

solutions that occur in the western states. Its action upon cement is such as would bring about the effects that have been noted at numerous points in the West, as well as those noted in some instances where wharves breakwaters, etc., have been destroyed by the action of sea water. The commonly held opinion that the magnesium sulphate in the sea water is most active in causing this destruction is confirmed by our data on the treatment with the single salts, which show that both magnesium ions and sulphate ions are capable of causing such disruption.

RECAPITULATION.

When set cement is leached with solutions of certain salts, the salts react with the calcium hydroxide of the cement, forming the corresponding hydroxides and calcium salts.

In the cases of the salts studied, sodium sulphate, sodium carbonate, magnesium sulphate, the calcium salts formed are insoluble, and therefore remain in the cement where they are formed. This is also the case with the magnesium hydroxide formed, but not with the sodium hydroxide, which is soluble, and therefore remains in the solution obtained as a filtrate.

The solid matter remaining in the cement is greater in weight and in space required than the calcium hydroxide which it displaces. The increased space necessary is only obtained by forcing apart the cement particles, thus breaking their hold upon each other, and cracking or weakening the cement.

The action of the sea water, a mixture of salts in solution, is such as would be expected from the action of the separate salts studied.

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BOILER WATER PURIFICATION.

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The purpose of this paper is to sketch the development of boiler water purification from a purely thermal process to a highly organized chemical system and in addition to give an idea of conditions actually met in various plants.

To aid us in this discussion I have made use of tabulations which will be referred to as Tables I, II, III and IV.

BOILER WATERS.

For convenience I have classified boiler water purifiers according to Table I and types of water according to Table II. Waters of the first group (Table II) are exceptionally soft and, unless all of the hardness is due to sulphate of lime, can be used in the plant with thermal treatment only. The precipitated carbonates and organic matter are blown out of the boiler at intervals.

Waters of the second group (Table II) can be used in boilers only under exceptional conditions without the use of some apparatus or chemical to disorganize their scaling properties. If the entire hardness were due to sulphates a live steam heater or chemical

purifier would at least be needed; a chemical softening plant would be better.

Saline waters, third group (Table II), are so called because of a preponderance of the chlorides of the alkalis and alkaline earths. As nearly all of our waters contain chlorides the minimum amount of such compounds necessary to place a water in this class is arbitrarily fixed at 170 parts per million or about 10 grains per U. S. gallon. Unless the chlorides are present in considerable quantity they are not difficult to handle in boilers.

TABLE I.—BOILER WATER PURIFICATION.

<i>Synopsis.</i>	
1. General—	Relating to the quality of water.
2. Scaling—	Corrosion, priming, foaming.
3. Mechanical Filtration.	
	1. Clear water basin; bars.
	2. Screens.
	3. Settling tanks in duplicate.
	4. Filters { Sand. Coke. Wood. Hot well. Open heater. Closed heater, pressure. { a tubes. b drips.
4. Thermal.	External Live steam heater. External sand filters. Economizers. Fire box heater. Mud drum. Internal Internal heater. Skimmer, dome-funnel.
5. Thermo-Physical.	Internal boiler purgers, coal dust, sawdust, kerosene, starch.
6. Thermo-Chemical, soda.	(a) Harrison. (b) Bonnell.
	Electro-Chemical, zinc-balls, aluminum.
8. Chemical—	Internal, boiler compounds.
9. Chemical—	External. (a) Intermittent. (b) Continuous. (c) Intermittent and continuous.
10. Specific Instances.	

TABLE II.—BOILER WATERS CLASSIFIED ACCORDING TO QUANTITY OF SCALE-FORMING SOLIDS.

Soft—To 50 parts per million.

- (a) Rain or snow.
- (b) Water from granite or quartz rock regions.
- (c) Returned water.
- (d) Swamps.
- (e) Lakes.
- (f) Large rivers.

Hard—Above 85 parts per million.

- (a) Springs.
- (b) Lakes.
- (c) Small rivers and creeks.
- (d) Wells.

Saline—Containing above 170 parts per million chlorides, of Ca, Mg, Na or K.

- (a) Sea.
- (b) Wells.
- (c) Mineral springs.

Alkaline—Carbonates or bicarbonates of the alkalis.

- (a) Western plains.
- (b) Springs.

Acid—Containing any strong mineral acid.

TABLE III.—BOILER WATER TREATMENT.

To 50 Parts per Million—Thermal.

From 50–170 Parts per Million:

1. Heaters.
2. Lime.
3. Soda, hot or cold.
4. Caustic soda.
5. Phosphate of soda.

From 170-250 Parts per Million:

1. Soda and heat.
2. Lime and soda ash.
3. Caustic soda and soda ash.

From 250-340 Parts per Million:

1. Soda and heat.
2. Lime and soda.

From 340-680 Parts per Million:

1. Heat and soda.
2. Lime and soda.

From 680-1020 Parts per Million:

1. Lime and soda.
2. Barium compounds.

From 1020-5100 Parts per Million:

1. Lime and soda.
2. Barium compounds.

Few eastern waters are alkaline to phenolphthalein before boiling (fourth group Table II). Those west of the Mississippi river often contain carbonates and bicarbonates of the alkalies with sulphate and chloride of soda. The treatment of such waters is very difficult.

Natural waters seldom have an acid reaction (fifth group Table II) due to the presence of a strong mineral acid. The water from coal mines may, however, carry sulphuric acid, and waters from springs are sometimes charged with hydrogen sulphide.

All waters contain carbon dioxide, sometimes in considerable quantity, and I believe that this is the basis of many boiler troubles.

Any natural water may contain organic matter, gases, suspended solids and dissolved minerals. We are not able to discuss the boiler reactions of any of these but the latter. Much study must be put on the others. Nor are we very sure of the action of dissolved minerals under the intricate processes of steam production. Their removal is an accomplished fact. The apparatus devised for such removal will now occupy our attention.

BOILER WATERS.

Steam waters are seldom free from suspended solids those from deep wells being the exception. Running streams carry sand, clay decomposing vegetable matter sewage and trade wastes. This is particularly true of rivers upon the banks of which our larger industries are found. Waters of this character, subject to rapid changes, should generally be led into settling basins (Fig. 1) or at least strained before passing to the pump. The simplest method of treatment is a wing dam (Fig. 2) placed nearly across the forebay in such a way that the intake water is drawn from a quiet pool at medium depth. Floating matter including grease and water plants is eliminated. Even with such precautions a screen is required (Fig. 3). This may be of copper or bronze and is furnished in many shapes—conical, cylindrical, or plain, set in a series of frames. These screens should remove the grosser suspended matter. The finer the mesh the better, consistent with working conditions provided the plant is running condensing.

If the water contains oil, a sand, coke or wood-fiber filter (Fig. 4) will be advantageous. I have found a 36-inch sand filter very useful in the removal of the sludge of wool-washing machines.

Considerable sewage and organic matter can be taken out with coke which should be broken to a coarse powder. Some engineers think coke softens water, chemists know differently.

Assuming that the water has passed the pumps reasonably clean which should always be the case, we usually find the closed heater (Fig. 5) next in line.

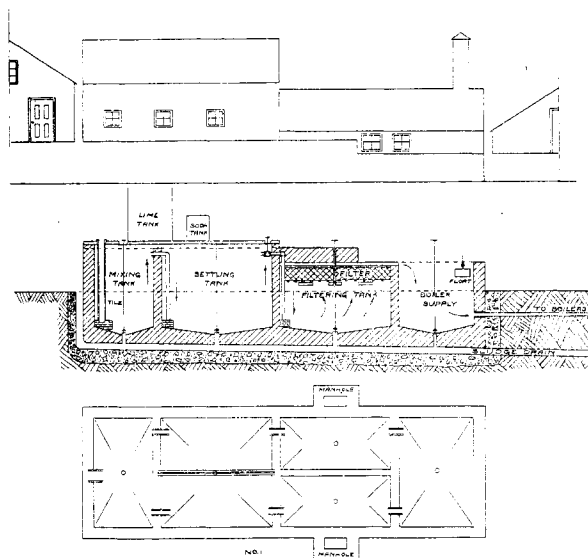


Fig. 1.

With steam on one side and raw cold water on the other the bicarbonates of calcium and magnesium are partially decomposed. Depending upon the speed with which the water is driven through the heater tubes, and the amount of heat supplied by the condensing steam the separated monocarbonates either lodge where they are set free or are driven into the

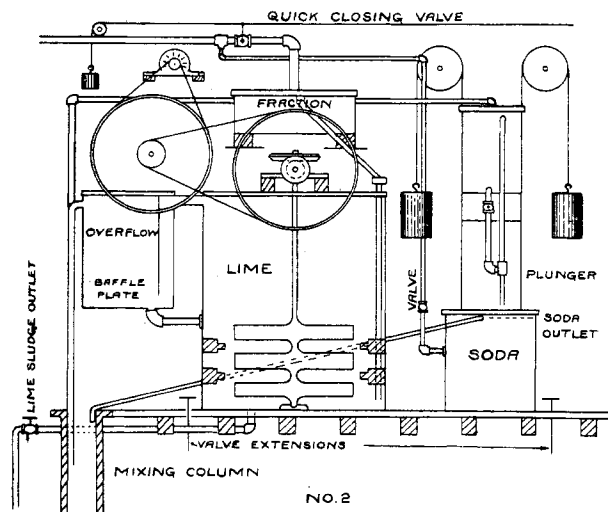


Fig. 2.

boiler, the reaction being continuous from the moment heat is applied. I often find the tubes of such apparatus and the boiler supply pipe filled with scale to a point where the water will scarcely pass. Such suspended matter as enters the boiler circulates with the water for a time and finally deposits or is blown out as sludge.

FIG. 1

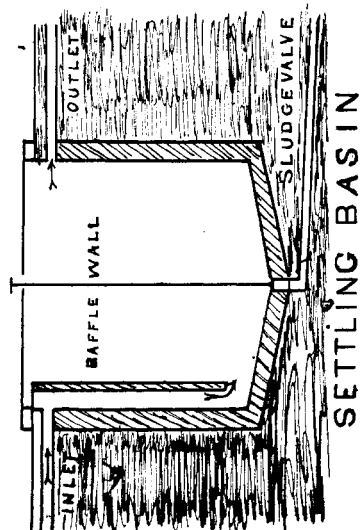


FIG. 4

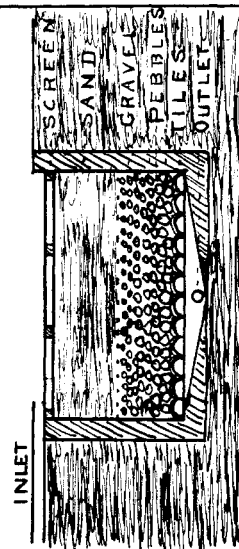


FIG. 2

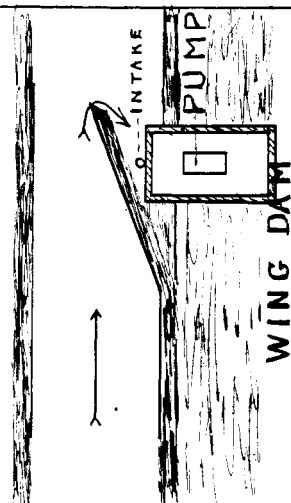


FIG. 5

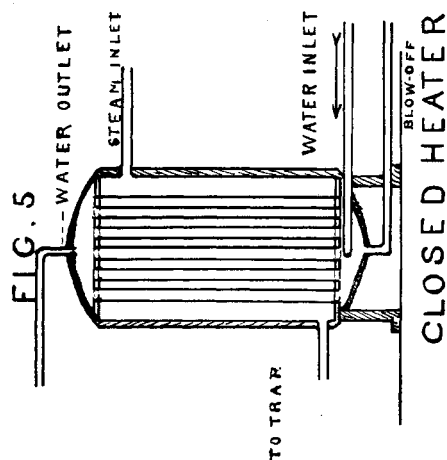


FIG. 3

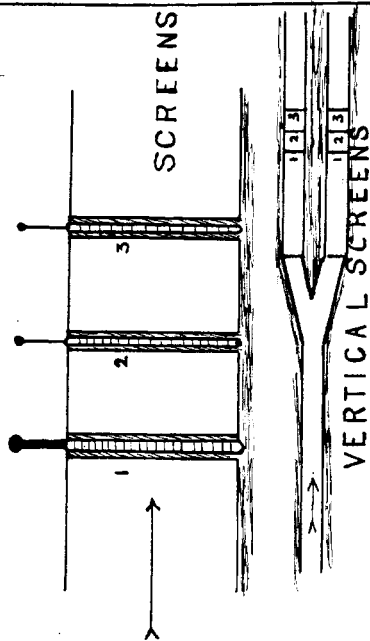
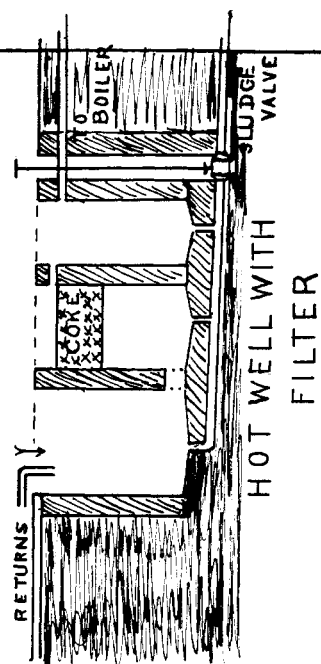
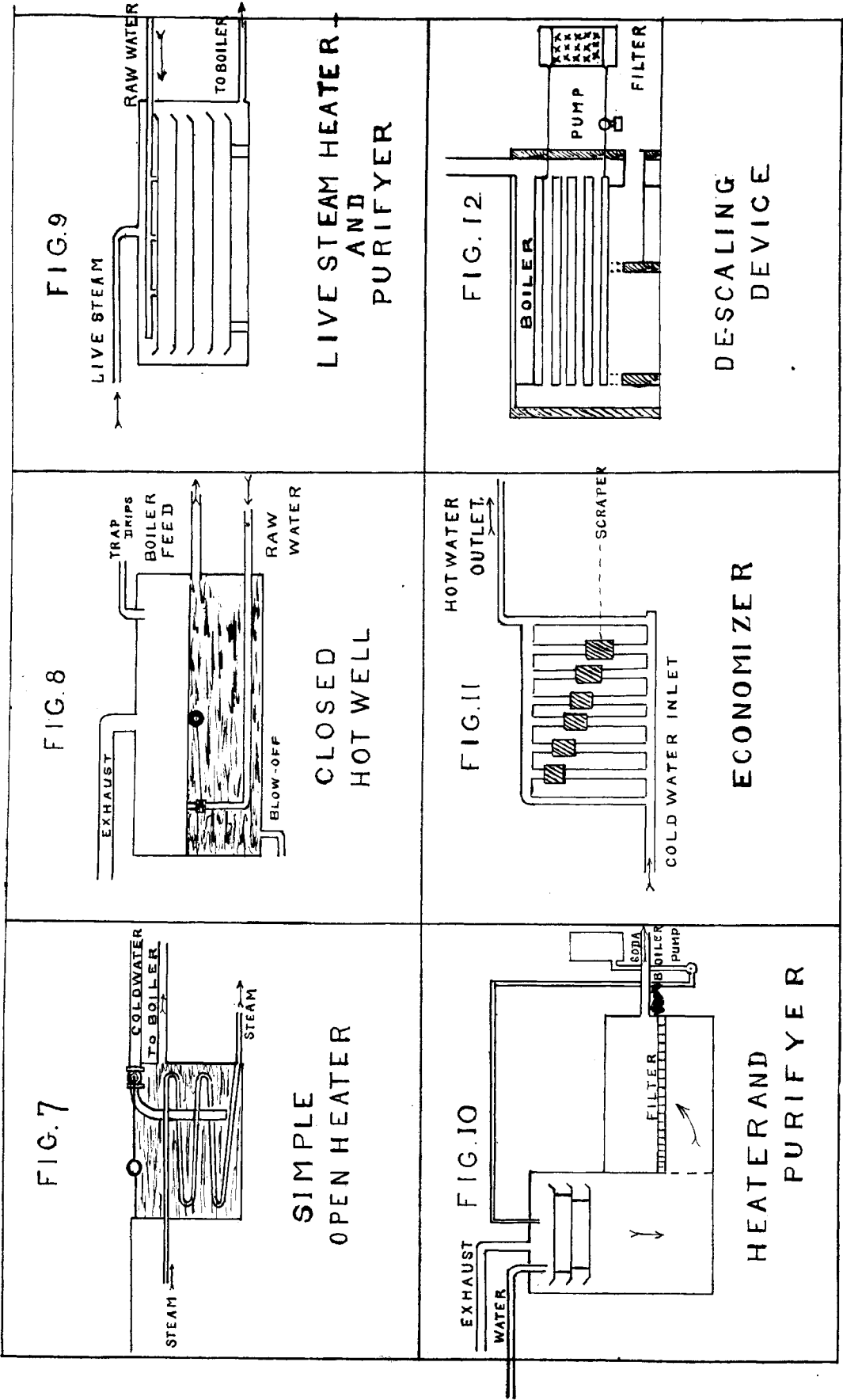


FIG. 6





The closed heater is a thermal purifier of uncertain action and its efficiency may approach zero when the tubes are scaled on one side and fouled with oil on the other.

I sometimes find hot wells (Fig. 6), some at atmospheric, others under steam pressure. In either instance raw water exhaust steam and return drips from the pumps and heating system are mixed. The thermal purification is begun at this point by a partial decomposition of carbonates.

In one instance the exhaust steam from several engines passes through two-inch tubes around which the raw boiler water flows on its way to the pump (see figure). These tubes collect scale rapidly in the hard water used.

The *live* steam purifiers (Fig. 9) take advantage of the insolubility of carbonates and gypsum at boiler pressures. Generally cylindrical in form this apparatus admits steam below or at the side of and water above removable trays. The scale separates from the thin layer of heated liquid. Periodically the trays are removed and cleaned.

In order that a live steam heater may be sufficient the temperature must be high, the circulation excellent and not too rapid. We have found 50 per cent. of the sulphates and 75 per cent. of the carbonates of hard water removed by this method.

An ingenious purifying apparatus (Fig. 12) consists of a sand filter connected with the boiler under pressure and through which the water is constantly pumped. Suspended matter is filtered out.

The economizer (Fig. 11) is one of our best efficient descalers as the temperature is often as high as 300° F. Such apparatus is really an auxiliary boiler.

Various devices have been gotten up to purify water by passing it through or at the side of the fire-box or bridge wall before entering the boiler. The difficulty with all classes of closed heating and descaling devices is their lack of cleaning facilities. Such heaters need as much scraping inside as the tubes of economizers.

The mud drum of the water tube boiler answers a double purpose—the collection and removal of precipitated calcium and magnesium compounds and of mud. If for no other reason, the water tube type boiler has large advantage over others due to this construction.

Still another type of thermal purifiers is placed in the boiler itself. One of the simplest of these is a cylinder about 10 inches in diameter running the length of, and immediately above, the flues. Raw water is admitted at one end and traverses the heated tube under boiler pressure and is delivered at the opposite end where it spreads out at the upper water level. This is useful in very hard water sections. This tube is cleaned by a steam jet daily.

Finally internal water purification is assisted by revolving or rocking buckets that scoop up the separated sludge.

Many practical men use coal dust, sawdust or starch-bearing vegetables in boilers. Potatoes have been used extensively. In any such instance an attempt is

made to furnish artificial centers of attraction for the depositing scale or to include colloidal materials that will prevent the formation of dense deposits. Logwood, chestnut and oak sawdust have answered the purpose sought.

Regarding the action of kerosene we have no theory. It is used in large plants very successfully. The liquid is added to the water, drop by drop, before entering the pump.

We now take up the sixth group—a class of apparatus depending upon heat to separate carbonates and upon soda ash to eliminate gypsum. One of the best known purifiers of this type consists of a hot well, soda supply tank and filter. Returned steam and water, soda and raw water enter the apparatus at the top. Trays are here provided to thoroughly mix the water and steam. Carbon dioxide gas at once separates the carbonates and sulphites precipitate, and all fall into the settling chamber, spreading laterally under a cloth filter. About one-half hour after the raw water enters the apparatus it passes to the boiler. The soda solution is pumped by a small piston attached to the boiler feed pump and is therefore positive in its action.

Very large installations have been introduced with success.

Similar to this is the soda-grits purifier. Caustic soda or soda ash or both are pumped into a raw water line leading to a hot well under pressure. From here the water is drawn through a quartz filter of coarse mesh. Once a day the water is by-passed while the filter flow is reversed and the filters cleaned.

In the case of soda ash heat treatment the water must be at a minimum temperature of from 176–185° F., preferably 190–200° F.

ELECTROCHEMICAL TREATMENT.

Several years ago a concern leased a lantern-shaped basket of white metal balls to be used in boilers to prevent the formation of scale. Shortly after these appeared I analyzed one of the balls and found it to contain 40 per cent. zinc, with lead, copper, tin, antimony and bismuth. Not long afterward a patent was granted on this combination of metals.

A great many installations were made under guarantee to prevent the formation of scale. After several months a mushy shapeless mass with a small nucleus of metal would be found in place of the ball.

Recently one of the owners of this process discussed their experience with me. He stated that balls of certain composition could be applied only to peculiar kinds and types of water and that others of different metals would have no action.

A still more remarkable claim is that one set of balls will act for a few months. Disintegration of the metal then ceases and another set of different composition must be used.

The whole experiment proved very interesting but as far as I know no definite scientific facts have been accumulated.

CHEMICAL TREATMENT—INTERNAL.

When scale begins to collect in a boiler the engineer

employs a "boiler compound" so called. This is a generic term applied to any material added to water just before it enters the boiler or added to the boiler itself after cleaning and washing out. These compounds are found on the market both in a liquid and solid state. The methods employed in their sale by unscrupulous manufacturers have brought the business into disrepute. Such compounds have usually been gotten up by unscientific men who have been at their wits' end to prevent the formation of scale in the boilers under their charge. In many instances some by- or wasteproduct of the plant itself has been found to possess anti-scaling properties.

This is illustrated by the use of spent tan liquor which will, when added to boiler water even in small quantities, rot and honeycomb scale that has formed and will prevent the accumulation of new deposits. This is also true of sugar and starch wastes.

The boiler feed-water in isolated sawmills in the woods often proves to be absolutely free from scale-forming constituents. Many patents have been issued for these practical recipes and scientific men have investigated the materials and have found that anti-scaling properties are due to the presence of two or three fundamental bodies.

The first of these is tannic acid which is a constituent of many barks and is found in quantity in oak, hemlock, quebracho, catechu, logwood and sumach. The boiler compound vender who tells you that he has a purely vegetable material imported from China, India or Africa usually employs the bark or wood in a finely powdered state or the extract. Experiments have been made under widely differing circumstances proving conclusively that free tannic acid attacks iron. The barks and woods that are used contain this principle in the form of a glucoside less active. Tannate of soda is still less corrosive.

The second group of boiler compounds depends for its active properties upon caustic soda, soda ash or sesquicarbonate of soda. Sometimes we have found hydrate or carbonate of potash. The use of this class of materials is the result of long experience in the manufacture of soda and alkalies generally. Unless highly concentrated and under very high pressure these alkalies preserve metal instead of destroying it.

The history of the caustic soda industry shows that this compound was originally concentrated in ordinary steam boiler shells and that more difficulty was experienced in the caking of the concentrated salt about the stay-bolts and tubes than from any corrosive action.

One of the most amusing circumstances in connection with the use of these compounds is the steady and persistent objection of the engineers of many plants to the use of soda ash or caustic soda but they will use compounds, the basis of which is one of these materials.

Another class of really efficient boiler compounds includes phosphate of soda which has active softening properties both when applied to old scale and that newly formed; further a large class of special chemicals

has been found to have an active effect in connection with the removal or prevention of scale. Their expense often precludes their use.

The patent office reports present an interesting record of the progress of this rule-of-thumb business to an interesting, scientific and accurate apportioning of chemicals to a boiler water, the result of analytical data and experience, and I am often surprised at the variety of chemical materials pressed into the service for this purpose. More recently barium aluminate has been applied.

The only bar to the use of impossible and injurious combinations is the boiler inspector whose business it is to inquire carefully into the history of any solid or liquid used in a boiler. One of the most interesting compounds that has come to my attention is permutite. This is a sodium zeolite which removes carbonates and sulphates of lime, magnesium and iron. It may be revived by common salt and used again and again. We understand it is used outside the boiler as a filter and purifier.

CHEMICAL TREATMENT—EXTERNAL.

The chemist is now able to predict with considerable accuracy the kind of treatment that a water demands to make it available for power plant use. His formulas are, however, of but little value in a written report to the engineer. They are usually placed on file or unfavorably discussed in connection with similar communications that were received the year before.

Every power plant necessarily becomes a separate study as far as its water problems are concerned and it is to the advantage of all interested parties to have a running record month by month of the quality of the water received, whether it be from well, lake, river or city supply. Such data become of the greatest value when an important question relating to scaling, corrosion or fouling of tubes occurs.

The writer has a water-softening plant in operation where the source of supply is a creek. Sometimes this water is red on account of aniline dyes; at other times it carries iron salts from pickling vats. In one particular instance the odor from the plant became intolerable and it was found that seepage from a pea-vine silo was contaminating the supply. In every instance a change in the water was accompanied by an inquiry from the owner as to the reason.

Other instances might be cited substantiating the claim that I have made—that a full history of the water should always be available.

If the quality of water supplied to a plant is such that it cannot be used in boilers without chemical treatment the study should be taken up further and the total cost of plant operation in excess of that required were the water not purified made the subject of investigation. Cost of coal, gaskets, boiler tubes, washing out, power-hammers, loss of service of boiler, interest on the investment should be taken into account, and if a softening plant can be installed and the initial expense, cost of labor and materials are less than in the first instance a purifying plant certainly becomes a profitable investment.

The character of the water will largely determine

the kind of purification plant to be used. There are waters which can be taken care of splendidly with soda ash and filtration. These are high in gypsum and may contain some carbonates. Waters that contain 30 or 40 grains of carbonates per gallon can be treated inexpensively, accurately and successfully with lime.

Waters containing carbonates and sulphates require both a lime and soda ash treatment. To proportion these to the water, changing as it may from hour to hour, is a very difficult matter and only by using very large reservoirs and accurate measuring devices can an average treatment be applied. There are several excellent systems in the market.

There are waters that are saturated with gypsum or nearly so. I have found from 95-106 grains per gallon in five deep wells in or near Syracuse, N. Y. Such water cannot ordinarily be used for boiler purposes by any method of soda-lime softening. Please do not understand that it is impossible to remove the calcium and magnesium salts from this water: it can be done accurately and successfully in the cold to a point representing the limit of solubility of hydrate of magnesium and carbonate of calcium. But such water shows a constant tendency to foam so that it is unsafe to use the steam generated in an engine. However, one of my clients has successfully operated for four years a boiler in a limestone quarry where the water contains 93 grams of gypsum per gallon. Foaming is unknown.

FOAMING.

Water containing oil, a large amount of sulphate of soda or salt is often hard to handle in the boiler. It rolls and bounds and frightens the fireman. It may cause great damage to the engines. If returned oil has accumulated and made the water troublesome it should be removed and a good separator installed. If a separator is already in place it should be cleaned. Mineral salts are usually concentrated in the boiler many fold. At a certain stage of this accumulation the water will foam. The lime soda process ex-

changes sulphate of soda for sulphate of lime. This should be blown out at regular intervals. There is no reason why it should be allowed to accumulate in the boiler.

A complete and careful analysis of a sample of water from the boiler will usually indicate the cause of foaming and the remedy is easily applied. On the other hand incorrectly arranged feed pipes may lead to this difficulty, or the fireman himself may be entirely to blame for it has been said that a poor fireman can foam any boiler.

CORROSION.

Even though water does not scale boiler tubes it may corrode the metal, in which case it is much more dangerous than scale. Immediate action should be taken to locate the cause and provide a remedy. It is safe under such circumstances to make the feed water slightly alkaline with caustic soda or soda ash. I have received a sample of boiler sludge containing when dried out 60 per cent. oxide of iron, due to acid water in the boilers.

A manufacturer at Buffalo, N. Y., uses well water that is saturated with hydrogen sulphide. This is used for cooling purposes. It is piped about the plant in lead tubes and has so badly corroded a 12-in. I beam that this will have to be replaced. The cooling system fed by this water requires new piping annually. It is unnecessary to say that such a supply should never be used in any power plant. Many expensive and deep wells would become available if there were a simple and inexpensive method of removing sulphuretted hydrogen.

One of the most severe cases of corrosion brought to my attention was not cured by 10 pounds of zinc slabs per week but was stopped by blowing down the boilers often. The excessive use of tannin compounds in a horizontal return tubular boiler apparently resulted in a large number of pin-holes in the tubes. The accumulated scale was coal-black.

In one instance I have found severe corrosion of metal where the water is high in gypsum, low in

TABLE IV.—SHOWING METHODS OF PURIFYING BOILER WATERS IN TYPICAL NEW YORK STATE PLANTS.

H. P.	Total hardness.		Heater.	Type of boiler.	Method of purification.
	Temp.	Perm.			
125	1	4	Closed	Return tubular	Compounds
250	1	4	Closed, hot well	Water tube	Soda ash
2000	1	4	Closed	Return tubular	Soda ash
300	1	4	None	Return tubular	Boiler compounds
250	7	1	Closed	Return tubular	Caustic soda
4000	7	1	Closed	Water tube	No treatment
100	2	8	Closed	Return tubular	Soda ash
100	9	1	Closed	Return tubular	Caustic soda
600	6	8	Closed	Return tubular	Caustic soda
1000	4	10	Pressure hot well	Return tubular	Lime-soda plant
3150	7	8	Closed	Water tube	Turbine returns
500	15	..	Closed	Return tubular	Boiler compounds
600	15	..	Closed	Water tube	Boiler compounds
600	15	..	Closed	Water tube	Caustic soda
300	4	12	Closed	Return tubular	Soda and filter
4000	3	14	Closed	Water tube tubular	Soda and sand filter
4000	5	17	Closed	Water tube	Lime-soda plant
4000	5	17	Closed	Return tubular	Lime-soda "
200	11	15	Closed	Return tubular	Lime-soda "
2000	11	15	Closed	Return tubular	Lime-soda "
600	11	15	Closed	Return tubular	Tannates
100	5	80	Closed	Return tubular	Soda ash outside the boiler

organic matter and containing no chloride of calcium or magnesium.

This subject requires a large amount of scientific study.

SUMMARY.

Water containing not more than 3 grains of sulphates and carbonates per gallon can usually be treated by heat alone.

Waters of medium hardness may be treated within or without the boiler, preferably without. Very hard water requires chemical treatment in a well designed softening plant. Some waters cannot be treated economically and are useless for boiler purposes.

The returned water from a plant is soft and free from mineral matter. If oil is present it should be removed and the water used as many times as possible. If it corrodes the boiler one or more grains of alkali per gallon may prevent this action.

Condensed water from steam turbines and surface condensers is oil-free. This is an argument in favor of their use.

Lime is ideal as a water-purifying agent as it practically removes the carbonates of lime and magnesium—it should be free from magnesium oxide.

Any softening agent that leaves sulphate of soda in solution favors foaming. The ideal purification removes the sulphate entirely.

Monthly analyses should be made and kept on file of the water from the intake and from the boilers.

Blowing down boilers will often save much labor and expense in the treatment and removal of tubes.

I wish to conclude this paper with a plea for more systematic investigation of the causes and prevention of scaling, corrosion, priming and foaming—conditions that present themselves in thousands of power houses annually.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 191.]

A NEW RAPID AND ACCURATE VOLUMETRIC METHOD FOR THE DETERMINATION OF MANGANESE AND ITS APPLICATION TO THE ANALYSIS OF IRON AND STEEL.

By F. J. METZGER AND L. E. MARRS.

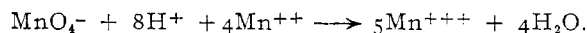
Received April 10, 1911.

It has been observed for some time¹ that the presence of manganese is a disturbing factor in the determination of ferrous iron in rock by the sulphuric-hydrofluoric acid method, and that the more hydrofluoric acid present, the greater the tendency to produce high results. This fact led to the supposition that in the presence of sufficient hydrofluoric acid, manganese and permanganic acid would react quantitatively, thus giving a method for the determination of the former.

Preliminary experiments proved that in the presence of sufficient hydrofluoric acid, the manganese, after the reaction, is all in the trivalent form; thus:



and $4\text{Mn}^{++} + 4^{(-)} \longrightarrow 4\text{Mn}^{+++}$, or



From this it is apparent that the value of the per-

¹ See Hillebrand, U. S. Geol. Survey, *Bull.* 422; "The Analysis of Silicate and Carbonate Rocks," pp. 162, 163.

manganate solution in terms of iron multiplied by 0.78682 (1911 atomic weights) gives the value in terms of manganese.

EXPERIMENTAL.

Solutions Used.—(1) Solution of potassium permanganate, approximately $N/30$; standardized against specially prepared Mohr's salt; 1 cc. = 0.001721 gram iron or 0.001354 gram manganese.

(2) A solution of manganous sulphate accurately standardized by precipitation as manganese ammonium phosphate and weighing as manganese pyrophosphate after ignition; 1 cc. = 0.002724 gram manganese.

Method.—Titrations were made in wax beakers, obtained by cutting off the tops of the ordinary white ceresine hydrofluoric acid bottles. A total volume of 100–150 cc. was used, containing 10 cc. sulphuric acid (1 : 2) and 25 cc. hydrofluoric acid. Measured volumes of the manganous sulphate solution were titrated in the presence of water, sulphuric and hydrofluoric acids with varying amounts of ammonium fluoride as follows:

No.	KMnO ₄ sol. used, cc.	Weight of ammon. fluoride present Grams.	Weight of Mn taken. Gram.	Weight of Mn found. Gram.	Error. Gram.
1.....	20.15	5	0.02724	0.02728	+0.00004
2.....	20.90	5	0.02833	0.02830	—0.00003
3.....	20.15	10	0.02724	0.02728	+0.00004
4.....	20.90	10	0.02833	0.02830	—0.00003

The endpoint is a distinct pink which lasts several minutes; the reaction proceeds somewhat slowly toward the end and the titration must be completed drop by drop. Sometimes there is a slight brown color at the end of the titration but the appearance of the pink end point is distinctly and easily seen. With amounts of manganese above about 40 mg., some experience is necessary for the recognition of the endpoint which is slightly masked by the brown color due to manganic salts. Ammonium fluoride increases the speed of the reaction but the effect of 10 grams is not sufficiently greater than that of 5 grams to justify the use of so much of the reagent.

Next, titrations were made similar to the above with varying amounts of ammonium fluoride and in the presence of 0.5 gram of iron (added in the form of ferric ammonium alum) in each titration. The results were as follows:

No.	KMnO ₄ sol. used, cc.	Weight of NH ₄ F present. Grams.	Weight of Fe''' present. Gram.	Weight of Mn taken. Gram.	Wt. of Mn found. Gram.	Error. Gram.
5.....	20.2	1	0.5	0.02732	0.02735	+0.00003
6.....	20.2	2	0.5	0.02724	0.02735	+0.00011
7.....	20.18	3	0.5	0.02724	0.02732	+0.00008
8.....	20.27	4	0.5	0.02729	0.02745	+0.00016
9.....	20.35	5	0.5	0.02754	0.02755	+0.00001
10.....	20.55	6	0.5	0.02778	0.02772	—0.00006
11.....	20.31	7	0.5	0.02749	0.02750	+0.00001
12.....	22.55	8	0.5	0.03054	0.03053	—0.00001
13.....	20.75	10	0.5	0.02806	0.02810	+0.00004
Sum of 13.	267.46	—	—	0.36164	0.36203	+0.00039

It is seen that the presence of ferric iron does not affect the accuracy of the method. One gram of ammonium fluoride completely decolorizes 0.5 gram of