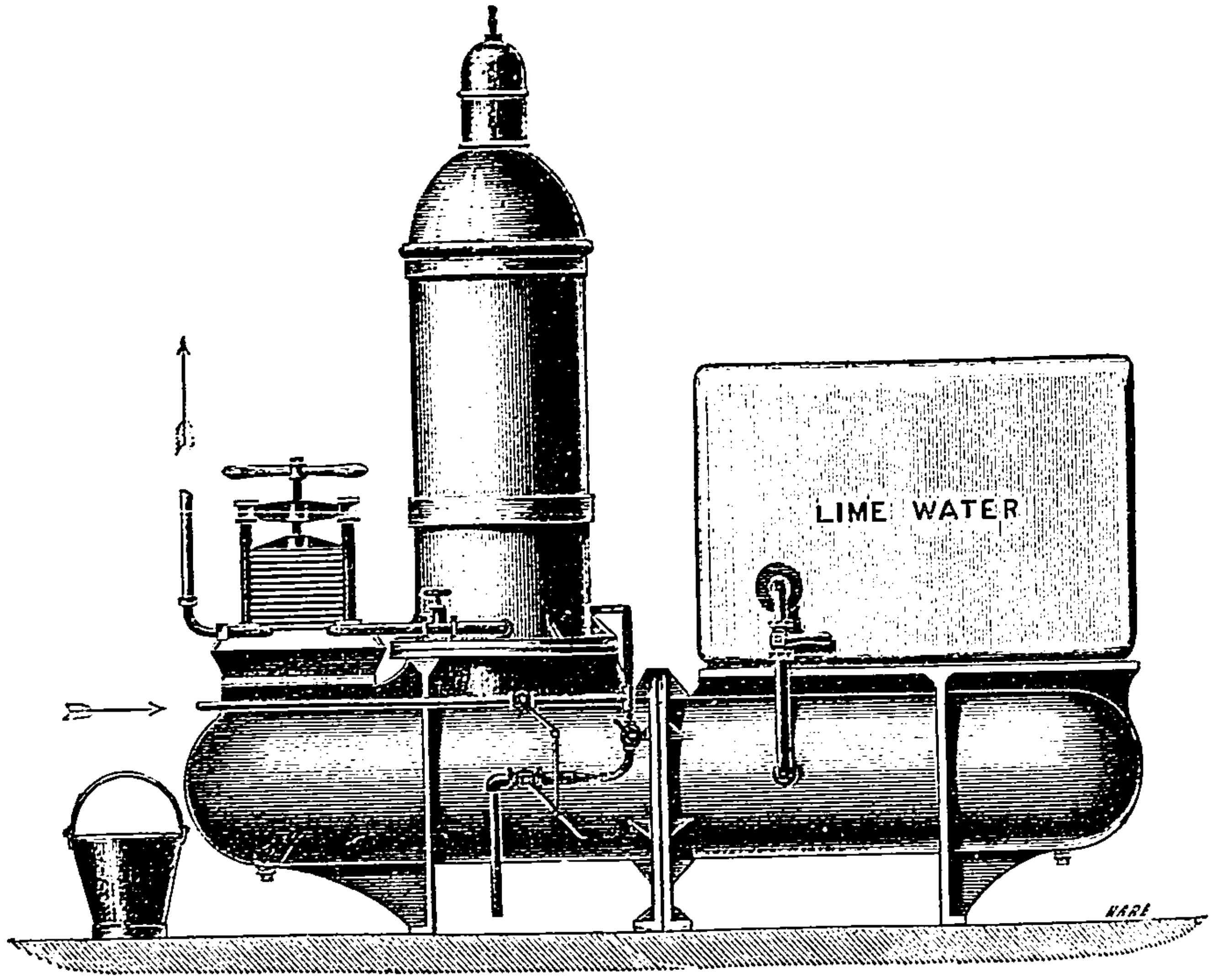

FIG. 41. Porter-Clark Water-softening and Filtering Plant (350 gallons per 12 hours).

Maignen uses a powder called "Anti-calcaire," of lime, carbonate of soda or caustic soda, and alum; the latter on dissolving gives aluminate of soda, which

aids in the precipitation and clarifying. The powder is contained in a vessel over the cistern (Fig. 44), and its delivery is regulated by a kind of water-wheel worked by the incoming stream of water; the wheel also aids in the mixing; the resulting mixture is cleared by a filtering bed placed in a second compartment of the cistern. A constant supply of water is required, and the results are generally good,

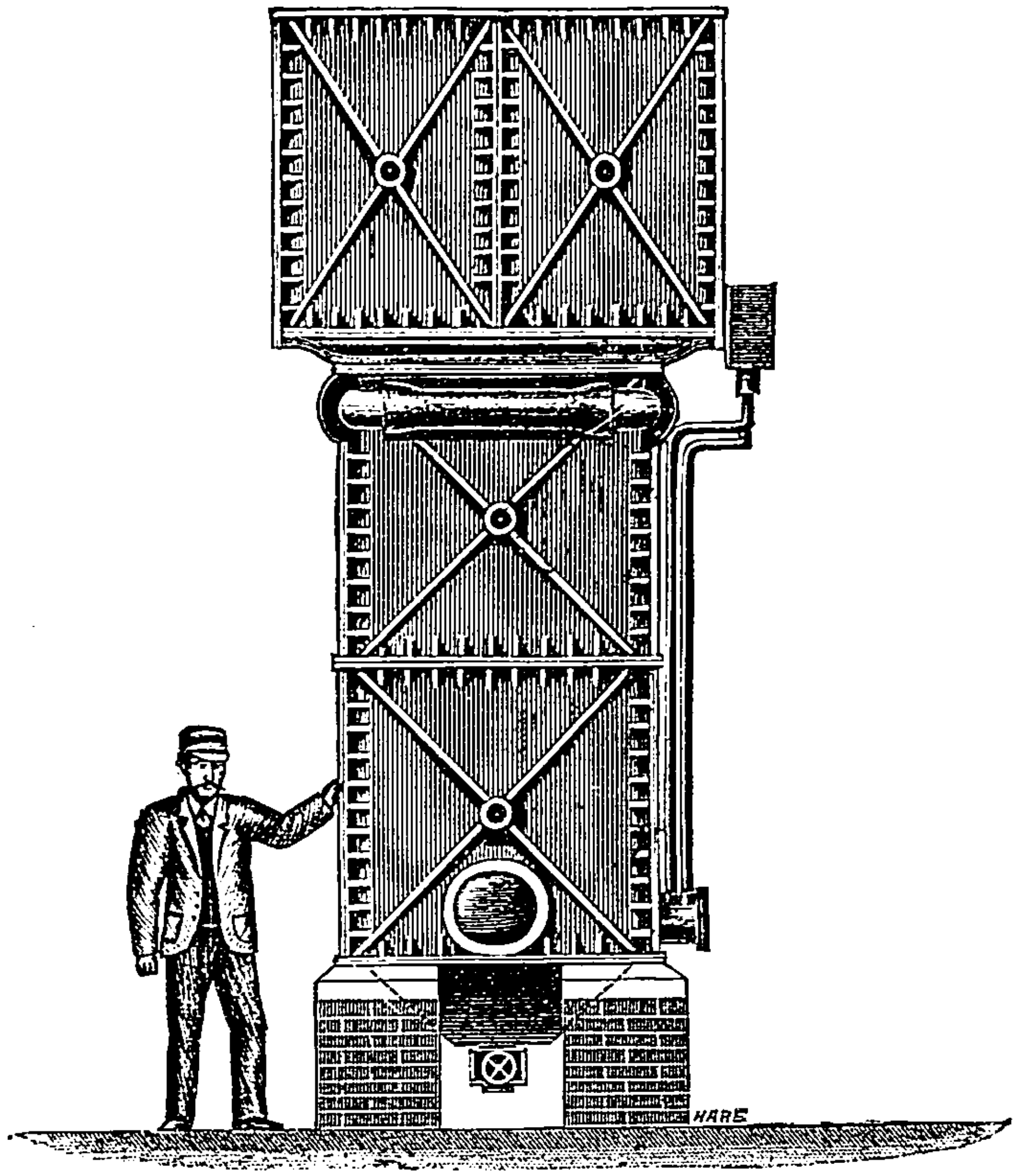

FIG. 42. Porter-Clark Water-softening and Filtering Plant ("Industrial" Purifier).

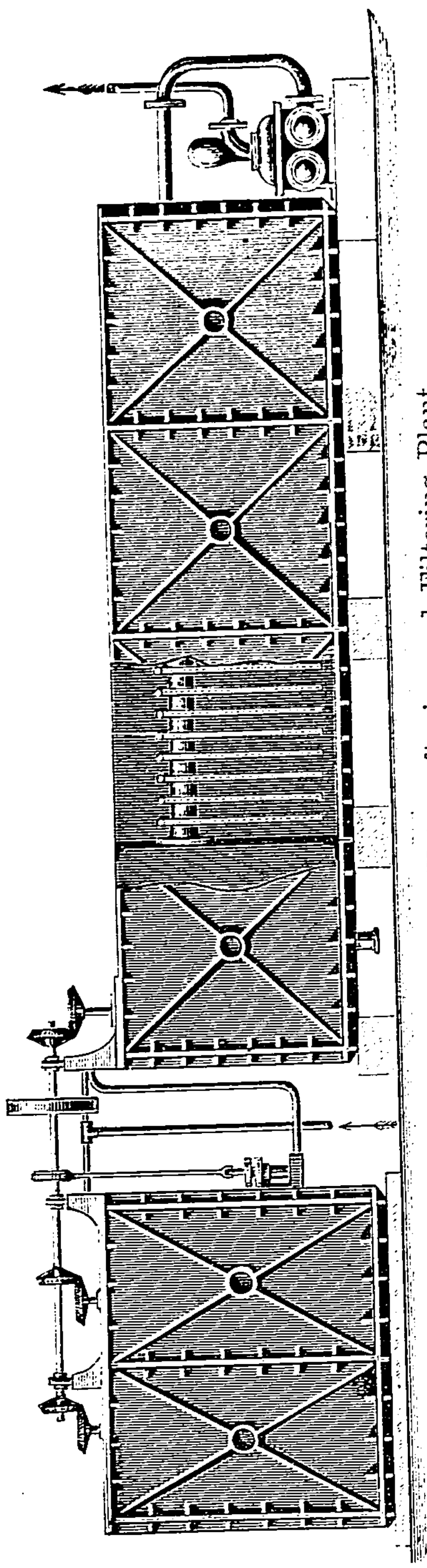

FIG. 43. Porter-Clark Water-softening and Filtering Plant.

but it has been already explained (p. 217) that the lime and soda should be added successively, and not together, for the proper reactions to be obtained.

3. *To remove the precipitate rapidly and completely.*—Settling reservoirs being slow in action and occupying much space, many other devices have been tried.

The Archbutt-Deeley process, as carried out at the Midland Railway Works, Derby, employs two tanks side by side. In one the water is mixed with lime, soda, and sometimes sulphate of alumina, in proportions determined by analysis. The solutions are injected through a rose by means of a steam blower. Since the particles of an old lime precipitate form

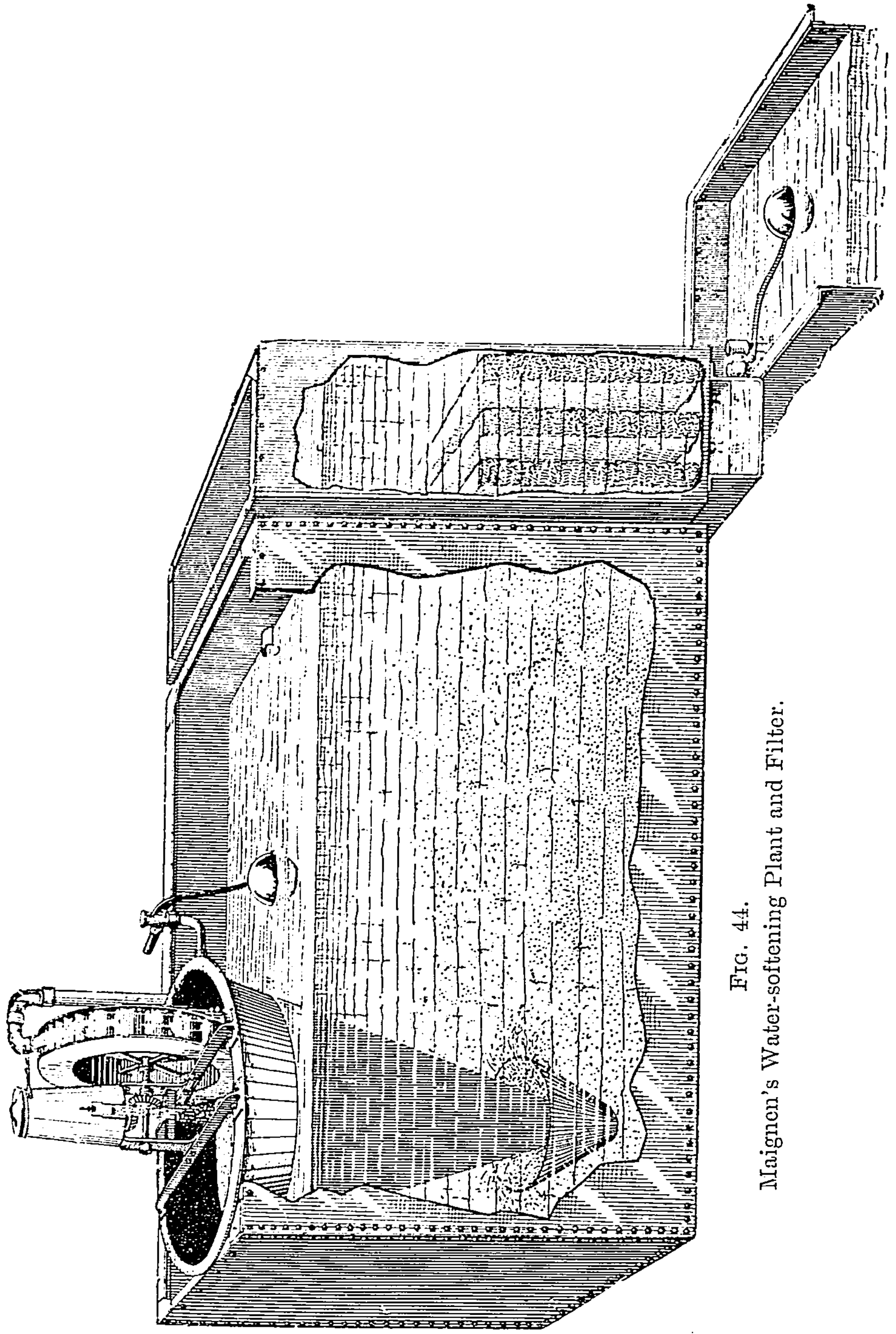

FIG. 44. Maignon's Water-softening Plant and Filter.

nuclei, round which the new deposit aggregates, they are left in the tank to promote the separation. By means of a three-way cock, a blower injects air in bubbles through perforated pipes at the bottom of the tank, stirring up the old precipitate and mixing the two. The settling then takes place rapidly, the water, practically clear, is run off in from half-an-hour to an hour into the second tank. Magnesian waters are apt to deposit hydrate or carbonate of magnesia in the cocks and tubes. To prevent this, the water is re-carbonated after the process by forcing in carbonic acid gas generated by a small coke stove. The method seems in great favour with brewers and steam users.

Atkins's process, as carried out at Southampton waterworks, is mainly distinguished by the form of filter used to finally clean the softened water after settling. The filtering medium consists of an endless band of cotton cloth travelling slowly. It first passes round a perforated horizontal revolving cylinder with a hollow axle, immersed for nearly its whole depth in a cistern containing the liquid to be clarified, so that the water filters inwards, leaving the deposit on the outside of the filter cloth.

More or less of a vacuum is maintained in the cylinder by pumps or by a fall in the outlet pipe, so as to aid the filtration by the pressure of the air. The cleared water passes out through the hollow axle. The cloth as it emerges is passed through a second part of

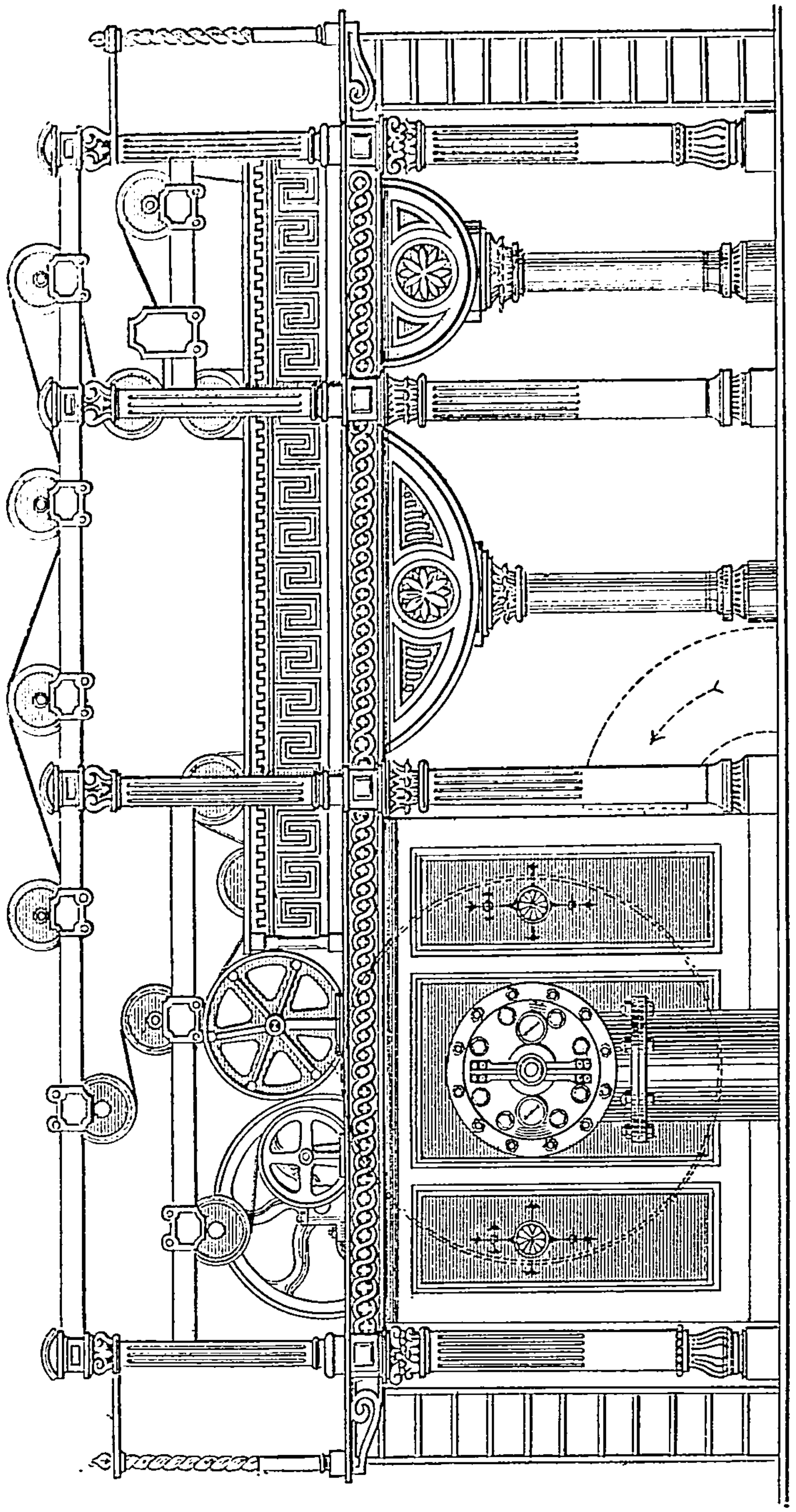

Fig. 45.—Atkins's Water Softener and Filter.

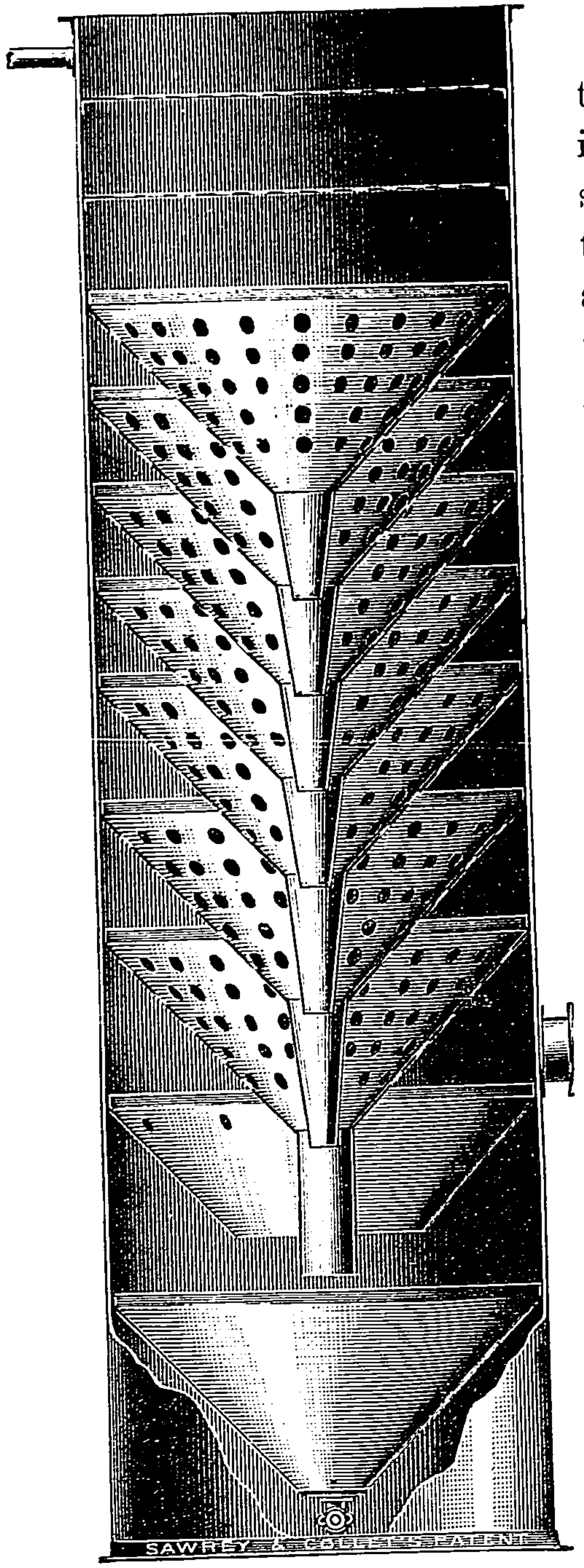

FIG. 46.—The Stanhope Tower.

the machine, where it is rinsed, boiled, steamed, and returned overhead by a series of rollers to the filtering tank. By this ingenious arrangement, the filtration and cleaning is made continuous, and it is claimed that a machine will soften 2,000,000 gallons per diem, at a cost of one farthing per 1,000 gallons (Fig. 45).

The "Stanhope Tower" (Fig. 46) has a series of sloping perforated shelves through which the water, mixed with lime and soda, ascends. In one form these take the shape of a series of funnels, on which the precipitate collects and slides down through a central tube to the base of the tower below, where the water enters. The deposit is drawn off by a sludge cock. The original form was patented by Gaillet and Huet. The towers are made rectangular or cylindrical, in various sizes, and are constructed to soften from 500 to 5,000 gallons per hour, "at a cost of one halfpenny per 1,000 gallons."

Wright's Patent Heater Condenser Company manufacture a form of apparatus (Fig. 47) in which the water is softened under pressure. This is said to be more applicable in cases of towns' supply, large institutions, or mansions, where the water has to be delivered at some distance from the softener, or where the tank is a considerable height above the outlet. A small reagent pump for the lime, or lime and soda, is fitted to the main pumps, so that every time they make a stroke the reagent pump makes one also. The incoming water passes over a small water-wheel working the lime-mixer. The deposition takes place on inclined plates. The filters, of charcoal, or of cloth if the water contains grease or matters that carbon will not arrest, are designed to work under a pressure of eighty pounds to the square inch. They are cleaned by reversing the current. The usual cost of chemicals is stated to be about 1*d.* per 1,000 gallons.

Another form of the apparatus specially intended for boilers combines a heater with the above pressure-softener (Fig. 48). It removes both temporary and permanent hardness down to three degrees, and

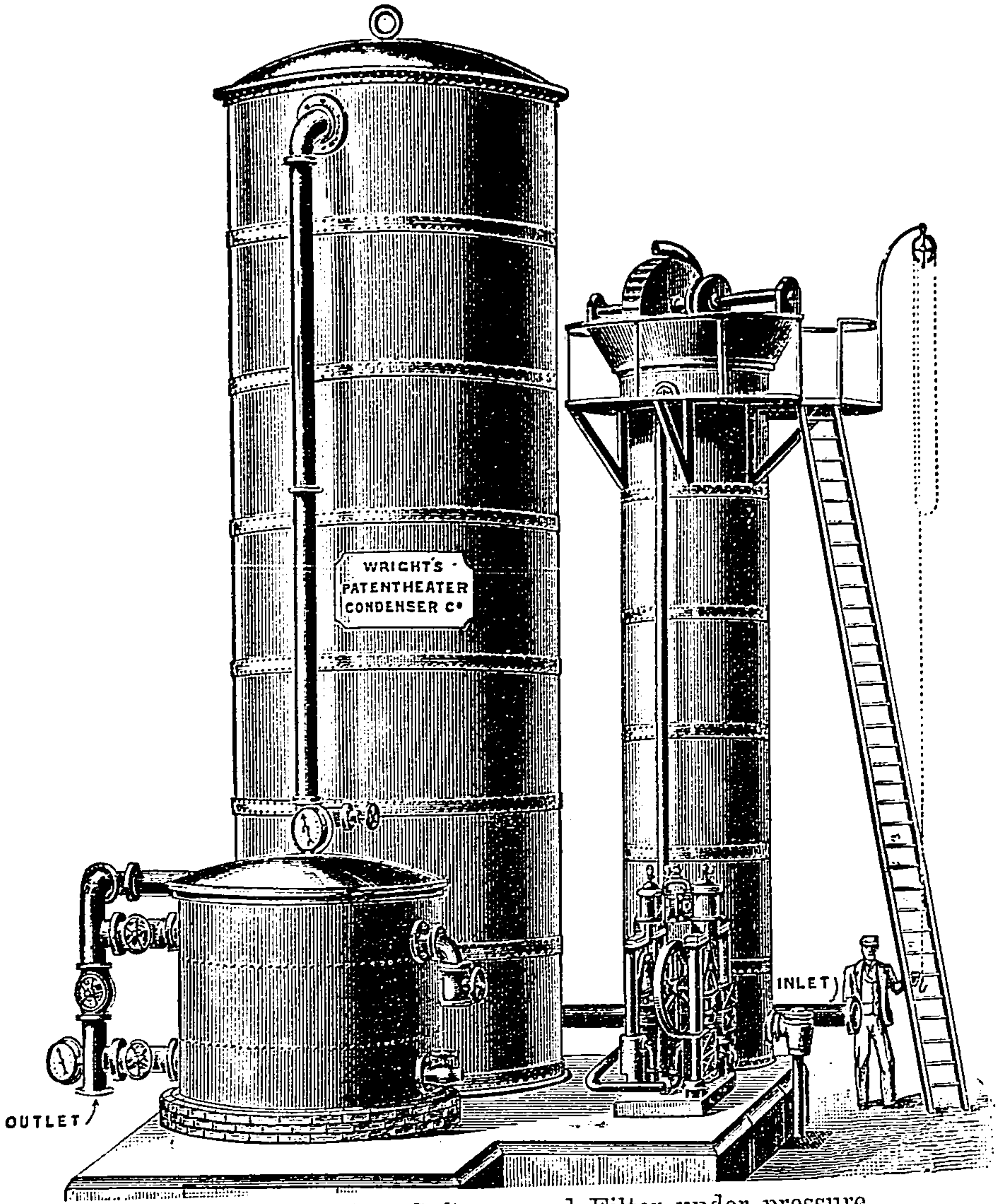

FIG. 47.—Wright's Softener and Filter under pressure.

raises the temperature to 210° F. before entering the boiler.

As to the economy of softening there can be no doubt. It is estimated that "a farthing's worth of lime saves about 30*s*. worth of soap." On the small

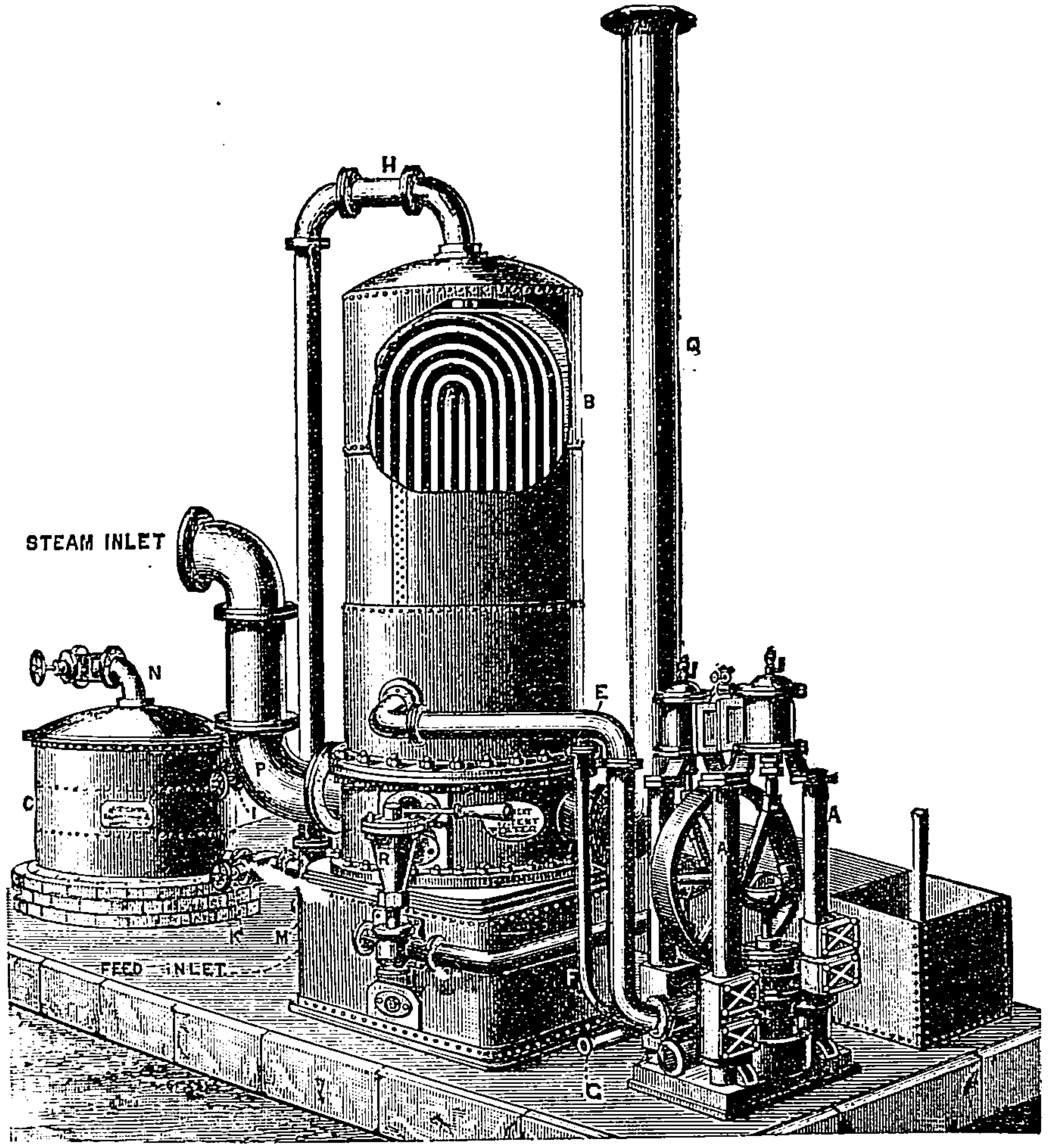

FIG. 48—Wright's Combined Softener and Heater

scale this would be about 1*d*. per 1,000 gallons under favourable conditions. Frankland considered that a town supply could be softened for £1 per 1,000,000 gallons.

Some analyses by the author, given in a report by Mr. Aldwinkle, the architect to the Metropolitan Asylums Board, February 6th, 1896, show the practical results obtained by some of these processes :—

Process.	Place.	Hardnesses in grains per gallon after softening. Total.	Tempy.	Permt.
1. Porter-Clark	Brookwood Asylum	3·1	0·7	2·4
2. Ditto	North London Railway Works, Bow	11·3	2·45	8·85
3. Atkins-Clark	Lambeth Workhouse	6·35	5·7	0·65
4. Ditto	Darenth Asylum	8·3	6·15	2·15
5. Archbutt-Deeley	McMurray's Paper-mills, Wandsworth	6·2	2·4	3·8

This table shows, as has been already explained, that lime effects almost a complete softening of a water like No. 1, which owes its hardness to calcium bicarbonate; whereas with No. 2, a magnesian water (this water had the original composition, total hardness, 16·4; permanent hardness, 10·8), little improvement is effected.

The same report gives interesting information as to the cost of the three processes, as applied to the special conditions at the Brook Hospital.

Hard waters, as a rule, are furnished by the following formations: Calcareous strata of Silurian, Devonian, and Coal Measures, Mountain Limestone, Lias, Oolites, Upper Greensand, Chalk.

Soft waters, by Igneous, Metamorphic, non-calcareous Cambrian, Silurian, Devonian, and Coal Measures, Lower Greensand, London and Oxford Clay, Bagshot Beds (hardness one to nine, average four), and non-calcareous gravel. Water from Gault Clay varies very much: some of it is soft and pure, some "of fair quality," hardness nine to eleven degrees; in Bedfordshire it often contains much lime and iron, derived from pyrites and coprolites. Lower Greensand and shale waters are frequently very ochreous. Water from Oxford and Kimmeridge Clays contains much vegetable matter, and is sometimes bituminous; other clays often include much sulphate of lime, and give waters of high permanent hardness. The New Red Sandstone waters are generally briny and quite unfit for drinking, besides containing much sulphate of lime and magnesian salts. Magnesian limestone also yields usually a bad supply.

A detailed description of the strata in their relation to waters will be found in the Appendix.