INTERNAL TREATMENT OF BOILER WATER FOR SMALL INDUSTRIAL PLANTS

By J. J. GANUCHEAU

IT IS not my intention to present before this group a complete treatise on boiler water or boiler water conditioning. I merely hope to bring to your attention certain facts with which you are already familiar, but through the hurry of more important things you may have failed to apply.

I wish to bring to your attention some of the common reactions encountered in boiler water conditioning.

These reactions may be found in a book by Blanning and Rich, "Boiler Feed and Boiler Water Softening."

I will give here only the reactions of the chemicals sometimes used in internal treatment.

From these reactions the chemist can choose the ones which apply to his particular water supply.

You will find the amount of chemicals used for internal treatment less than that required for external treatment. While the amounts are smaller than for external treatment, nevertheless, enough chemicals must be added to give the water a zero hardness.

CHEMICAL EQUATIONS

I. *Temporary Hardness Removal*:

(a) Calcium Bicarbonate

Caustic Soda—$Ca(HCO_3)_2 + 2NaOH = Na_2CO_3 + 2H_2O$.

Sodium aluminate—$Ca(HCO_3)_2 + Na_2Al_2O_4 = CaAl_2O_4 + Na_2\ CO_3 + CO_2 + H_2O$.

Heat—$Ca(HCO_3)_2$ + Heat $= CaCO_3 + CO_2 + H_2O$.

Di-sodium phosphate—$Ca(HCO_3)_2 + Na_2HPO_4 = CaHPO_4 + 2NaHCO_3$.

(b) Calcium carbonate (Residual in Solution)

Di-sodium phosphate — $3CaCo_3 + 2Na_2HPO_4 = Ca_3(PO_4)_2 + 2Na_2CO_3 + H_2O + CO_2$.

(c) Magnesium Bicarbonate

Caustic Soda—$Mg(HCO_3)_2 + 4NaOH = Mg(OH)_2 + 2Na_2CO_3 + 2H_2O$.

Sodium aluminate — $Mg(HCO_3)_2 + Na_2Al_2O_4 = MgCl_2 + Na_2CO_3 + CO_2 + H_2O$.

Di-sodium phosphate — $Mg(HCO_3)_2 + Na_2HPO_4 = MgHPO_4\ t + 2Na\ HCO_3$.

(d) Magnesium Carbonate

Caustic Soda—$MgCO_3 + 2NaOH = Mg(OH)_2 + Na_2CO_3$.

II. *Permanent Hardness Removal*:

(a) Calcium Sulphate

Soda Ash—$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$.

Sodium aluminate—$CaSO_4 + Na_2Al_2O_4 = CaAl_2O_4 + Na_2SO_4$.

Di-sodium phosphate—$CaSO_4 + Na_2HPO_4 = CaHPO_4 = Na_2SO_4$.

(b) Magnesium Sulphate

Caustic soda—$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$.

Di-sodium phosphate—$MgSO_4 + Na_2HPO_4 = MgHPO_4 + Na_2SO_4$

(c) Calcium Chloride

Soda Ash—$CaCl_2 + Na_2CO_3 = CaCo_3 + 2NaCl$.

Sodium aluminate—$CaCl_2 + Na_2Al_2O_4 — CaAl_2O_4 + NaCl$.

Di-sodium phosphate—$CaCl_2 + Na_2HPO_4 = caHPO_4 + 2\ NaCl$.

(d) Magnesium Chloride

Caustic Soda—$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl$.

Soda Ash—$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$.

Di-sodium phosphate—$CaCl_2 + Na_2HPO_4 = CaHPO_4 + 2NaCl$.

III. *Gas Removal*

(a) Oxygen

Sodium sulphite—$2Na_2SO_3 + O_2 = 2Na_2SO_4$.

Iron—$4\ Fe + 3O_2 = 2Fe_2O_3$.

Tannins or starch are usually added. Their function is to keep the precipitated matter in suspension. We have found corn starch quite satisfactory.

The objects of internal boiler water treatment are:

1. Scale prevention.
2. Dry steam.
3. Efficiency.
4. Prevention of corrosion or pitting.

The achievement of good results in this direction can be gotten by a careful study of each boiler plant as an individual problem. The chemist is often asked to treat a water away from his laboratory. When this is the case, I cannot over-emphasize the importance of sending a questionnaire to the engineer to find out what are his present conditions, and what his troubles are.

If it is at all possible, the chemist should make a personal examination of the boiler plant to get first hand information of the conditions existing in that particular plant. You will find low feed water temperature, containing much oxygen, exhaust steam with plenty of lubricating oil in it, etc.

If a questionnaire is requested, this questionnaire should be accompanied by a gallon sample of the boiler feed make up water.

This water should be given a complete analysis, particular attention being given to the total hardness, total solids, chlorides, and the total sulphate in the sample.

At its best internal treatment is not the most acceptable way to treat boilers. But, taking into consideration the high initial cost of external treatment for small plants, good results can be obtained by intelligently applying through internal treatment, chemicals to greatly improve if not entirely cure bad boiler water trouble.

As brought out in an excellent bulletin entitled "Instructions for the Treatment of Boiler Feed Water and for the Operation, Care and Repair of Feed-Water Apparatus—Navy Department Bureau of Engineering, 1933," most boiler waters contain some kind of impurity which is undesirable. Even evaporated water would give trouble if it were not properly deaerated. The prevention of scale, corrosion, priming and foaming are of most importance to the engineer. Most waters will require some sort of treatment to effect these desirable results. By far the most objectionable of scale forming salts is calcium sulphate. This builds up a hard, flint-like scale which increases in thickness until tube failure occurs. Another bothersome scale is calcium silicate, or other silicate scale which forms glass-like and dense scales which being poor conductors of heat might also result in tube failure.

Quoting the Navy bulletin—"Contrary to what was formerly believed, scale is not formed by the formation of the crystals of the salt in the body of the boiler water and later settling and baking of these crystals on the evaporating surface. Scale is formed by the salts whose solubility *decreases* with increase in temperature. The scale is deposited directly on the metal since the hottest water is that which in contact with the metal surface."

The method of scale prevention is to add to the water highly soluble chemicals such as sodium carbonate and sodium phosphate; these react with the scale forming calcium sulphate to form soluble sodium sulphate and a harmless sludge consisting of either calcium carbonate of calcium phosphate.

The theory of corrosion has been admirably handled by R. E. Hall in "A Physico-Chemical Study of Scale Formation and Boiler-Water Conditioning," Bulletin 24, Mining & Metallurgical Investigation, page 88 in this bulletin. Hall shows the importance of maintaining the proper alkalinity to prevent corrosion. The maintenance of *high* (210° F.) feed water temperature; the higher the temperature, the less oxygen can be dissolved by the water. The amount of sodium sulphite recommended by S. T. Powell—Power, June-July, 1935, for the prevention of corrosion is as follows: "Pounds of commercial sodium sulphite required per 1000 gallons of feed water for each milliliter per liter of dissolved oxygen is 0.139."

The other important principle is the prevention of bad boiling conditions such as priming and carryover, or foaming. The greater the amount of dissolved solids in a boiler the greater the tendency to foam or froth when it is boiled rapidly. A considerable amount of suspended solids will also cause foaming by stabilizing the steam bubbles by increasing the film thickness giving them more strength, the steam bubbles may fail to break and enter the dry pipe. Small particles of water will, therefore, be carried along with the steam.

Necessity for daily study of water analyses.

Any satisfactory system of boiler feed-water treatment must be used properly to be successful. This requires a daily analysis of the boiler water, a study of the results obtained, and prompt application of such corrective measures as may be necessary. This is accomplished easily and quickly providing the general subject of feed water treatment is understood. The minutes required to daily examine the boiler water analyses to determine whether boiler conditions are correct, will pay dividends both in the decrease in the manual labor and the material costs which the continuous maintenance of proper conditions is certain to effect. The analysis of the boiler water should be made at the boiler. We have found a single titration using phenolpthalen to give good results.

The three important tests to run on boiler water are:

1. Alkalinity.
2. Hardness.
3. Concentration.

The directions for running these, with some modification, as prescribed by the U. S. Navy, are as follows:

Instructions for Making Water Test

1. Each milliliter of the twentieth normal (N-20) acid solution required by a 50 ml. sample represents 0.1 per cent of normal alkalinity. The alkalinity is determined as follows: .

(a) Rinse the 50 ml. pipette with some of the water to be tested.

(b) Fill the pipette to the zero mark and transfer exactly 50 ml. of sample into the clean 250 ml. Erlenmeyer flask.

(c) Add 2 or 3 drops of phenolphthalein indicator, which will give the sample a deep pink color.

(d) Fill the burette and drain to zero.

(e) Add the twentieth-normal acid solution from the burette while stirring the sample continuously. Add only a drop at a time as the color begins to fade, until the pink color entirely disappears.

(f) Read the burette.

(g) The burette reading (in milliliters) multiplied by 0.10 equals the per cent normal alkalinity of the sample. For example, a burette reading of 5.2 ml. represents an alkalinity of 0.52 per cent normal.

Hardness

2. The strength of the soap solution is such that each milliliter required by a 50 ml. sample represents 1 grain per gallon of hardness. A small amount of soap solution, the "lather factor," is required to form a lather on a sample of pure water. This "Lather Factor," which should be written in pencil on the roughened area on the shoulder of the soap bottle, must be subtracted from all determinations of soap hardness. The hardness of a boiler water is determined as follows:

(a) Pipette 50 ml. of water sample into the 8 ounce bottle.

(b) Fill the burette and drain down to zero.

(c) From the burette add to the sample an amount of soap equal to the "lather factor," stopper the bottle, shake vigorously. Lay the bottle on its side on the bottom of the cabinet and start a stop watch.

(d) If the lather persists and completely covers the surface of the water for 5 minutes, report "zero hardness."

(e) If the lather does not persist, add more soap solution, stopper and shake. Lay the bottle on its side in the bottom of the cabinet and start a stop watch.

(f) Repeat (e) until a lather is obtained which completely covers the surface of the water for 5 minutes.

(g) Read the burette.

(h) From the burette reading (in milliliters) subtract the "lather factor" which at all times should be marked in pencil on the roughened area on the shoulder of the soap bottle.

(i) The burette reading, minus the "lather factor" equals the hardness of the sample in grains per gallon.

The amount of the soap solution to be added under (e) above will vary between 1 drop and a half a milliliter. A few titrations on waters of different hardness values will aid in gauging a proper addition. Too much should never be added.

We have found by actual practice, the maintaining of an alkalinity between .4 and .7 per cent normal which is 10 to 17 grains per gallon alkalinity in terms of NaOH to give very good results. When this alkalinity is maintained, the water usually has a zero soap hardness.

Concentration

3. The concentration ratio can be determined by:
   a. Chloride ratio in feed water and boiler water.
   b. By concentration hydrometers.

We have found hydrometers very satisfactory for controlling the amount of blowdown.

The sulphate ratio as recommended by the A.S.M.E., should be strictly adhered to.

Acknowledgment

Credit is given the Navy bulletin from which most of this material was obtained.

LITERATURE REFERENCE

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A NOTE ON THE ANALYSIS OF TUNG FRUITS

GROWN UNDER DIFFERENT CONDITIONS IN MISSISSIPPI

By R. S. McKINNEY and G. S. JAMIESON

SIX large samples of tung fruits were sent by B. T. Abbott, colonization agent of the Illinois Central Railroad Company at Jackson, Mississippi, to Dr. C. C. Concannon of the Department of Commerce, who gave them to us for investigation. According to descriptions accompanying the samples, they had been collected as indicated in Table I.

TABLE I

	Sample	Age of Trees Years	Soil Types	Locality) (Miss.)	Cultivation
1	Composite	4	Orangeburg	Yeaton	Cultivated
2	Composite	4	Orangeburg	Yeaton	Uncultivated
3	Composite	4	Ruston	Yeaton	Uncultivated
4	Composite	5	Orangeburg	Lyman	Cultivated
5	Single tree[1]	10	Loess	Natchez	Uncultivated
6	Single tree[2]	12	Loess	Port Gibson	Uncultivated

[1] Total crop was 184 pounds of fruit.
[2] Total crop was 135 pounds of fruit.

The average weight of the fruits of each sample was determined, as wells as the percentages of the nuts and kernels. The moisture and oil contents of the kernels were also determined, together with the iodine number of their respective oils.

In order to get a representative sample for the determination of the oil content it was necessary to take about 60 grams of the tung nut kernels and grind them to a meal which would pass through a 6-mesh sieve. After thoroughly mixing the ground kernels, portions of about 5 grams were accurately weighed for the determination of oil by the well-known method described in the Department of Agriculture's Service and Regulatory Announcement No. 133, with the following modification: The extraction with the special petroleum ether is continued for one hour, and the meal is ground in a mortar and extracted for another hour. This treatment of grinding and extracting is repeated (usually three more times) until the weight of the oil obtained is negligible.

Of the various directions suggested for the determination of the iodine number by the Wijs method, it was found in the case of tung oil that more concordant results were obtained by following the method given in the 1930 Tentative Standards of the American Society for the Testing of Materials, which recommends that 160 to 190 mg. of the oil be allowed to react for 30 minutes with 25 cc. of the Wijs solution in a dark place at a temperature between 21° and 23° C.

After making a number of experiments according to these directions, we found that approximately 160 mg. of oil gave an iodine number more than a unit above that given by about 190 mg. It was found also that a Wijs solution 25 days old gave results about two units lower than a freshly prepared solution. In view of these findings, it was decided not to use a Wijs solution older than 8 days and to take portions of about 175 mg. of the oils.

All the results obtained with the tung fruits and their oils are given in Table 2.

It will be observed that the oil content of the kernels of the fruit from the cultivated trees was 64.7 and 70.1 per cent, whereas that of the other samples ranged from 53.6 to 67.6 per cent. For comparative purposes a sizable sample of tung fruits grown near Gainesville, Florida, was sent to us by B. F. Williamson. The kernels from these fruits gave 67 per cent of oil and 2.3 per cent of moisture. The extremely low moisture content of these kernels and the kernels from the Mississippi tung fruits accounts in part for the higher oil content than that reported in most instances in the literature. A portion of this difference may be due in the present case to the more complete extraction of the oil.

TABLE 2
Tung Fruits, Nuts, Kernels and Oils

Sample	Aver. Wt. Fruit Grams	Percent Nuts in Fruits	Percent Kernels in Nuts	Percent Kernels in Fruits
*1..................	27.3	58.2	63.6	37.0
2..................	25.7	52.1	62.7	32.7
3..................	22.8	50.5	58.9	29.7
*4..................	30.4	56.4	64.1	36.2
5..................	19.9	66.4	62.0	41.2
6..................	23.1	51.2	52.8	27.0

Sample	Moisture in Kernels Percent	Oil in Kernels Percent	Iodine Value of Oil (Wijs)
*1..................	2.3	70.1	164.7
2..................	2.5	67.6	164.7
3..................	2.6	67.6	166.2
*4..................	2.7	64.7	163.2
5..................	1.7	54.9	163.1
6..................	2.0	53.6	165.5

*Cultivated.