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THE TREATMENT OF WATER FOR BOILER USE.

INTRODUCTION

The Bureau of Standards receives numerous requests for information regarding the use and treatment of water for heating purposes, steam generation, and industrial processes wherein difficulties are encountered from scale formation, corrosion, and hardness. The information which is usually given in each individual case has been compiled in the form of a letter circular to obviate the necessity of preparing a large number of individual letters on the same subjects.

The difficulties which are usually experienced in the use of water for industrial purposes result from the dissolved gases and mineral matter in the water. These are the result of the solvent, mechanical, and chemical action of the water in contact with the atmosphere and the earth's surface. The character and extent of this action vary with conditions such as the season of the year, the nature of the soil encountered, atmospheric pollution, and the presence of industrial wastes. In handling all problems involving the use of water a chemical analysis is essential. Water analyses are of two distinct types. One type indicates the possibility of any contamination from sewage or industrial waste which will render the water supply unsafe for human consumption. This is known as a sanitary chemical analysis. The other type indicates the amounts of mineral and gaseous matter present which will affect the use of the water for industrial purposes. This is known as a mineral analysis or sometimes as a "boiler water analysis". Typical forms of reporting the two types are given herewith:

Sanitary Chemical Analysis

Total solids
Loss on ignition
Carbonate or temporary hardness
Non-carbonate or permanent hardness
Chlorine
Oxygen consumed
Albuminoid ammonia
Free ammonia
Nitrites
Nitrates

Mineral Analysis

Suspended matter
Total solids
Loss on ignition
Silica
Aluminum
Iron
Calcium
Magnesium
Sodium
Potassium
Sulphate
Chloride
Bicarbonate
Total hardness

In many cases where the source of a water supply is in general use, mineral analyses may be obtained from municipal authorities, state chemists, state geologists, or from published analyses of the U. S. Geological Survey, Washington, D. C. If analyses are not available from such sources, it may be necessary to have an analysis made by a state chemist or a commercial analyst. In having an analysis made, the chemist should be informed in detail the definite object of the analysis. The best procedure is to consult the chemist before sending a sample of the water. His directions regarding the method of obtaining and forwarding the sample should be implicitly followed.

EFFECTS OF THE USE OF UNTREATED WATER IN BOILERS

Scale Formation

The formation of scale in a boiler results from changes in the solubility and chemical composition of the mineral matter in the water as the temperature of the water is raised. Under this condition the calcium, magnesium, silicon, iron and aluminum compounds in the water tend to precipitate and form an incrustation on the boiler walls and tubes or to settle to the bottom in the form of a sludge. The salts of sodium and potassium remain in solution up to their saturation values. While boiler scales are of varied composition, (R. E. Hall, Ind. Eng. Chem., 17, 283, 1925, lists fourteen different types of scale) probably the majority of them contain either calcium carbonate, calcium sulphate, or silicates as their preponderant constituents. In a general way, the physical character of a boiler scale will depend upon the nature of its chief constituent. A calcium carbonate scale will tend to be soft and loosely adherent. A calcium sulphate or a silicate scale will tend to be dense, hard, and closely adherent.

The presence of any considerable amount of scale in a boiler is objectionable because its heat-insulating property increases the fuel consumption. The presence of scale is also a hazard since cracks in the scale will admit water to the heated metal beneath the scale with consequent danger of explosion. F. N. Speller in his book, "Corrosion - Causes and Prevention" states that: "The presence of a more or less porous scale sometimes assists corrosion by increasing the temperature of the metal, by producing a high concentration of salts under the scale, and by favoring the decomposition of magnesium salts and other such compounds."

Corrosion

Fundamental theories regarding the reactions which take pl the in the process of corrosion are discussed in detail in ma liography. texts listed under books and general information in th

It has been generally established that the initial action is solution of the metal in water. This is followed by the oxidation of the metal in solution with the formation of insoluble iron oxides which are familiarly known as rust. Corrosion under water, as in boilers and piping, differs from corrosion in the atmosphere in the physical character of the rust formed, the ease with which the corrosive action continues, and the more unequal distribution of the attack resulting in severe corrosion at certain points or areas with the formation of pits and ultimately of holes or failures.

The results of a large amount of experimental work, which has been done by numerous investigators, indicate that within readily attainable limits the composition of the metal has little effect upon the rate of corrosion of iron and steel of ordinary composition submerged in an average water supply. Ferrous alloys, such as high chromium iron, are of course more resistant, but their present cost prohibits their general use in large installations. Of the many factors, other than the character of the metal, probably the two which exercise the controlling influence in corrosion under water are the dissolved oxygen in the water and the degree of acidity of the water.

In the presence of most natural waters the amount of corrosion which takes place is proportional to the dissolved oxygen content of the water. By dissolved oxygen is meant the oxygen from the air which is dissolved in the water and not the oxygen which is a part of the compound of oxygen and hydrogen which is known as water. It has been demonstrated experimentally that corrosion can be controlled at will, all other factors being constant, by increasing or decreasing the dissolved oxygen content. The amount of dissolved oxygen which may be present in most natural waters depend chiefly upon the temperature and the amount of aeration to which the water has been subjected.

The degree of acidity of a natural water is usually governed by the amount of carbon dioxide, which is also a constituent of the atmosphere, dissolved in the water. In the operation of a boiler the amount of carbon dioxide may be increased by breaking down of the unstable bicarbonates of calcium and magnesium present in the water. In waters of abnormal composition the presence of hydrogen sulphide, or of mineral or organic acids resulting from acid-forming constituents in the soil or from industrial wastes and sewage, may be other contributing factors toward the production of acidity. Acidity is not a fundamental cause of corrosion, since corrosion may take place in its absence, but its presence serves to increase the rate and extent of the corrosion.

A factor which is of importance in governing the amount of corrosion taking place under water is that of film formation. The rust which is initially formed may serve to retard the further progress of corrosion by producing a partially protective film on

the surface of the metal. The stability of this film is dependent upon the degree of acidity or alkalinity of the adjacent water, since the ferrous hydroxide which composes the film has a slight solubility and its solution has a definitely alkaline reaction. In the presence of strong alkalies in the water the solubility of the film is decreased and the film becomes protective. In the presence of acids in the water the alkalinity of the film is destroyed, its solubility increased, and the protective action lost. The formation of protective films is the chief natural agency tending to retard corrosion. In addition to the simple rust film other protective films of a more complex nature, either naturally or artificially produced, may be present. Scales consisting of silicates and carbonates of iron, calcium, and magnesium, which may result from the presence of these substances originally in the water or from their intentional addition, will provide further protection. The absence of these materials accounts in part for the greater amount of corrosion which frequently occurs in localities where the water is low in dissolved mineral matter in comparison with regions where the water is highly mineralized and scale-forming.

Hydrogen Embrittlement

Another form of metal failure associated with corrosion is that of hydrogen embrittlement. This manifests itself in peculiar cracks developing below the water-line in boilers. The definite process by which this takes place is still a matter of discussion. It is associated with feed waters that are high in sodium carbonate and low in sulphates, either naturally or as the result of boiler water treatment. Its occurrence from natural causes is limited to a few geographical districts.

Foaming and Priming

Foaming and priming are intimately related. Foaming has been defined as the formation of bubbles on the surface of the water and in the steam space. Priming has been defined as the passage of fine particles of water from the boiler along with the steam causing so-called "wet steam". The distinction is not a sharp one and many authorities regard the terms foaming and priming as interchangeable. While there has been no definitely accepted theory in regard to foaming and priming, it is generally agreed that they are the result of certain types of boiler design, in which a complex interior and numerous tubes and a small steam space play a part, and of the chemical composition of the water. Present day knowledge indicates that foaming is usually caused by the presence of a high concentration of sodium salts together with a suspension of finely divided insoluble matter. The latter may be particles of loosened scale or of organic and inorganic suspended matter present in the feed water.

The chief detrimental effect resulting from foaming and priming is the carrying, either in solution or suspension, of solids over into the steam line. These solids will be deposited in superheater tubes, valves, and at other points along the path the

steam travles. In superheater tubes the solids will be deposited by evaporation and will seriously affect the efficiency of the superheater system. The abrasive action of the solids in contact with turbine blades or deposited in valves will cause serious erosion. In many cases the deposition of solids in valves will cause serious stoppage.

METHODS OF TREATMENT OF WATER

Softening and Scale Prevention

Softening or the removal of the scale-forming and hardness constituents from water is accomplished by either of two methods. The chemical method consists in adding to the water certain reagents which convert the dissolved scale-forming constituents into an insoluble form. In the treatment of water previous to its use in a boiler or for an industrial purpose the scale-forming constituents are removed by settling or filtration. In the treatment of water within the boiler by the use of "boiler compounds" the scale-forming constituents are removed periodically in the form of a sludge. The physical method consists either in bringing the water to the boiling temperature before it enters the boiler, whereby the soluble bicarbonates of calcium and magnesium are broken down and the resulting carbonates and hydroxides are precipitated, or by distilling the water in so-called evaporators, by which means the water is rendered practically free from all mineral matter.

Preliminary Softening by Chemical Action

The two most frequently used methods of preliminary softening, using chemical reactions, are the "lime-soda" and the base-exchange-silicate or so-called "zeolite" treatments.

The "lime-soda" treatment consists in adding to the raw water, previous to its use , hydrated lime in amount equivalent to the free carbon dioxide and the calcium and magnesium bicarbonates present, and soda ash (anhydrous sodium carbonate) in amount equivalent to any calcium sulphate and calcium and magnesium chlorides present. The function of the lime is to combine with the free carbon dioxide and the bicarbonates of calcium and magnesium present. The calcium carbonate formed is fairly insoluble and settles out. Magnesium carbonate is fairly soluble and much of it remains in solution. However if lime is added in sufficient excess all the magnesium carbonate is converted to magnesium hydroxide which, being insoluble, is precipitated. The function of the soda ash is to react with the constituents causing the non-carbonate or permanent hardness by converting the sulphates and chlorides of calcium and magnesium to insoluble carbonates and hydroxides, with the accompanying formation of sodium sulphate and sodium chloride.

In the "cold softening process" the reagents are usually added to large quantities of the water in proportions determined by analysis. The reactions which take place bring down a large part of the calcium and magnesium present in the form of a sludge. This sludge will also mechanically entrap and precipitate a large part

of the suspended and colloidal matter present in the water. The sludge is allowed to settle and the softened water is filtered or drawn off. Two methods of applying the "lime-soda" process are in general use. These are the intermittent and the continuous methods. In the intermittent method a tank full of raw water is treated with the calculated amounts of lime and soda ash, thoroughly mixed, and allowed to stand for some time to permit the sludge to settle, after which the softened water is drawn off into a storage tank. The water may or may not be filtered after treatment. In the continuous method the softening agents are added to a continuous flow of the raw water and the treated water is passed through an irregularly arranged series of baffles which retards the progress of flow and permits the sludge to settle. The softened water emerges in a steady stream at the outlet.

"Hot process softening" is essentially the same as the continuous method of "cold softening" with the exception that the apparatus is provided with a means of heating the water to at least 200 degrees Fahrenheit. Exhaust or live steam is generally used for this purpose.

In softening by the "lime-soda" process the extent to which the softening will be complete will depend upon temperature, thoroughness of mixing, period of sedimentation, and other factors. Even under ideal conditions of operation a certain amount of the scale-forming constituents will remain in the treated water, owing to their solubility and to incomplete subsidence. However, the softened water is usually sufficiently free from scale-forming matter to render the water suitable for boiler use. The comparative values of the intermittent and continuous types of softener depend upon the local operating demands. The chief advantage of the intermittent softener is the greater time permitted for sedimentation which insures a cleaner, softer water. The advantages of the continuous type are the continuous supply of softened water and the smaller apparatus required. The choice of a system depends upon the particular kind of service required.

In the base-exchange-silicate method the softening material is a bed of porous silicate mineral which has the property of retaining either calcium and magnesium or sodium and potassium as part of its chemical composition. On passing a water containing calcium and magnesium through a bed of this material the calcium and magnesium are automatically retained in the silicate mineral and the effluent contains an equivalent quantity of sodium or potassium released from the silicate mineral. The silicate mineral upon exhaustion or saturation with calcium and magnesium is regenerated by allowing a solution of sodium chloride to flow through the bed of mineral, the displaced calcium and magnesium being contained now in the wash water. Practically the silicate mineral or so-called "zeolite" acts thus as a carrier for sodium.

By this method the calcium and magnesium are reduced to a negligible quantity so long as the base-exchange property of the

mineral is maintained, the completeness of the softening reaction being a noteworthy property of this method. It is obvious that, since the reactions involve practically an exact exchange of sodium or potassium for calcium and magnesium, the water can not be overtreated. Incomplete softening, or undertreatment, can occur only when the base-exchange-silicate has become saturated with calcium and magnesium, a point which can be readily ascertained by the simple means of determining the total hardness of the treated water.

This method of treatment does not affect the nature of the negative or acid radicals present in the water. Free carbon dioxide and the bicarbonate radical remain unchanged, the latter now being present as sodium bicarbonate. This method is therefore very useful and effective for producing a very soft water, but the presence of carbon dioxide, both in the free state and that which is liberated from the sodium bicarbonate in the boiler, may make the water so treated more corrosive than water treated by the "lime-soda" method. In a publication, "Zeolite Water Treatment in a Large Central Heating Plant", by A. H. White, J. H. Parker, E. P. Partridge and L. F. Collins, Reprint Series No. 1, July 1927, Department of Engineering Research, University of Michigan, the authors have described successful experiments in treating the effluent from a base-exchange-silicate softener with sufficient sulphuric acid to neutralize about 50 per cent of the sodium bicarbonate present. The carbon dioxide is subsequently eliminated by heating the water in a deaerator and the water leaving the deaerator has a desirable degree of alkalinity.

Frequently with very hard waters, especially those high in carbonate hardness, a system combining precipitation by the "lime-soda" method and further treatment of the partially softened water by the base-exchange-silicate method may be advantageously used. The object of such a system is to remove the greater part of the carbonate hardness with lime and the non-carbonate hardness by the base-exchange-silicate.

The choice of a softening system depends upon numerous factors. In general the "lime-soda" method works best with waters of constant composition such as well waters. It decreases the total mineral content of the water, although it does not completely remove the hardness. It is comparatively inexpensive to operate. It requires more or less careful supervision and is best adapted to the requirements of large installations such as: power plants, central heating systems, and railroads. It is suitable wherever complete removal of hardness is not sought. The base-exchange-silicate method is best adapted to waters of varying composition since it is almost automatic in operation and requires less supervision. It reduces the total hardness to a negligible amount. It does not decrease the total mineral content of the water, and as usually applied, it does not eliminate dissolved carbon dioxide. It is best adapted to the requirements of small installations such as: hospitals, hotels, residences, and where, in the case of laundries and specialized industries, completely softened water is especially desirable.

Boiler Compounds

Boiler compounds are substances which are introduced directly into the boiler for the purpose of preventing scale formation. They are used where no preliminary softening of the water is employed. Treatment with boiler compounds is frequently the most feasible method for small plants or for marine use where a softening plant would be either too expensive or not applicable. For large systems their use is frequently unsatisfactory. The chief purpose of a boiler compound is to precipitate the scale-forming matter in the boiler in such a form that adherence to the boiler walls is diminished or even prevented. Under proper conditions the calcium and magnesium salts are precipitated in the form of a loose sludge which may be periodically removed by "blowing down" and washing out the boiler. A second possible purpose of a boiler compound is to reduce corrosion by increasing the alkalinity of the boiler water. A third object is to prevent foaming by changing the surface tension of the water in the boiler.

Nearly all boiler compounds contain as basic materials strongly alkaline sodium salts. These may be soda ash (sodium carbonate), caustic soda (sodium hydroxide), water glass (sodium silicate), sodium aluminate, or trisodium phosphate. Many boiler compounds consist wholly of one or more of these reagents. In others there are present organic materials such as starch or tannin extract. The list of the latter substances is a long one, but they all have a common purpose. Such substances influence the physical character of the precipitated matter and prevent it from adhering to the boiler walls. The presence of castor oil is effective in preventing foaming by reducing the surface tension of the water.

Most of the materials which enter into the composition of proprietary boiler compounds have a useful purpose. There is, however, no universal compound which can be used successfully without a knowledge of the composition of the feed water and without an accurate apportionment of the compound to the scale-forming material in the water. To the prospective purchaser of a boiler compound two courses are open. He should either consult a manufacturer of a boiler compound, who maintains a service of examining the feed water and will make recommendations based upon his analysis, or employ a chemist to examine the water and prescribe treatment.

Softening by Distillation

Distillation consists in vaporizing the raw water and collecting

it as a distillate. The source of heat employed is usually a system of steam coils. The condensate collected from the steam used for heating is also utilized. Water converted into vapor and condensed is practically free from solid matter unless it is carried over mechanically or is produced by corrosion of the containers. When collected on a large scale this effect frequently happens and the water is never entirely free from solid material. However, distillation is the only method by which it is possible to completely eliminate the mineral matter from water.

The evaporator finds a particular field of usefulness where boilers are operated at high ratings involving high pressures and temperatures, conditions in which greater purity of the feed water is necessary. The greatest advantage in the use of this method is, of course, the high purity of the water. It eliminates boiler scale, priming, foaming, embrittlement, and the expense of "blow downs" and boilers out of commission. The chief disadvantages are the cost of fuel, the initial cost of equipment, and the danger from corrosion unless the water is rendered free from dissolved oxygen.

Prevention of Corrosion

The methods employed for the prevention of corrosion depend upon the removal of dissolved oxygen, the regulation of the alkalinity of the water, and the production of protective films.

The removal of dissolved oxygen is accomplished by either or both of two methods. They may be designated as (a) chemical and (b) physical or mechanical. The chemical method removes the oxygen by allowing it to exert its corrosive action before the water is used. The raw water is allowed to pass through scrap iron or strips of iron, the purpose of which is to eliminate the oxygen by the formation of iron rust. This is customarily referred to as deactivation or deoxygenation. Since the rate of reaction is relatively slower in cold water, it is usual to heat the water before passing it through the deactivator. The scrap iron or strips of iron are contained in a steel chamber similar to a pressure filter. The scrap iron or strips have to be replenished about every two years and the temperature should be carefully regulated. Aside from this, little attention is required and such systems are particularly suited to small installations such as private homes, apartment houses, and hotels.

The physical or mechanical method is employed in the majority of cases where it is desirable to remove oxygen from feed water on a large scale. The method is commonly referred to as deaeration. This method consists, in general, in heating the water, preferably to boiling, under either atmospheric or reduced pressure. One type employs an explosive boiling of the water as it

passes through the apparatus. The deaerator is kept under a partial vacuum. The incoming water is heated to a sufficiently high temperature that a flash of steam takes place as it enters the chamber. As a result of the reduced pressure the gases are swept out of the water. In another type the gases are removed by discharging steam into the bottom of the deaerator tank. In another type the water, which is partially heated, flows over a bank of tubes heated internally with live steam. The types which are employed all utilize the same general principle and differ only in mechanical details. One system is sometimes employed wherein the bulk of the dissolved oxygen is first removed by a mechanical method and the residual oxygen is finally removed by chemical means.

The use of either deactivation or deaeration requires an initial investment in equipment, which is frequently high, but is justified by the large savings effected in the reduction of corrosion of the boiler and heating system.

Regulation of Alkalinity and Film Formation

Regulation of the alkalinity and the formation of protective films are closely related and are accomplished in much the same manner. Increasing the degree of alkalinity to a point above that at which extensive corrosion may take place results in film formation, the simplest film being iron hydroxide which is initially formed on the surface of the metal. As long as the desired alkalinity is maintained this iron hydroxide will remain insoluble and act as a protective film. The alkalinity can be maintained by the use of such materials as lime, soda ash, caustic soda, trisodium phosphate, etc. More complex reactions, which result in the formation of protective films, take place between the alkaline material added and the mineral constituents of the water. Thus a material like sodium silicate not only increases the alkalinity but forms silicates of iron, calcium, and magnesium which serve as very protective coatings. Sodium silicate is the basic material in numerous "boiler water treatments" sold on the market for preventing corrosion. The use of film-forming and alkaline materials is desirable in small installations, in which the removal of dissolved oxygen is not feasible, and in localities where the water presents unusally severe conditions, such as high acidity or low mineral content.

Prevention of Foaming and Priming

The addition of a small amount of castor oil is the most effective means of stopping foaming. Frequently the use of a water filtered free from suspended matter and the more frequent removal of accumulated sludge from the boiler will reduce foaming and priming.

REMOVAL OF SCALE FROM BOILERS AND RUST FROM PIPING

Frequently inquiries are received regarding the removal of scale and rust from boilers and piping. Extensive information on this subject is lacking in the literature. Reference is made to mechanical removal by scraping, chiselling, and drilling. Several devices are offered on the market for mechanically descaling boiler tubing. It may be said that in comparison with the use of strong reagents, mechanical removal is, in general, a more advisable practice in so far as the safety of the underlying metal is concerned. However, the use of strong solutions of hydrochloric acid has been recommended by several authorities, who claim not only a saving in labor cost but also very little attack of the metal if care is exercised. The use of this reagent should not be attempted except by experienced operators. The use of very strong solution of soda ash or caustic soda has been known to loosen scale. Likewise the change to a very soft water will tend to dissolve scale deposits in time. Some work has also been done on the use of carbon dioxide as a scale solvent. The use of carbon dioxide is apparently successful where the nature of the scale and other conditions are favorable. A boiler scale which contains a high percentage of silica can be loosened and removed by this treatment. The explanation given is that the silicates are mixed with a small amount of calcium carbonate and the latter tends to be dissolved by the carbon dioxide in solution, permitting the bulk of the scale to be loosened from the boiler walls. No definite instructions for the removal of rust and scale can be given that will fit all cases.

Water piping which is clogged with rust and so located in a building that removal of the piping for cleaning will be attended by considerable expense can sometimes be cleaned with hydrochloric acid. It is necessary that the pipe be in fairly good condition and more or less uniformly thick walled. Treatment with the acid will, of course, dissolve the rust and will also tend to attack the metal. Recent literature contains references to the use of so-called inhibitors for this purpose, materials which prevent the acid from attaking the metal but do not interfere with its solvent action upon the rust. The use of hydrochloric acid alone is frequently permissible where the metal parts are of heavy construction, as in the case of engine jackets of marine motors and cooling chambers of compressors.

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Detailed discussion of methods can not be given in the limited confines of a letter circular. Such information may be obtained from the literature, references to which follow. The literature on water treatment and corrosion is very extensive and frequent repetitions occur. The list of references given here is by no means

complete, but is believed to be representative of present day knowledge. For a more detailed list of publications dealing with water and water treatment, reference is made to "Chemical Abstracts" published by the American Chemical Society, the volumes of which may be found in most public libraries, and in the libraries of universities, colleges, and technical schools.

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