THE EFFECT OF LIME-SODA ASH TREATMENT ON FOAMING CHARACTERISTICS OF BOILER WATER.

by

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I. INTRODUCTION

Water treatment for steam production is almost universal in present day industries. The type of treatment varies with the type and quantity of raw water to be used. For boiler feed water purification, the removal of the scale forming and corrosive constituents is the most important treatment. The lime-soda ash method is widely used for locomotive feed water treatment because of its relative cheapness, and its efficiency in removing the undesired constituents.

One of the difficulties encountered in the operation of boilers using treated water, instead of raw water, is the greater tendency to foam. Foaming is a formation of bubbles, or foam, on the surface of the water inside a boiler. This foam may range in thickness from a layer barely covering the surface, to a mass that fills the entire steam space above the water. When this foam layer is of such height that it reaches the steam outlet, serious damage may be done when these particles of water, which contain a large amount of metallic salts, are carried over with the steam.

Since foaming is usually associated with a high concentration of dissolved salts, railroad steam locomotives probably have more foaming difficulty than other industrial boilers. One explanation for this is the fact that steam condensate is not returned to the boiler and dissolved salts from the feed water rapidly concentrate in the boiler unless a frequent blowdown schedule is maintained. Excess blowdown is undesirable as it causes heat loss due to the removal of part of the hot boiler water.

The majority of the previous work on foaming has been based on the foaming concentrations of single salt solutions, and little information is available on mixtures of salts in solution or on foaming conditions of natural waters. It seemed desirable to determine foaming concentrations of natural waters that had been properly treated, and to compare the characteristics of each.

The two types of water studied in this investigation were the "relatively soft" New River water, and the "relatively hard" well water used at the Virginia Polytechnic Institute. Both of these waters are used in industrial boilers, and have been known to foam if the dissolved salts were allowed to concentrate in the boiler.

The purpose of this investigation was to determine the effect of various degrees of lime and soda ash treatment on the foaming characteristics of Virginia Polytechnic Institute boiler water and New River boiler water, at atmospheric pressure and at a constant evaporation rate.

II. LITERATURE REVIEW

Definitions

Foaming. Foulk (10) defined foaming as simply the formation of foam on the surface of the water. This foam might range in thickness from a layer barely covering the surface to a mass that filled the entire steam space above the water.

Priming. Webster (41) defined priming in connection with boilers as conveying water out of the boiler with the steam. Foulk and Rysnar (21) gave the following reasons for priming:

1. The formation of a sufficiently thick layer of foam on the surface of the boiler water to reach the steam outlet.
2. Violent ebullition or other mechanical agitation throwing slugs of water against the steam outlet.
3. Lifting of the boiler water by the sudden formation of steam bubbles throughout its mass.

History

Early Knowledge of Foaming. Stromeyer (39) wrote about foaming in 1893: "Information on this subject is as yet almost nonexistent." Eighteen years later, Stabler (38) evidently felt that little information had been added, for he began a discussion of foaming and priming with the statement that they "are probably the least understood of boiler phenomena."

In 1925, Foulk (11) stated that sodium salts apparently were the only definite chemical substances to which foaming and priming were generally attributed, but he had not been able to find a record of any experiments which indicated that sodium salts alone were the cause of the trouble. The belief had unquestionably originated from the fact that in the great majority of waters, sodium salts were the only ones that concentrated in the boiler.

In 1890, Lord Raleigh (36) stated that upon boiling a strong salt (NaCl) solution, only a slight foam layer was formed on the surface of the solution. In 1904, Tatlock and Thompson (40) reported a laboratory boiler which contained over 30,000 parts per million of sodium salts but showed no trace of carry-over. Koyl (30), in 1900, fed into boiling water pure sodium carbonate up to several hundred grains per gallon without producing foam. However, if just a trace of insoluble powder such as calcium carbonate was fed into the water, it would foam vigorously.

In 1921, Bancroft (8) wrote that in order to get a foam the only essential was that there be a distinct surface film;

that is, the concentration of the surface layer should differ from the mass of the liquid. All true solutions would therefore foam if there were a marked change of surface tension with concentration, regardless of whether the surface tension increased or decreased.

In 1945, Williams (42) stated that the main objectives of feed water treatment were to protect the boiler and its heating surfaces from scale, corrosion, and embrittlement. Unfortunately, with the methods of treatment commonly used, the troubles with foaming have increased. This was clearly illustrated by the following statement made in 1943 in an American Railway Engineering Association (A.R.E.A.) Bulletin(6): "A generation or so ago, with little water treatment, the major action of dissolved solids was to form scale, and foaming was not a problem. By proper treatment of water supplies, scale is no longer a problem, but the introduction of alkaline sodium compounds has increased the foam-producing capacity of the water supplies."

Theory

<u>Causes of Foaming and Priming</u>. In 1924, Foulk (13) gave the causes for foaming and priming as being either physical or chemical, or a combination of both. In 1947, Place (35) stated that foaming is basically a result of chemical conditions, and boiler water concentration and composition are

the important factors involved.

Physical Factors. Foulk (13) listed the physical factors as:

1. The design and operation of the boiler. The more complex the interior (tubes, stay bolts, etc.) the more likely it was to foam.

2. The smaller the steam space the more likely that water would be carried over with the steam.

3. Violent ebullition might occur for a few seconds from the sudden evolution of steam following a period of superheating. A similar situation might occur when a piece of scale falls from the tubes and hot water comes in contact with red hot metal. Rapid opening of the steam valve might have the same effect.

High pressure boilers are less likely to foam than low pressure ones. However, the American Boiler Manufacturers Association (33), based on experience, has decreased the permissible concentration of dissolved solids in boiler water with increased pressure.

Chemical Substances: According to Foulk (11), substances that caused foaming were: organic matter, impurities, oily matter, soap, saline matter, alkalies, and suspended solids.

Boilers. Joseph and Hancock (29) stated that behavior in experimental boilers and commercial boilers showed good agreement. Foulk and Brill (17) reported that exact agreement between laboratory and commercial boilers was not always the case. In 1939, Foulk and Ryznar (21) experimented with two different types of experimental boilers -- a water tube boiler and a cylindrical boiler. They found that up to concentrations of 40,000 parts per million sodium chloride, the foam height in each case was essentially the same. However, they stated that only a long series of experiments could determine whether the behavior of the water in experimental and commercial boilers was the same.

Priming Values of Salt Solutions. In 1935, Foulk and Brill (17) used a water tube experimental boiler to determine the concentration when carry-over began of solutions of pure compounds. The final averages of the concentration at which various pure salt solutions began to prime are shown in Table I, page 8.

In 1938, Foulk and Ulmer (22) used the same boiler as Foulk and Brill (17) to determine the concentration at which various pure salts began to prime. The results of their findings are shown in Table II, page 10.

Surface Tension. According to Jacoby and Thompson (28), "When a substance dissolves in a liquid, it is generally found to be adsorbed in the liquid surface. If its concentration in the surface is greater than in the body of the liquid, it is said to be positively adsorbed, and the

Table I

Priming Values of Pure Salt Solutions

Substance in Solution	Concentration of Dissolved Solids When Priming Began ppm
Sodium Chloride	4235
Sodium Carbonate	3946
Sodium Hydroxide	3151

Foulk, C. W. and Brill, H. C. Solid Matter in Boiler Water Foaming, III. Effect of Calcium Carbonate and Magnesium Hydroxide Precipitated Inside the Boiler. Ind. Engr. Chem., 27, 1430-5. (1935).

surface tension of the liquid is lowered. If its concentration in the surface is less than in the body of the liquid, it is said to be negatively adsorbed and the surface tension is increased. In both cases a film may be formed, and both conditions may contribute to film stability. In other words, although foaming is usually associated with a lowering of surface tension, foaming is not actually dependent upon surface tension.

"Dissolved substances exerting a film-stabilizing action are generally conceded to be surface active, which means that they tend strongly to concentrate in the surface layer and thereby modify its properties. The stabilizing effect of dissolved substances, while not dependent upon surface tension, is associated mainly with a lowering of surface tension since they have no appreciable effect on mechanical properties such as surface viscosity."

In 1931, Foulk and Miller (20) experimented with surface tension in respect to foam height and per cent film formation. Both static and dynamic surface tension were measured. Dynamic surface tension meant a measurement made on the surface within a small fraction of a second after the formation or extension of the surface. Such measurements were made by determining the distance between the nodal points on a stream flowing from an elongated orifice. The measurements were made within a small fraction of a second

Table II

Priming Values of Pure Salt Solutions

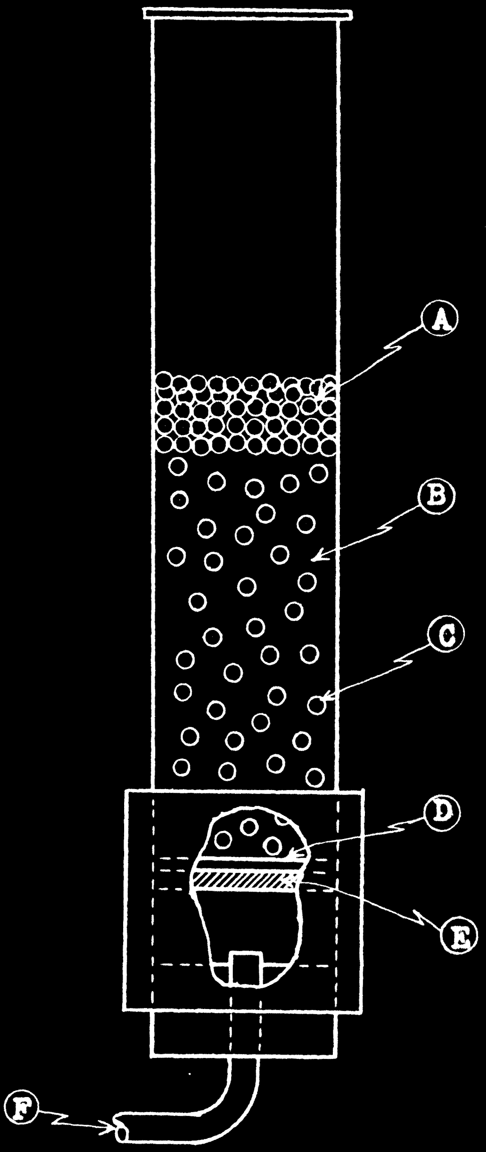
Substance in Solution	Concentration of Dissolved Solids When Priming Began ppm
Sodium Aluminate	5619
Sodium Chloride	4274
Sodium Carbonate	3946
Sodium Hydroxide	2988
Sodium Sulfate	2960
Calcium Chloride	2886
Sodium Phosphate	2566

Foulk, C. W. and Ulmer, Richard. Solid Matter in Boiler Water Foaming, IV. Additive Effects of Salts and Behavior of Gelatinous Precipitates. Ind. Engr. Chem., 30, 158-60. (1938).

after the formation of the surface. Static surface tension was measured after there had been time for the difference in concentration between the surface and the bulk of the solution to establish itself.

Per Cent Film Formation. The apparatus as shown in Figure No. 2, page 13, was used by Foulk and Miller (20) for studying the behavior of two bubbles in contact in a solution. It consisted of a bent tube, A, opening under a small glass bell, B, so placed that a bubble issuing from the tube would be caught and held in such a way that a second issuing bubble would touch it. The bubbles would exhibit only one of two possible behaviors. On touching each other they could either coalesce to form one larger bubble, or they would not coalesce but would roll past or flatten against each other. Per cent film formation was the per cent of pairs of bubbles that failed to coalesce under the same conditions.

The Dynamic Foam Meter used by Foulk and Miller (20), as shown in Figure No. 1, page 12, was designed by Hansley (25). It was an arrangement for blowing air through a porous septum into a column of liquid. The air was filtered through cotton wool and passed through soda lime to remove carbon dioxide. The upper zone, A, consisted of true foam and the lower zone, B, of a column of liquid through which air bubbles rose. The height of the foam zone was



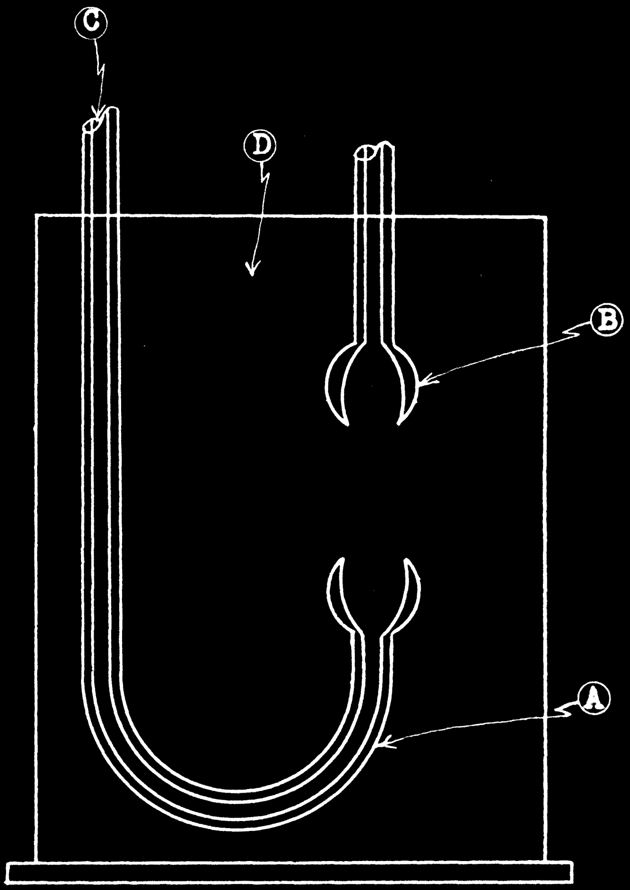
LEGEND

A Foam Zone
B Liquid Column
C Air Bubble
D Porous Septum
E Soda Lime
F Air Inlet

Figure 1

Dynamic Foam Meter

Foulk, C. W. and Miller, J. D. Experimental Evidence in Support of the Balanced Layer Theory of Liquid Film Formation. Ind. Engr. Chem., 23, 1283-8, (1931).



LEGEND

A Bent Tube
B Glass Bell
C Air Inlet
D Liquid

Figure 2

Apparatus for Determination
of Per Cent Film Formation

Foulk, C. W. and Miller, J. D. Experimental Evidence in Support of the Balanced Layer Theory of Liquid Film Formation. Ind. Engr. Chem., 23, 1283-8, (1931).

proportional to the stability of the foam bubbles, or film, and to the rate at which the foam bubbles were moving up the tube.

By use of the Dynamic Foam Meter and Bubble Testing Apparatus, Foulk and Miller (20) experimented with several salts, as shown in Table III, page 15, and found that:

1. The more concentrated the salt solution:
    a. The greater the difference between static and dynamic surface tension.
    b. The greater the foam height.
    c. The greater the per cent film formation.
2. The dynamic surface tension of positively adsorbed salts was greater than the static surface tension.
3. The dynamic surface tension of negatively adsorbed salts was less than the static surface tension.
4. Solutions containing both positively and negatively adsorbed salts tend to cancel the foaming tendencies of each other by producing equality of concentration between surface and mass of the solution.

Figure 3, page 16, shows graphically the relationship of molar concentration versus the reciprocal of the foam height as shown in Table III, page 15. The reciprocal of the foam height was used in order to produce curves that were similar to those found in this investigation.

Table III

Effect of Concentration Upon Difference Between Static and Dynamic Surface Tension, Foam-Zone Height, and Percentage Film Formation.

	Surface Tension				
Molar Conc.	Static dynes per cc.	Dynamic dynes per cc.	Difference dynes per cc.	Foam-Zone Height cms.	Film Formation %
Sodium Sulfate (Negatively Adsorbed)					
1.0	74.9	72.6	2.3	7.6	82
0.8	74.7	72.4	2.3	6.5	69
0.6	73.9	72.5	1.4	6.1	53
0.4	73.5	72.4	1.1	5.4	37
0.2	73.0	72.3	0.7	3.2	16
0.05	72.3	72.2	0.1	1.6	4
Sodium Chloride (Negatively Adsorbed)					
1.0	73.8	72.5	1.3	5.6	44
0.8	73.3	72.3	1.9	5.4	35
0.6	72.9	72.3	0.6	5.1	25
0.4	72.5	72.2	0.3	5.1	17
0.2	72.4	72.2	0.2	2.8	8
0.05	72.2	72.2	0.0	1.9	1
Sodium Sulfocyanate (Positively Adsorbed)					
1.0	71.2	71.6	0.4	4.8	28
0.8	71.5	71.7	0.2	3.9	22
0.6	71.5	71.8	0.3	2.3	17
0.4	71.7	71.8	0.1	1.2	9
0.2	71.9	72.1	0.2	1.2	2
0.05	72.3	72.2	+0.1	1.1	0.3

Foulk, C. W. and Miller, J. D. Experimental Evidence in Support of the Balanced Layer Theory of Liquid Film Formation. Ind. Engr. Chem., 23, . 1283-8, (1931).

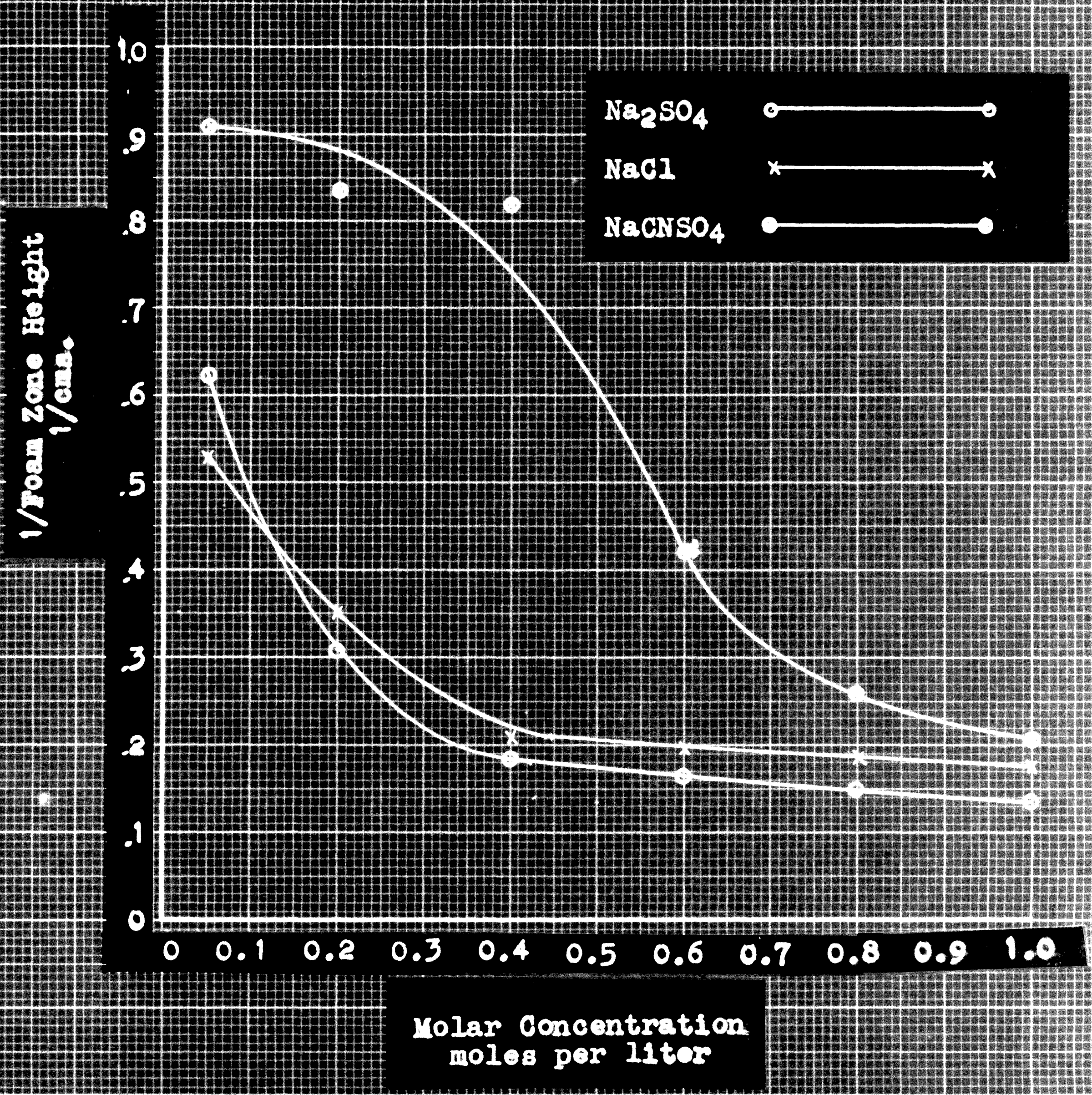


Figure 3

Molar Concentration versus 1/Foam Zone Height

Table III, page 14, Foulk, C. W. and Miller, J. D. Experimental Evidence in Support of the Balanced Layer Theory of Liquid Film Formation. Ind. Engr. Chem., 23, 1283-8, (1931).

Bubble Stabilization. In 1933, Foulk and Grove (18) advanced the idea that an increase of the stability of the bubbles, which in a way was similar to the stabilization of emulsions, was presumably caused by the action of electric double layers surrounding the individual bubbles. In 1938, Adams (1) expressed the opinion that the stabilization of the bubbles might depend on the building up of insoluble crystalline films such as carbonates, hydroxides, or sulfates, precipitated around the bubbles by the process of evaporation.

In 1944, Cassel (9) stated that "the question as to why the presence of electrolyte in the water under other-wised unchanged conditions enhances the formation and stabilization of more numerous bubbles than occur in less concentrated solutions has not yet been satisfactorily answered."

Balanced Layer Theory of Film Formation. In 1929, Foulk (14) stated that "in solutions, the solute is either more or less concentrated in the surface layer than in the interior of the liquid. Now since diffusion pressure tends to produce and maintain uniformity of concentration throughout a solution, this difference in concentration between the surface and the mass of the liquid must result from a movement of a portion of the dissolved matter against diffusion pressure; that is, work is done by the system against diffusion pressure, and therefore, if equality of concentration between surface and interior is to be restored, work must be performed on the system. In other words, such a system will resist a force tending to bring about an equality of concentration, or expressed in simpler terms, it will resist a tendency to mix the surface layer with the rest of the liquid.

"If then, two surfaces of a solution are made to approach each other under the urge of some small mechanical force, a resistance will be set up when the two surfaces become very close together because pushing the two surfaces together has a tendency to mix them. If the mechanical force is not too great, an equilibrium will be reached -- the force pushing the two surfaces together will be balanced by the physico-chemical forces tending to maintain the two layers at each surface. The net effect is the formation of a thin film of liquid with two layers of unequal concentration on each side, or the film can equally be pictured as a three-layer system in which the two outside layers have the same concentration, but differ from that of the inside layer."

In 1931, Foulk and Miller (20) attempted to depict the two cases of surface-bubble formation as shown in Figure 4, page 19. A, is a solution exhibiting negative adsorption of dissolved matter in the surface, and, B, is one showing positive adsorption. The light hatching around the

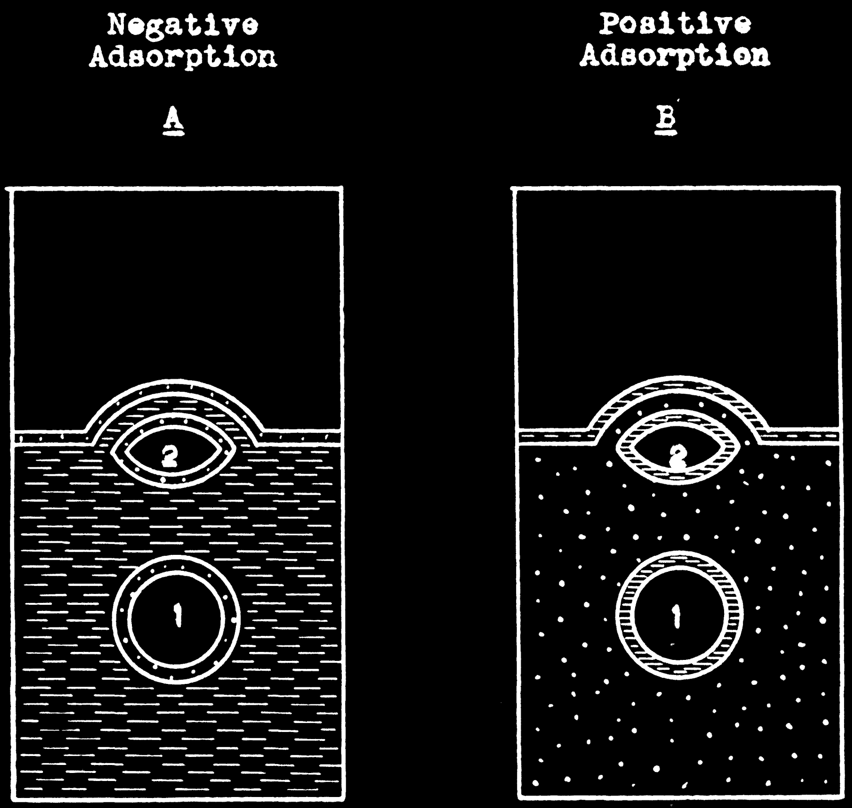


Figure 4

Surface-Bubble Formation

Foulk, C. W. and Miller, J. D. Experimental Evidence in Support of the Balanced Layer Theory of Liquid Film Formation. Ind. Engr. Chem., 23, 1283-8, (1931).

interior of bubble 1, represents, on an exaggerated scale, the interior thin layer of less concentration than that of the mass of liquid. At 2, this bubble is represented as having risen to the top and having pushed up a portion of the surface layer, also less concentrated than the bulk of the solution. Between these two surface layers is a thin layer of the solution of the bulk concentration. The two surface layers are pictured at 2, as having ceased their approach to each other because any further approach would result, in effect, in mixing them; that is, it would cause uniform concentration of the three layers, the two surfaces, and the interior one of bulk concentration. This tendency to mix is resisted by the physico-chemical forces which brought about the differences in concentration, and consequently a film is formed. Exactly the same set of conditions is pictured at B, except that positive adsorption is exhibited at 1. At 2, there are again two surface layers differing in concentration from the bulk of the solution, and between them is one of bulk concentration.

In 1946, Place (34) stated that the majority of carry-over problems boiled down to control of foaming in the boiler. At low ratings and with large diameter drums, sufficient time is allowed for destruction of the foam films and liberation of the entrapped steam and foam, and carry-over may not become a problem, even with high boiler water concentrations, and with considerable foam generated in the boiler. At higher ratings and with smaller drums, the rate of foam generation tends to exceed the rate at which the foam films can be destroyed and boiler water concentration limits are usually lower.

Theory of Carry-over. In 1947, Mumford (32) offered a theory for carry-over based on the idea that chemicals in water from which steam is made are concentrated in a film surrounding the steam bubble and that operating pressure and chemical concentration are related to steam contamination. His belief was that the soluble material must remain undissolved in the liquid and most likely concentrated in the film surrounding the steam bubble, to a degree dependent upon the size of the bubble and the thickness of the film. The surface tension rises with the concentration of dissolved matter and the film strength could be high even at the high temperatures accompanying high pressures. Little actual knowledge was available on the subject of bubble diameter, but Mumford stated that bubble diameter should decrease with increased pressure because the degree of concentration, and, therefore, the surface tension increases with pressure. His theory was that strong films would be formed around bubbles of steam and the film strength would increase rapidly with increase in pressure even in dilute boiler waters. The foregoing would appear to be confirmed by the fact that the American Boiler Manufacturers Association (33), based on experience, decreased the permissible concentration of dissolved solids in boiler water with increase in pressure as shown in Table IV, page 23. These recommended limits for solids are not necessarily exactly applicable to each individual case. They are limits of a general nature -- providing a good starting point.

Effect of Undissolved Solids. Foulk (13) experimented on the stabilization of foams by solid matter in solutions boiling at atmospheric pressure. At least 100 trials were made with various kinds of insoluble powders -- pumice, sulfur, pyrolusite, bone black, galena, boiler scale, precipitated calcium carbonate, and lime stone. When the above substances were boiled in distilled water, no appreciable foaming was observed. If solutions of sodium salts were used instead of distilled water, it was found, "when present in sufficient concentrations" any one of the sodium salts together with any one of the insoluble materials mentioned above produced a white foam. Among the solids tried, powdered boiler scale and limestone were found to be most effective as foam producers.

In 1927, Joseph and Hancock (29) recorded experiments with a small laboratory boiler operated at pressures over 100 pounds and also experiments with commercial boilers. In all cases their evidence showed that the presence of finely divided solid matter had no effect on the foaming and priming of the boilers. On the other hand, the Water Service Committee of the American Railway Engineers Association for 1929 (5)

Table IV.

Recommended Limit of Dissolved Solid Concentration in Boiler Water

Pressure psi gage	Dissolved Solids ppm
0 - 300	3500
301 - 450	3000
451 - 600	2500
601 - 750	2000
751 - 900	1250
901 -1500	1000

Nieland, W. L. Control and Economics of Boiler Blowdown. Combustion, 16, 35, (1944).

gave data in the operation of certain commercial boilers which showed that the presence of solids in the boiler increased the water in the steam due to foaming and priming.

Foulk (14) found that different kinds of solid matter stabilized the foams of salt solutions in greatly different degrees, and some kinds of solid matter lost their foam-stabilizing properties on prolonged boiling in a salt solution.

In 1934, Foulk and Whirl (23) found that the usual boiler solids, though initially possessing high foam-stabilizing properties, rapidly lost them at the high temperatures (pressures) of steam boilers. Foulk called it "aging of the sludge." They said that the cause of this loss of foam-stabilizing power is a progressive lessening of the solid matter's resistance to wetting. If the solid wetted instantly, as in the case of ground flint, the particles sank at once, and therefore, did not collect on the bubble films and stabilize the bubble. This resistance to wetting might have been due to traces of oil in the solids or might have been a natural property of the material. The density of the solids played a minor role in the resistance to wetting.

<u>Foaming in Size Separation by Froth-flotation</u>. In 1942, Schuhmann (37) stated that "separation of minerals by the froth-flotation process involves two essential steps: (1) chemical preparation of the mineral surfaces to make the particles of one mineral air-adherent while leaving the remaining

mineral particles water adherent, and (2) production of a froth from the water suspension of ore particles and separation of this froth from the suspension. Badger and McCabe(7) stated that to obtain a persistent froth it is necessary to increase the viscosity of the bubble films. Some agents used as frothers are, cresylic acid, pine oil, other soft and hardwood oils, and special mixtures of alcohols and ketones. The agent concentrates the mineral particles so as to form an interface that is more viscous than either the frothing agent or the water or the mixture of the two. It is the presence of the solid matter that contributes to the viscosity of the bubble films in the froth. The material in this paragraph was inserted only for information, and was not used in this investigation.

Evidence For and Against Theory that Suspended Solids Increase Foaming. In 1935, Foulk and Brill (17) found evidence both for and against the theory that suspended solids increase foaming. Calcium carbonate formed in the boiler by the decomposition of the bicarbonate decreased foaming. Calcium carbonate precipitated by pumping sodium carbonate into calcium chloride solution in the boiler had no effect on foaming. Calcium carbonate precipitated by pumping calcium chloride into sodium carbonate solution in the boiler increased foaming, but the precipitate lost this property after several hours in the hot boiler.

In 1938, Foulk and Ulmer (22) found that calcium carbonate in presence of sodium chloride had little effect on foaming; aluminum hydroxide, precipitated outside the boiler, increased foaming; ferric hydroxide, precipitated outside the boiler, increased foaming; and magnesium hydroxide, precipitated in the boiler in the presence of an excess of sodium hydroxide, reduced foaming.

Foulk and Ulmer (22) stated that "an inspection of the evidence offered by Foulk and Ulmer, Joseph and Hancock, Holmes, Peters, Foulk and Whirl, and Foulk and Brill, shows that the effect of suspended solids on the foaming of boiler water was not always the same. By experimenting with one kind of solid at a time, it was found that some kinds increased foaming and others had no effect or actually decreased it. It was also shown that several kinds of solids which at first increased foaming, lost that property while in the boiler, and that the speed of such loss was greater, the higher the temperature of the water. These facts have been true both for solids introduced from the outside and for solids precipitated inside the boiler."

Theory of Antifoams. In 1924, Foulk (13) stated that "the destruction of foam is due to the destruction of the stabilizing action of the solid matter rather than to any change in the surface tension." This theory was supported by the statement in an American Railway Engineers Association Bulletin (6) which stated, "that there is no evidence that the action of antifoam compounds is based on surface tension changes."

In 1944, Cassel (9) reported that foam inhibiting agents do not work at the water-steam interface, supposedly facilitating the coalescence of bubbles, but at the heating surfaces and the surface of suspended particles. "In other words, it appeared that by properly conditioning these interfaces, the number of bubble nuclei could be drastically reduced so that fewer but larger bubbles are formed before coalescence could be of significance." However, Cassel does not give a method for properly conditioning the interfaces.

According to Jacoby and Thompson (28), all boiler antifoam materials of greatest value possess at least two properties in common -- surface activity and substantial insolubility in water. The effect of soluble surface active substances on liquid films showed the mechanism of the rupture of a doublefaced film as consisting of the thinning of this film due to a drainage of liquid from it as shown in Figure 5, page 28. The collapse of a foam bubble caused by this drainage and thinning may be accompanied by the sudden formation in the adsorption layers of dehydrated aggregates of the surface active material. This sudden "coagulation" of molecules and formation of dehydrated aggregates, which are unable to redisperse themselves on the bubble film is termed by the physical chemist as "syneresis." This syneresis, when the bubble film is thinning, causes the surface active material to take

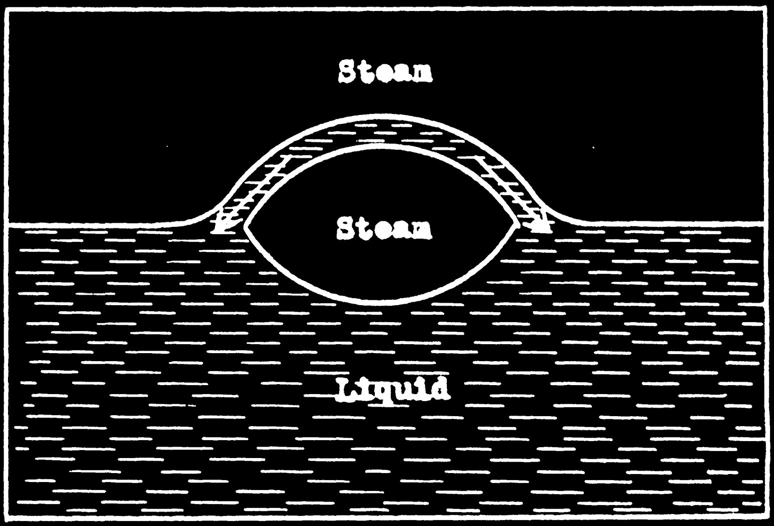


Figure 5

Thinning of Bubble Film
due to Liquid Drainage

Jacoby, A. L. and Thompson, W. H. Improvement of Steam Quality. Paper presented at the Seventh Annual Water Conference of the Society of Engineers of Western Pennsylvania. Pittsburg, Pennsylvania, January 6-8, 1947.

the form of islands or patches on the film. The continuity of adsorption layers and homogeneity of the bubble film are thus destroyed, high local differences in surface tension result, and the bubble is broken. It was believed by Jacoby and Thompson (28) that this phenomenon of syneresis was responsible for the foam-destroying action of antifoam materials.

According to Jacoby (27), the theory of antifoam action referred to above suggests that hydrogen bonding promotes antifoam action by enhancing the syneretic effect and creating a greater tendency for the monolayer to reach the "solid or brittle" state.

Antifoam Compounds. In 1924, Foulk (13) stated that castor oil was the only known antifoam compound. However, in 1944, Williams (42) stated that amide types of antifoams had been found to give better results than the castor oil compounds. In 1945, Gunderson (24) stated that surface-active compounds which are good antifoam agents included: (1) compounds containing quaternary groups, e.g. tetracetylammonium bromide; (2) di- or trialkylated amines; (3) acylmono - or dialdyl amides; (4) esters with at least two chains of 10 carbon atoms each, such as dodecyl ester of lauric acid or 9-octadecenyl ester of oleic acid.

Industrial Purification of Water

The purification of water for steam production (12) consists in removing or destroying the scale forming and corrosive constituents. It happens that those impurities that destroy soap, or make the water hard, are also the ones that cause scale in steam boilers, and therefore the removal of them is the most important kind of purification. These impurities are the dissolved calcium and magnesium compounds, and the elimination of them from water is called "softening."

Lime-Soda Ash Process. All of the carbonate or temporary hardness constituents and that part of the permanent hardness due to magnesium compounds can be precipitated from water by means of lime (calcium oxide). The remaining hardness can then be precipitated by means of soda ash (calcined sodium carbonate).

Reactions with Lime.

$$CaO + H_2O = Ca(OH)_2$$

$$H_2CO_3 + Ca(OH)_2 = CaCO_3 + H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$$

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$$

Reactions with Soda Ash.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

If the calcium is combined as sulfate or nitrate, sodium sulfate or sodium nitrate will be left in the water instead of sodium chloride.

Calculation of Required Amount of Chemicals. According to Hoover (26), the amount of chemicals needed for treatment of boiler feed water are calculated by use of the following formulas:

Lime.

Free and half bound CO_2 (ppm) x 0.0106 + total Mg (ppm) x 0.019 = lbs. CaO/1000 gallons.

Free and half bound CO_2 is equal to approximately 44 per cent of the methyl orange alkalinity.

Soda Ash.

Non-carbonate hardness (ppm) x 0.009 = lbs. Na_2CO_3/1000 gallons.

Alum.

1/4 lb. per 1000 gallons of clear water. If water is not clear, additional alum should be used. The maximum for very muddy water should be 1/2 lb. per 1000 gallons.

Methods of Analyses. The American Public Health Association (2)(3)(4) outlined the standard water analyses for testing of boiler water. These tests are outlined in the Experimental Section of this thesis on page 48 .

III. EXPERIMENTAL

Purpose of the Study

The purpose of this investigation was to determine the effect of various degrees of lime and soda ash treatment on the foaming characteristics of Virginia Polytechnic Institute boiler water and New River boiler water, at atmospheric pressure and at a constant evaporation rate.

Boiler water foaming has long been a major problem in the production of steam for railroad locomotives. Not only is it costly to remove part of the boiler water by blowdown at intervals in order to keep the concentration of the dissolved solids below the foaming concentration, but it is still more costly if the foam is allowed to be carried over with the steam into the mechanism of the machinery. The lime-soda ash method of treatment was selected because of its relative cheapness and its wide use for treatment of water for railroad locomotives.

Plan of Investigation

The following plan of investigation was followed:

1. A review of the literature was made to study previous work that had been done on the study of foaming, present knowledge of causes of foaming, and methods for the reduction or elimination of foaming, in boiler waters.

2. By use of standard glass laboratory equipment, apparatus was assembled to simulate a steam boiler. (Figure 6, page 40.)

3. The relatively hard well water used at Virginia Polytechnic Institute was collected from the tap in the laboratory, and the relatively soft New River water was collected from the Norfolk and Western Railroad's boiler plant at Radford, Virginia.

4. The raw water was tested for hardness, alkalinity, chlorides, and dissolved solids; and the amount of lime and soda ash needed for the desired treatment was calculated and added to the raw water in the treating. Individual treatments were made for per cent alkalinities of approximately 10, 15, 20, 25, 30, and 35.

5. Twenty-four hours after treatment, the water was tested for hardness, alkalinity, chlorides, and dissolved solids; and the per cent alkalinity, or degree of treatment, was calculated. The water was always treated to at least 10% alkalinity to insure against corrosion, embrittlement,

cracking, and scale forming constituents.

6. The treated water was boiled in the simulated steam boiler at atmospheric pressure, constant volume of 500 ml., and at a constant evaporation rate of 20.8 ml./min., until the foam layer was 3¼ inches which was sufficient height for the foam to be carried out of the flask through the steam outlet. The process was then stopped and the boiler water was allowed to cool to room temperature.

7. The boiler water was tested for hardness, alkalinity, chlorides, dissolved solids, and suspended solids; and the per cent alkalinity was calculated.

8. The foaming tendencies of Virginia Polytechnic Institute boiler water and New River boiler water were compared, based on the dissolved solids concentration of the boiler water with respect to the per cent alkalinity.

9. Mineral analyses of the raw and treated waters were made for the purpose of attempting to correlate the composition of the water with its foaming tendency.

10. The results of this investigation were compared with results of previous investigations.

Materials

Acid Sulfuric. A. C. S. std., sp. gr. 1.84, assay 95-96%, lot No. E-207018. Used for preparation of standard solutions for alkalinity determinations. J. T. Baker Co., Phillipsburg, New Jersey.

Acid Nitric. A. C. S. Std., sp. gr. 1.42, assay 70%, lot No. 209027. Used in the mineral determination. General Chemical Co., New York, New York.

Acid Hydorchloric. A. C. S. Std., sp. gr. 1.1878, assay 37%, lot No. 70421. Used in the mineral determination. E. I. Du Pont de Nemours and Co., Inc., Grasselli Chemicals Dept., Wilmington, Delaware.

Acid Oxalic. Crystals, C. P., lot No. 51846. Used in the mineral determination. J. T. Baker Co., Phillipsburg, New Jersey.

Ammonium Hydroxide. 28% NH_3, code 1293, lot No. E209002. Used in the mineral determination. General Chemical Co., New York,New York.

Ammonium Carbonate. Powder, C. P., lot No. 38. Used in the mineral determination. General Chemical Co., New York, New York.

Alum. Commercial Grade, 17% Al_2O_3. Used as the coagulent for the treated water. Davidson Chemical Co., Columbus, Ohio.

Barium Chloride. Crystals, C. P., lot No. 32729. Used in the mineral determination. Merck & Co., Rahway, New Jersey.

Barium Hydroxide. Crystals, C. P., lot No. 2647. Used in the mineral determination. J. T. Baker Co., Phillipsburg, New Jersey.

Castile Soap. Powder, C. P., lot No. 42345. Used for preparation of standard soap solution for hardness tests. J. T. Baker Co., Phillipsburg, New Jersey.

Calcium Carbonate. Powder, C. P., lot No. 42806. Used for preparation of standard hardness solution. Merck & Co., Rahway, New Jersey.

Gas. Pyrofax. Used as fuel for Fisher burner. Natural Gas Distributors, Roanoke, Virginia.

Lime. Commercial Grade, "Chemical Hydrate", 93.1% calcium hydroxide. Used for water treatment. National Gypsum Co., Bellefonte, Pennsylvania.

Alcohol. Methyl, Absolute Refined, code No. 1214PB. Used in preparation of standard soap solution for hardness tests. Phipps & Bird Co., Richmond, Virginia.

Paint. Aluminum, ready mixed, No. 470, Rust Preventative. Used for painting the inside of the treating tank. Rust Oleum Co., Evanston, Illinois.

Phenolphthalein. Solution No. 222, lot No. 119. Used as an indicator in water tests. National Aluminate Corp., Chicago, Illinois.

Potassium Chromate. Crystals, C. P., lot No. 112743. Used in preparation of indicator for chloride tests. J. T. Baker Co., Phillipsburg, New Jersey.

Methyl Orange. Solution. Used as an indicator in water tests. General Chemical Co., New York, New York.

Soda Ash. Powder, Commercial Grade, 99,6% sodium carbonate. Used for water treatment. Wyandotte Chemicals Corp., Wyandotte, Michigan.

Sodium Carbonate. Powder, C. P., lot No. 41246. Used in preparation of standard dissolved solids solutions. J. T. Baker Co., Phillipsburg, New Jersey.

Sodium Chloride. Crystals, C. P. lot No. 9645. Used in preparation of standard dissolved solids solutions. J. T. Baker Co., Phillipsburg, New Jersey.

Sodium Ammonium Phosphate. Crystal, C. P. lot No. 6342. Used in the mineral determination. J. T. Baker Co., Phillipsburg, New Jersey.

Silver Nitrate. Crystals, C. P., lot No. 11146. Used in the chloride determination. J. T. Baker Co., Phillipsburg, New Jersey.

Water. Virginia Polytechnic Institute. Relatively hard well water which had been treated with chlorine. Obtained from tap in laboratory and used as raw water for treatment with lime and soda ash for use as boiler feed water.

Water. New River. Relatively soft river water which had no previous treatment. Obtained from Norfolk and Western Railroad Boiler Plant at Radford, Virginia. Used as raw water for treatment with lime and soda ash for use as boiler feed water.

Water. Distilled. Used to prepare all standard solutions used in this investigation. Stokes Still, copper lined. Chemistry Stock Room.

Apparatus

Flask. Pyrex,round bottom, 1000 ml. Used as the boiler in the laboratory apparatus for foaming test of boiler water. (Figure 6, page 40.)

Funnel. Pyrex, long stem. Used as feed inlet to flask in laboratory apparatus for foaming tests of boiler water.

Funnel. Separatory, 250 ml. Used as feed regulator to flask in the laboratory apparatus for foaming tests of boiler water.

Condenser. Pyrex, 24 inches long. Used to condense steam from the flask in the laboratory apparatus for foaming tests of boiler water.

Nalcometer. Model CMA-4, v. 110 a.c., cycles 25-60, serial No. 1894. Used for the determination of total dissolved solids in boiler waters. Manufactured by National Aluminate Co., Chicago, Illinois.

Oven. Drying, electric, Serial No. 100-2761, Cat. No. 1250, Temp. range 35 to 180° C., v. 110, amps. 5.5, cycles 60, watts 100, phases 1, Type A. Used for evaporation of water samples. Manufactured by Precision Scientific Co., Chicago, Illinois.

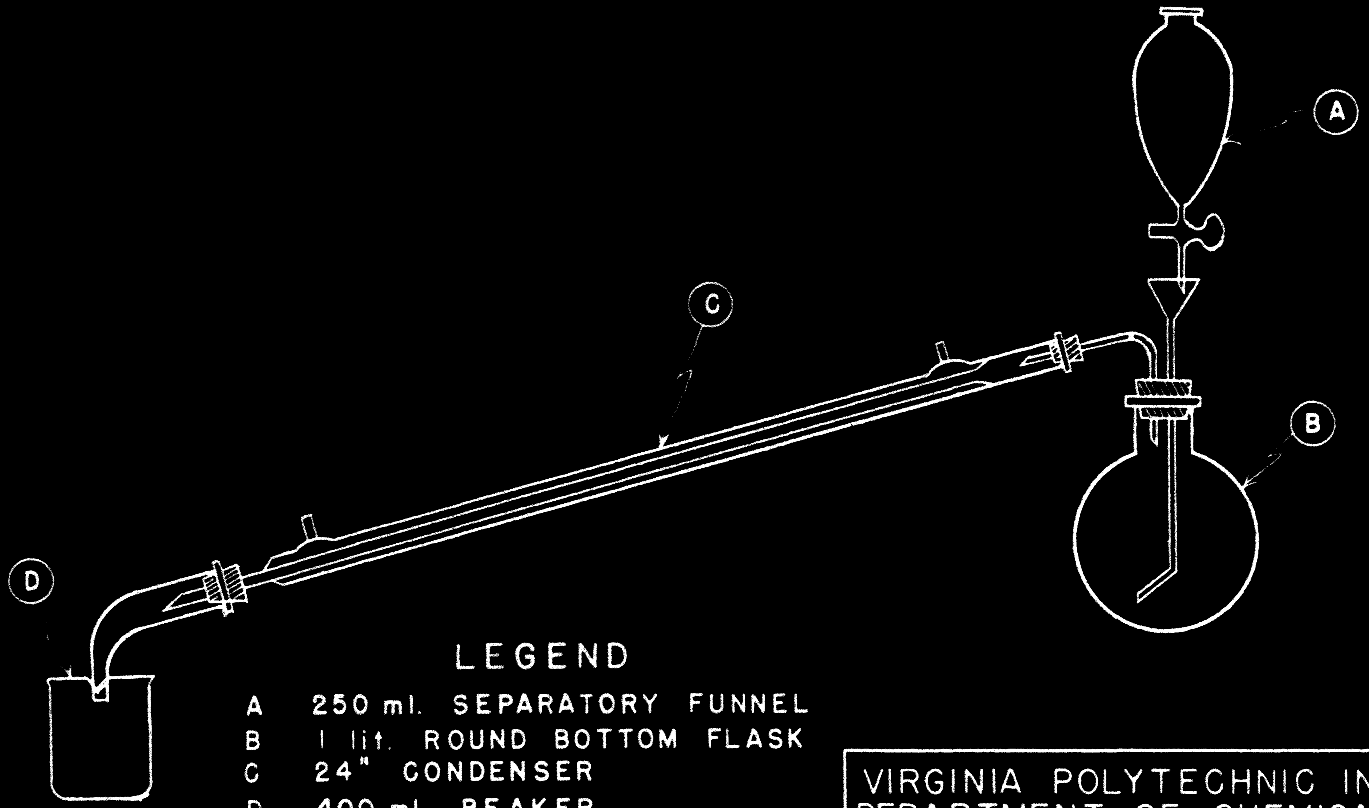
Balance. Chainweight, Type DLB No. 15345. Used to weigh all samples in analytical work. Manufactured by William Ainsworth and Sons, Denver, Colorado.

Furnace. Electric, v. 220 a.c., maximum temp. 1350° F. Used for igniting samples in mineral analysis. Manufactured by Allied Cooley Electric Corp., Indianapolis, Indiana.

Plate. Hot, round, Serial No. ROPH 7066, v. 120, watts 660. Used for heating samples in the water analysis procedure. Manufactured by Fisher Scientific Co., Pittsburgh, Pennsylvania.

Tank. Treating, steel, 30 gallon capacity. Used for treatment of raw water. Obtained from the Chemical Engineering Unit Operations Laboratory.

Burner. Fisher. Used to heat water in flask of the foaming test apparatus. Manufactured by Fisher Scientific Co., Pittsburgh, Pennsylvania.



LEGEND

A 250 ml. SEPARATORY FUNNEL
B 1 lit. ROUND BOTTOM FLASK
C 24" CONDENSER
D 400 ml. BEAKER

VIRGINIA POLYTECHNIC INSTITUTE
DEPARTMENT OF CHEMICAL ENGR.
Blacksburg, Virginia

LABORATORY ASSEMBLY FOR
FOAMING TESTS OF BOILER WATER

Drawn by: PEH	Date: June 12, 1948
Checked by: RAF	Figure: 6
Approved by: RAF	Scale: None

Rack. Funnel, wooden. Used to hold funnels for filtrations in analytical determinations.

Paper. Filter, Scimatco, No. 9-790, 11.0 cm., ash 0.0008 gram. Used to filter precipitate in analytical determinations. Manufactured by Fisher Scientific Co., Pittsburgh, Pennsylvania.

Dishes. Evaporating, porcelain, Coors, 3" diameter. Used for evaporation of water samples.

Crucibles. Porcelain, 20 ml. capacity, Coors. Used to ignite samples in the analytical determinations.

Thermometer. Glass, -15° to 360° C., 1° graduations. Used to read temperature of electric drying oven. Brothcom, New York, New York.

Thermometer. Glass, with armor, 50° to 120° F., 1° graduations. Used to read temperature of water samples. National Aluminate Co., Chicago, Illinois.

Miscellaneous Equipment. Including ring stands, clamps, tripods, rubber tubing, rubber stoppers, cork stoppers, tongs, asbestos pads, tongs.

Miscellaneous Glassware. Including water bottle, indicator bottles, graduated cylinders, watch glasses, beakers, desiccator, volumetric flasks, gallon jugs, funnels, shaking bottles, burrettes, adapter, beakers.

Procedure

Construction and Assembly of Equipment

The equipment used in this investigation was divided into three major categories. These were: water treating equipment, apparatus used for foaming tests, and analytical equipment.

Water Treating Equipment. The water treating equipment consisted of a 30 gallon steel drum, which was first thoroughly cleaned and then painted with rust preventive aluminum paint. The tank was open at the top and a 3/8 inch water line from the tap was available either for use as raw water or for cleaning purposes. A 1/2 inch drain line from the bottom of the tank was connected to the floor drain. A 24 inch wooden paddle was used for agitation.

Apparatus for Foaming Tests. All of the pieces of apparatus used in the foaming test equipment were obtained from the chemical stock room. (Figure 6, page 40). All of the apparatus was supported by means of ring stands and clamps.

A one-liter, Pyrex, round-bottom flask was used as the simulated boiler, and was supported by a clamp at the neck of the flask. A No. 7, two-hole rubber stopper was inserted in the top of the flask. A funnel with a 10 inch stem was put into one of the holes in the stopper. A 45° bend was made in the stem, 1 inch from the end, which was inside the flask. The funnel was so placed that the end was approximately 1/2 inch from the bottom of the flask. In the second hole of the rubber stopper, a piece of 3 mm. inside diameter soft glass tubing was inserted so that it extended 1 inch down the neck of the flask. Two inches above the stopper, the glass tubing was bent at 105° and then extended 2 inches more. This served as the steam outlet and was connected by means of a No. 1, one-hole rubber stopper, to a 24 inch Pyrex water condenser, which was supported by a ring clamp.

A 250 ml. separatory funnel was supported by means of a ring clamp just above the funnel that extended down into the round bottom flask. The end of the stem of the separatory funnel extended 3/8 inch below the rim of the funnel.

Tap water was used as cooling water in the condenser and rubber tubing was used for both the inlet and outlet water. The rate of cooling water was approximately 2 liters per minute. The condensate was collected in a 400 ml. beaker, which was marked at 250 ml. A Fisher burner was used to heat the water in the round bottom flask, and rubber tubing was used for connecting the gas main to the burner.

Analytical Equipment. All of the pieces of equipment used in the analytical determinations, with the exception of the Nalcometer, were obtained from the chemical stock room. Burettes were supported on ring stands and held in place by means of burette clamps.

Collection of Water

Both Virginia Polytechnic Institute water and New River water were used in the foaming tests. Hence, two separate methods of conveying the water to the treating tank had to be devised.

Virginia Polytechnic Institute Water. As previously explained in this section under "Water Treating Equipment", a 3/8 inch water line from the tap was available to the top of the treating tank. The tank was initially scrubbed with water and then the tap water was turned on and allowed to run freely while the drain in the bottom of the treating tank was open. After five minutes, the drain valve was closed and the tank was allowed to fill to the desired level.

New River Water. New River water was collected from the Norfolk and Western Railroad's Stationary Boiler Plant at Radford, Virginia. The pumping station was located on the New River just opposite the city of Radford. Water was pumped from the New River to a large over-head storage tank which was connected by a pipe line to the boiler plant. The hose from which the water was collected was connected to this line. The hose was flushed for three minutes before any water was collected. Six five-gallon glass carboys were thoroughly cleaned and rinsed with the water before they were filled. They were transported to and from Blacksburg by automobile.

The treating tank was initially scrubbed with Virginia Polytechnic Institute water and then rinsed with approximately two quarts of New River water before filling to the desired level.

Sampling of Water

Raw water, treated water, and boiler water were sampled for testing purposes. Hence, three separate methods of sampling were employed.

Raw Water. A one gallon jug which had been previously cleaned both inside and out, and rinsed with the water to be sampled, was dipped into the treating tank immediately after it was filled to the desired level. The jug was filled one-third full with water from each of the bottom, middle, and top portions of the tank. Before samples were taken from the jug for testing purposes, the jug was shaken to insure uniform mixing.

Treated Water. A one gallon glass jug was thoroughly cleaned and rinsed with the water to be sampled. By means of a rubber siphoning tube, the jug was filled one-third full with water from each of the top, middle, and bottom portions of the tank. Before samples were taken from the jug for testing purposes, the jug was shaken to insure uniform mixing.

Boiler Water. After the foaming concentration had been determined, the boiler water was allowed to cool in the flask. Samples were removed by means of pipettes and at the same time, the flask was swirled in order to insure uniform mixing.

Determination of Foaming Point

After the treated water had been tested and found satisfactory for boiler use, one gallon was siphoned from the treating tank into a gallon jug by means of rubber tubing. Care was taken to keep the end of the tubing that was in the tank about three inches from the surface of the water. Care was also taken so as to disturb the water in the tank as little as possible to avoid causing the sludge that had settled on the bottom of the tank to rise and mix with the treated water.

A 500 ml. mark was made on the liter round bottom flask, B, as shown in Figure 6, page 40, and treated water added through the funnel up to this mark. 250 ml. of treated water was added to the separatory funnel, A, and the stop cock was closed. Cooling water from the tap was circulated through the condenser, C, and a 400 ml. beaker, D, with a 250 ml. mark, was placed so as to collect the condensate.

A Fisher burner was placed beneath the flask with the top of the burner 1½ inches from the bottom of the flask.

The gas was turned on and the time was recorded when the water began to boil. The stop cock on the separatory funnel was opened and the feed was regulated so as to keep the water at the same level in the flask. When 250 ml. had been evaporated, as indicated by the empty separatory funnel and the condensate level at the 250 ml. mark in the beaker, the time was recorded, the condensate beaker replaced with a similar empty beaker, and 250 ml. of feed water was added to the separatory funnel. The time difference was noted and recorded. The intensity of the flame and the rate of feed were adjusted so as to give an evaporation rate of 250 ml. per 12 minutes.

The phenolphthalein and methyl orange alkalinity tests were made on a 58.3 ml. sample of the distillate. This procedure was discontinued after the first few runs because no alkalinity was found in the condensate until actual carry-over of foam through the 3 mm. glass tubing that served as the steam outlet was observed,

More feed water was siphoned from the feed tank and boiling was continued. Constant evaporation rate was maintained by checking the level in the flask, feed rate, and condensate. The amount of water evaporated before the water in the flask foamed sufficiently to fill the entire space in the flask above the water with foam, varied from eight to forty liters -- depending upon the degree of treatment of the water.

When the foam reached sufficient height in the flask to be carried over through the steam outlet, the burner was removed from beneath the flask in order that the water would subside. The steam outlet was located 3½ inches above the water level in the flask. After approximately 15 seconds, the burner was replaced beneath the flask and boiling was continued. If the water again foamed sufficiently that carry-over was observed, the feed water and the gas were both turned off. If the water did not foam sufficiently for carry-over to be observed, the boiling was continued until carry-over was again observed.

The boiler water in the flask was allowed to cool to room temperature and was then tested as explained in the following section, "Testing of Water".

Testing of Water

Raw water, treated water, and boiler water were tested in the same manner except for slight differences explained herein. The symbols in parentheses following the name of the test are the standard symbols used for water analysis. (2)(3)(4)

Hardness (H). Fifty-eight and three tenths ml. of the water to be tested were measured into an 8-ounce shaking bottle. Standard soap solution was added from a burette in small amounts at a time, (prepared as shown on page 64) with vigorous shaking after each addition.

If a false end point or "Ghost Point" was found, it was recorded as this was the dividing line between the calcium and magnesium salts. The addition of soap solution was continued until a one inch lather was secured which would last for at least five minutes. The number of ml. of soap solution, minus 1.0 ml. as the lather factor, gave the total hardness of the water in grains per gallon in terms of calcium carbonate. The difference between the end point and the "Ghost Point" gave the hardness due to magnesium in grains per gallon in terms of calcium carbonate.

Phenolphthalein Alkalinity (P). Four drops of phenolphthalein indicator were added to 58,3 ml. of the sample in a white porcelain evaporating dish. N/50 sulfuric acid was added from a burette until the pink color disappeared. The amount of standard acid required to change the water from pink to colorless measured the hydroxides plus one-half the normal carbonates in grains per gallon in terms of calcium carbonate. In the case of the two raw waters, the addition of phenolphthalein indicator did not turn the sample pink, thus indicating only bicarbonates, and no hydroxides or normal carbonates present in the water. For boiler water, a 1/4 sample, or 14.75 ml., was used and the amount of N/50 sulfuric acid required was multiplied by 4 in order to get the phenolphthalein alkalinity in grains per gallon in terms of calcium carbonate.

Methyl Orange Alkalinity (M). The same sample from the phenolphthalein alkalinity determination was used, and two drops of methyl orange indicator were added and the sample turned yellow. N/50 sulfuric acid was added from a burette until the faintest pink coloration appeared. The methyl orange alkalinity, or total alkalinity, in grains per gallon calcium carbonate was equal to the total number of ml. of N/50 sulfuric acid added to the sample. For boiler water, the total amount of N/50 sulfuric acid required was multiplied by 4 in order to get the total alkalinity in grains per gallon in terms of calcium carbonate. The amounts of hydroxide, normal carbonates, and bicarbonates in the sample were determined by means of Table V, page 51.

Sodium Chloride (NaCl). One ml. of potassium chromate indicator was added to the same sample as used for the alkalinity determination. Standard silver nitrate solution was added from a burette until a reddish coloration was detected. The detection of the end point was facilitated by comparison of the color in the porcelain evaporating dish with that in a similar vessel containing the same quantity of indicator in 58.3 ml. of distilled water to which 0.3 ml. of standard silver nitrate solution had been added. The total number of ml. of standard silver nitrate solution used, minus 0.3 ml., was equal to the amount of sodium chloride in the sample in grains per gallon sodium chloride. In the case of the boiler water, the total number of ml. used, minus 0.3 ml.,

Table V

Relations between Alkalinity to Phenolphthalein and that to Methyl Orange in Presence of Hydroxide, Carbonate, and Bicarbonate.

Result of Titration*	Value of Radicle Expressed in terms of Calcium Carbonate		
	Hydroxide	Carbonate	Bicarbonate
$P = 0$	0	0	M
$P < 1/2\ M$	0	2P	M-2P
$P = 1/2\ M$	0	2P	0
$P > 1/2\ M$	2P-M	2(M-P)	0
$P = M$	M	0	0

*M = Total alkalinity in presence of methyl orange
P = Alkalinity in presence of phenolphthalein

Anon. "Standard Methods of Water Analysis", p. 36, American Public Health Association, New York, New York. (1933), 7th ed.

was multiplied by 4 in order to get the sodium chloride content in grains per gallon.

Dissolved Solids (DS). The water to be tested was filtered through a No. 9-790, Scimatco, 11 cm., filter paper. A 50 ml. sample was measured in a pipette and added to a preweighed evaporating dish which had been dried for one hour at 105° C. in the drying oven, and cooled in a desiccator. The sample was covered with a watch glass and placed in the drying oven and evaporated to dryness at 105° C. The evaporating dish was cooled in a desiccator and reweighed. The difference in weight multiplied by 1.166 gave the dissolved solid content of the sample in grains per gallon.

Dissolved Solids by Use of Nalcometer (DS). The Nalcometer was used only for the determination of dissolved solids in boiler water as it was found to be outside the limit of accuracy below 30 grains per gallon dissolved solids. Approximately 50 ml. of the sample to be tested was put into the test cylinder provided with the Nalcometer, and 2 drops of phenolphthalein were added to turn the sample pink. 2N sulfuric acid was added drop by drop until there was just the slightest pink coloration left in the sample. If too much acid was added, more of the sample was added in order to make the sample barely pink in color. The electrode was submerged in the test cylinder, and the temperature of the sample was determined by means of a 50° to 120° F. thermometer. The temperature reading was set on the T scale by means of the course and the fine adjustment knobs. The scale selector knob was turned to the II scale which has a maximum reading of 1000 grains per gallon dissolved solids, and the dissolved solid content was read directly from the II scale. If the reading on the II scale was below 150, the scale selector knob was turned to the I scale which has a maximum reading of 150 grains per gallon, and the dissolved solid content was read directly from the I scale.

The electrode must be completely submerged in the sample when the readings are taken. The theory of the Nalcometer is based upon the difference in electrical conductivity of salt solutions of different strengths. The sample does not have to be filtered first because the solid particles do not affect the electrical conductivity of the solution.

Suspended Solids. A 50 ml. sample of the water to be tested was measured in a 50 ml. pipette and added to a pre-weighed evaporating dish which had been dried for one hour at 105° C. in the drying oven, and cooled in a desiccator. The sample was covered with a watch glass and placed in the drying oven and evaporated to dryness at 105° C. The evaporating dish was cooled in a desiccator and reweighed. The difference in weights minus the difference in weights of the dissolved solid sample, multiplied by 1.166 gave the suspended solid content of the sample in grains per gallon. Duplicate samples were tested to check the accuracy of the results.

Per Cent Alkalinity (%M). Per cent alkalinity was the amount of excess alkalinity in the dissolved solid content of the water. It was calculated by the following formula:

$$\frac{\text{Total Alkalinity (M)} - \text{Hardness (H)}}{\text{Dissolved Solids (DS)} - \text{Hardness (H)}} \times 100 = \text{Per cent Alkalinity (\%M)}$$

In this investigation, per cent alkalinity was used as a standard for measurement of treatment excesses.

Treatment of Water

The water used in this investigation was treated only by the lime-soda ash method of treatment. Alum was used in each case as a coagulate.

Treatment with Lime. The amount of commercial hydrated lime (calcium hydroxide) used in each batch treatment was determined from the following formula:

Free and half bound CO_2 (ppm) x 0.0106 +

Total magnesium (ppm) x 0.019 = lbs. CaO/1000 gallons.

The amount of free and half bound carbon dioxide was assumed to be 44% of the total alkalinity (26).

The result of the value obtained from the above formula was multiplied by the following conversion factors to change from pounds of CaO/1000 gallons to grams of $Ca(OH)_2$/25 gallons.

a. $\frac{25}{1000}$ to convert from 1000 gallons to 25 gallons.

b. 453.6 to convert from pounds to grams.

c. 17.1 to convert from grains/gallon to ppm.

d. 1.43 to convert from CaO to $Ca(OH)_2$.

The calculated amount of lime needed was weighed on the balance in a dry evaporating dish and added to the raw water in the treating tank. A camel's hair brush was used in order to get all of the lime from the dish. The water was stirred vigorously for about five minutes after the addition of the lime. In each case of treatment a certain per cent of additional lime was added, depending upon the excess degree of treatment that was desired.

Treatment with Soda Ash. The amount of commercial soda ash (sodium carbonate) used in each batch treatment was determined from the following formula:

Non-carbonate hardness x 0.009 = lbs. soda ash/1000 gallons.

The same conversion factors as used in the lime determination apply in the determination of soda ash with the exception of d.

The calculated amount of soda ash needed was weighed on the balance in a dry evaporating dish and added to the water that had lime previously added. A camel's hair brush was used in order to get all of the soda ash from the dish. The water was stirred vigorously for about five minutes after the addition of the soda ash. In each case of treatment, a certain per cent of additional soda ash was added depending upon the excess degree of treatment that was desired.

Treatment with Alum. The amount of alum (aluminum sulfate) needed in each batch treatment was based on the relationship of 1/4 pound of alum for 1000 gallons of clear water, and 1/2 pound of alum for 1000 gallons of muddy water. In all cases of treating Virginia Polytechnic Institute water, the equivalent of 1/4 pound per 1000 gallons was used. However, the different collections of New River water varied from slightly muddy to very muddy, and the equivalent of 3/8 to 1/2 pound per 1000 gallons was used depending upon the clearness of the raw water. The calculated amount of alum needed was weighed on the balance in a dry evaporating dish and added to the water to which lime and soda ash had previously been added. The water was stirred vigorously for approximately five minutes after the addition of the alum. The water was stirred every fifteen minutes for one hour and then was allowed to stand for at least 24 hours before using.

The actual amounts of chemicals added for different batch treatments are shown in Table VI, page 57. A sample calculation of the amounts of chemicals needed for the desired treatment is shown on page 67 .

Table VI

Amount of Chemicals Added for Lime-Soda Ash Treatment of Raw Water

Run No.	Lime grams	Soda Ash grams	Alum grams	Water gallons
Virginia Polytechnic Institute Raw Water				
3	27.0	4.00	3.0	25
4	28.0	3.50	3.0	25
5	26.0	3.25	3.0	25
6	8.9	1.04	0.9	10
7	29.0	4.25	3.0	25
9	30.0	4.50	3.0	25
11	30.0	5.25	3.0	25
12-13	28.0	3.25	3.0	25
New River Raw Water				
14-17-18	8.25	2.55	4.5	25
15-16-18-19	9.25	2.30	4.0	25
19-20	10.00	2.50	4.0	25

Mineral Analysis

A mineral analysis was run on both the raw and treated water according to "Standard Methods of Water Analysis" (4). All results were determined in grains per gallon, and all analyses were run in duplicate in order to check the accuracy of the results.

Determination of Silica (SiO_2). The sample to be analyzed was filtered through No. 9-790, Scimatco, 11 cm. filter paper. By use of a 100 ml. pipette, 100 ml. of the filtered sample was added to a 400 ml. beaker and evaporated on the electric hot plate. When the sample was almost to dryness, 100 ml. more of the sample was added and this procedure was continued until 500 ml. had been evaporated. When the 500 ml. sample was nearly dry, 1.0 ml. of 1:1 hydrochloric acid was added, and after moistening the sides of the beaker in order to recover any matter that may have clung there, the sample was evaporated to dryness. It was baked on the electric hot plate for one-half hour. The residue was moistened with distilled water and a few drops of 1:1 hydrochloric acid was added. The sample was heated to boiling and was filtered through No. 9-790, Scimatco, 11 cm., filter paper. The filter paper was washed three times with hot distilled water.

The filter paper containing the precipitate of silica and silicates, was folded and placed into a small porcelain crucible which had been weighed on the chainweight balance. The crucible was placed in the laboratory furnace at 1200° F. for one hour, removed, and allowed to cool for 1/2 hour in the desiccator. It was reweighed on the balance and the difference in the two weights was reported as silica (SiO_2).

Determination of Iron and Aluminum (Fe_2O_3). The filtrate from the silica determination contained iron, aluminum, calcium, and magnesium. The filtrate was heated on the hot plate to boiling and was oxidized with 5.0 ml. of concentrated nitric acid. The sample was concentrated to about 25 ml. and ammonium hydroxide was added drop by drop until the solution was slightly alkaline, as determined by the change of color from red to blue of litmus paper to which a portion of a drop of the sample had been added. The sample was boiled for one minute to expel the excess ammonia, and was then filtered through No. 90790, Scimatco, 11 cm. filter paper and washed three times with distilled water.

The precipitate contained iron and aluminum. The filter paper containing the precipitate was placed in a small preweighed crucible and ignited at 1200° F. in the laboratory furnace. The crucible was removed from the furnace after one hour, and placed in the desiccator to cool. After 1/2 hour the crucible was reweighed and the difference in the two weights was reported as ferric oxide (Fe_2O_3) plus aluminum oxide (Al_2O_3).

Determination of Calcium (Ca). The filtrate from the iron-aluminum determination contained calcium and magnesium. The filtrate was boiled on the hot plate and concentrated to approximately 100 ml. To this was added 15 ml. of a concentrated solution of ammonium oxalate in 3 ml. portions at a time. The solution was stirred at intervals and kept warm until the precipitate settled readily and the supernatant liquid was clear. This usually required approximately 1/2 hour. The solution was filtered through No. 9-790, Scimatco, 11 cm. filter paper and the precipitate was washed five times with distilled water.

The precipitate contained calcium oxalate. The filter paper containing the precipitate was put in a small preweighed porcelain crucible and ignited at 1200° F. in the laboratory furnace for one hour. The crucible was removed from the furnace, and allowed to cool for 1/2 hour in the desiccator. The crucible was reweighed and the difference in the two weights was recorded as calcium oxide. The weight of calcium was determined by multiplying the weight of calcium oxide by 0.715.

Determination of Magnesium (mg). The filtrate from the calcium determination contained magnesium. The solution was acidified with 5 ml. of 1:1 hydrochloric acid. The solution was boiled on the hot plate and concentrated to approximately 150 ml. To this was added 25 ml. of a saturated solution of microcosmic salt ($NaNH_4HPO_4$). The solution was allowed to cool and ammonium hydroxide was added drop by drop until the solution was slightly alkaline to litmus paper. The solution was allowed to stand for four hours and then was filtered through No. 9-790, Scimatco, 11 cm. filter paper, and washed three times with a 3% solution of ammonium hydroxide.

The filter paper containing the precipitate was put in a small preweighed porcelain crucible and ignited at 1200° F. in the laboratory furnace for one hour. The crucible was removed from the furnace, placed in the desiccator, and allowed to cool for 1/2 hour. After cooling, the crucible was reweighed and the difference in the two weights was recorded as magnesium pyro-phosphate ($Mg_2P_2O_7$). The weight of magnesium was determined by multiplying the weight of magnesiumpyrophosphate by 0.219.

Determination of Sulfates (SO_4). A 500 ml. filtered sample was evaporated on the hot plate and the silica was removed as outlined in this section under "Determination of Silica". To the filtrate from the silica precipitate was added 20 ml. of a hot solution of barium chloride. The solution was stirred at intervals and kept warm until the precipitate settled readily. This required approximately 1/2 hour. The solution was filtered through No. 9-790, Scimatco, 11 cm. filter paper and washed three times with distilled water. The precipitate contained barium sulfate.

The filter paper containing the precipitate was put in a small preweighed porcelain crucible and ignited at 1200° F. in the laboratory furnace for one hour. The crucible was removed, placed in the desiccator, and allowed to cool for 1/2 hour. After cooling, the crucible was reweighed and the difference in the two weights was recorded as barium sulfate. The weight of the sulfate was determined by multiplying the weight of the barium sulfate by 0.4114.

Determination of Sodium (Na). The filtrate from the sulfate determination was evaporated on the hot plate to approximately 25 ml. The beaker containing the filtrate was then placed in the drying oven and evaporated to dryness at 105° C. The beaker was then heated barely to redness by means of a Fisher burner to remove ammonium salts. Approximately 25 ml. of distilled water was added to the residue. To this was added 20 ml. of a saturated barium hydroxide solution and the mixture was heated to boiling on the hot plate.

After 1/2 hour, the solution was filtered through No.9-790, Scimatco, 11 cm. filter paper and washed three times with hot distilled water. Approximately 5 ml. of ammonium hydroxide and 25 ml. of a saturated solution of ammonium carbonate were added to the filtrate, and the mixture was heated on a steam bath until the calcium and barium carbonates settled. This usually required approximately 1/2 hour. The mixture was filtered through No. 9-790, Scimatco, 11 cm. filter paper, and washed five times with distilled water.

The filtrate was evaporated on the hot plate to approximately 25 ml. The beaker containing the filtrate was then placed in the drying oven and evaporated to dryness at 105° C. The beaker was removed from the drying oven and heated barely to redness by means of a Fisher burner to remove ammonium salts. Approximately 15 ml. of distilled water was added to the residue and the mixture was filtered through No. 9-790, Scimatco, 11cm. filter paper, and then washed three times with distilled water. The filtrate was collected in a white porcelain evaporating dish. A few drops of 1:1 hydrochloric acid were added to the filtrate and it was placed in the drying oven and evaporated to dryness at 105° C. The evaporating dish was removed from the drying oven and placed in the laboratory furnace at 600° F. and heated barely to redness to drive off ammonium salts. The evaporating dish was removed from the furnace, and allowed to cool in the desiccator for 1/2 hour. The evaporating dish was then weighed on the balance. The residue was taken up in a few ml. of distilled water, filtered through No. 9-790, Scimatco, 11 cm. filter paper and washed three times with distilled water. The evaporating dish was again dried in the drying oven at 105° C. for one hour. The evaporating dish was placed in the desiccator and allowed to cool for 1/2 hour before it was reweighed on the balance. The difference in the two weights was recorded.

The filter paper containing the precipitate was put into a small preweighed crucible and ignited at 1200° F. in the laboratory furnace for one hour. The crucible was removed from the furnace, placed in the desiccator and allowed to cool for 1/2 hour before being weighed on the balance. The difference in the two weights was recorded. The weight difference of the crucibles subtracted from the weight difference of the evaporating dishes, gave the weight of sodium chloride and potassium chloride. The weight of the mixed chlorides expressed as sodium was found by multiplying the mixed chloride weight by 0.3934.

Preparation of Solutions

Since none of the solutions used in the analytical determination of water was available, all had to be made by using distilled water and materials that were available.

Preparation of Standard Soap Solution. Approximately 100 grams of dry white Castile soap were dissolved in one liter of 80% methanol, and were allowed to stand for four days. The solution was filtered and 100 ml. of the filtrate were added to one liter of 80% methanol. The soap solution was standardized with standard calcium chloride solution. One ml. of the calcium chloride solution was equivalent to 0.2 mg. of calcium carbonate. To a shaking bottle were added 58.3 ml. of distilled water, and soap solution was added in 0.2 ml. portions. Between each addition of soap solution, the bottle was agitated by shaking for approximately 30 seconds. The soap solution was adjusted so that 1.0 ml. of soap solution would give a one-inch lather which would last for at least five minutes. One mg. calcium carbonate in 58.3 ml. of distilled water is equivalent to one grain per gallon calcium carbonate. Water samples of 58.3 ml. equivalent to 1, 2, 3, 4, 5, and 6 grains per gallon calcium carbonate were prepared and soap solution was added as described above, except 0.5 ml. portions were added until the end point was approached. The soap solution was adjusted so that the amount of soap solution required to give a one inch lather which would last for five minutes would be one ml. greater than the equivalent calcium carbonate in the sample. For example, if the sample was equivalent to 3.0 grains per gallon calcium carbonate, the soap solution was adjusted so that 4.0 ml. would give a one-inch lather that would last for at least five minutes.

Preparation of Standard Calcium Chloride Solution. To 10 ml. of dilute hydrochloric acid was added 0.2 gram of pure calcite (calcium carbonate). The solution was evaporated to dryness twice to expel the excess acid. The residue was dissolved in distilled water and made up to one liter. One ml. is equivalent to 0.2 mg. of calcium carbonate.

Preparation of Standard Sodium Chloride Solution. One gram of fused, C. P., sodium chloride was dissolved in one liter of distilled water. One ml. equals 1.0 mg. sodium chloride.

Preparation of Standard Silver Nitrate Solution. To one liter of distilled water were added 2.922 grams of C. P. silver nitrate. Ten ml. of standard sodium chloride solution were diluted to 58.3 ml. with distilled water and poured into a porcelain evaporating dish. One ml. of potassium chromate was added as an indicator. The salt solution was titrated with silver nitrate solution, and the silver nitrate solution was adjusted so that 10.3 ml. were equivalent to 10. mg. sodium chloride in 58.3 m. of distilled water. The silver nitrate solution was checked with different concentrations of salt solutions. A "blank" of 0.3 ml. was used in each case.

Preparation of Potassium Chromate Indicator. Twelve and five-tenths grams of C. P. potassium chromate were dissolved in 50 ml. of distilled water. A few drops of silver nitrate solution were added to produce a slight red precipitate. The solution was filtered and the filtrate was made up to 250 ml. with distilled water.

Preparation of 2N Sulfuric Acid Solution. Twenty-seven and five tenths ml. of 96.8% sulfuric acid, sp. gr. 1.84, were diluted to 500 ml. with distilled water.

Preparation of N/50 Sulfuric Acid Solution. To 2.5 liters of distilled water were added 1.37 ml. of 96.8% sulfuric acid, sp. gr. 1.84. The solution was adjusted so that when titrated with methyl orange as the indicator, 25.0 ml. were equivalent to 25.0 ml. of N/50 sodium carbonate solution.

Preparation of N/50 Sodium Carbonate Solution.

Seventy-four hundredths grams of C. P. sodium carbonate was dissolved in one liter of distilled water.

Preparation of 1:1 Hydrochloric Acid Solution.

Two hundred and fifty ml. of 37% hydrochloric acid, sp. gp. 1.1878, were diluted with 250 ml. of distilled water.

Preparation of Standard Dissolved Solid Solution for Adjustment of Nalcometer. One and six tenths grams of sodium chloride and 1.6 grams of sodium carbonate were dissolved in two liters of distilled water. The exact dissolved solid content in grains per gallon was determined by evaporating a 50 ml. sample in the drying oven, and weighing the evaporating dish both before and after evaporation.

Sample Calculation

The following is the calculation for run 9 of the amount of chemicals used for treating 25 gallons of Virginia Polytechnic Institute raw water to 40% alkalinity. The raw water tested as follows:

H	M	2P	Mg
12.8	10.9	0.0	1.46

Calculation for Lime:

0.44 x M x 0.0106 + Mg x 0.019 = lbs. CaO/1000 gallons

By substituting,

0.44 x 10.9 x 0.0106 + 1.46 x 0.019 = 0.0787

Using conversion factors as outlined on page 55,

0.0787 x 25/1000 x 453.6 x 17.1 x 1.43 = 21.8 grams lime
per 25 gallons for zero per cent treatment.

For 40 per cent alkalinity,

0.40 x 21.8 + 21.8 = 30.2 grams lime for treatment of
40 per cent alkalinity.

(30.0 grams lime actually added to 25 gallons raw water).

Calculation for soda ash:

Non-carbonate hardness x 0.009 = lbs. Na_2CO_3/1000 gallons

By substituting,

1.9 x 0.009 = 0.0171

Using conversion factors as outlined on page 55,

0.0171 x 25/1000 x 453.6 x 17.1 = 3.3 grams soda ash per
25 gallons for zero per cent treatment.

For 40 per cent alkalinity,

0.40 x 3.3 + 3.3 = 4.6 grams soda ash for treatment of
40 per cent alkalinity.

(4.5 grams soda ash actually added to 25 gallons raw
water).

Calculation for alum:

0.25 lb. for 1000 gallons of clear water.

0.25 x 453.6 x 25/1000 = 2.9 grams alum for 25 gallons of clear raw water.

(3.0 grams alum actually added to 25 gallons raw water.)

Data and Results

Raw Water, Treated Water, and Boiler Water. In this investigation, the term "raw water" referred to the water before treatment with lime and soda ash. "Treated water" referred to the water which had been treated with lime and soda ash, and was used as feed water for the simulated boiler. "Boiler water" referred to the water in the flask after carry-over due to foaming had been observed.

The following tables and figure give the observed data and the results calculated during the course of this investigation.

Analysis of Virginia Polytechnic Institute and New River Raw Waters, Treated Waters, and Boiler Waters. Table VII, page 71, shows the comparison between Virginia Polytechnic Institute and New River, "raw waters", treated waters, and "boiler waters". The amount of lime and soda ash needed for treatment was calculated from the raw water analyses. The degree of treatment is shown in the treated water analyses by the per cent alkalinity. The boiler water analyses show the composition of the boiler waters at their foaming points.

Relationship Between Hardness and Alkalinity of Virginia Polytechnic Institute and New River, Raw Waters, Treated Waters, and Boiler Waters. Table VIII, page 72, simplifies the interpretation of the analyses of the Virginia Polytechnic Institute and the New River, raw waters, treated waters and boiler waters, as shown in Table VII, page 71, by separating the hardness into carbonate and non-carbonate hardness, and by separating the total alkalinity (M) into caustic alkalinity, bicarbonates, and carbonates. The reduction of the hardness after treatment and the relationship between the carbonates and caustic alkalinity of the treated and boiler waters show the suitability of the treated and boiler waters for boiler use.

Mineral Analysis of Virginia Polytechnic Institute and New River, Raw Waters and Treated Waters. Table IX, page 73, shows the comparison between the mineral analyses of the Virginia Polytechnic Institute and the New River, raw waters and treated waters.

Effect of Treatment Variations on Foaming Concentrations. Figure 7, page 74, shows graphically the variation of the dissolved solids concentrations of the boiler waters at their foaming points with change in per cent alkalinity, of the Virginia Polytechnic Institute boiler water, and of the New River boiler water, taken from Table VII, page 71.

Table VII

Analysis Of Virginia Polytechnic Institute and New River, "Raw" Waters, "Treated" Waters, and "Boiler" Waters.

Run Number	Date Tested	Hardness (H)	Methyl Orange Alkalinity (M)	Phenolphthalein Alkalinity x 2 (2P)	Chlorides (NaCl)	Dissolved Solids	Per Cent Alkalinity $\frac{M-H}{DS-H} \times 100$	Suspended Solids	Feed Water Evaporated
		grains/gallon $CaCO_3$			grains/gal. NaCl	grains/gallon	%M	grains/gallon	liters
Virginia Polytechnic Institute "Raw" Water									
3	4/16/48	12.4	10.4	0.0	0.4	13.8	0.0	-	-
4	4/20/48	12.6	10.6	0.0	0.4	14.1	0.0	-	-
5	4/23/48	12.4	10.4	0.0	0.4	13.6	0.0	-	-
6	4/27/48	12.6	10.6	0.0	0.4	-	0.0	-	-
7	4/30/48	12.8	10.8	0.0	0.4	-	0.0	-	-
9	5/8/48	12.8	10.9	0.0	0.4	13.8	0.0	-	-
11	5/12/48	12.8	10.9	0.0	0.4	14.0	0.0	-	-
12 & 13	5/17/48	12.8	10.9	0.0	0.4	13.8	0.0	-	-
Virginia Polytechnic Institute "Treated" Water									
3	-	1.5	2.7	3.2	0.4	4.9	35.4	-	-
4	-	2.4	3.8	5.6	0.4	5.1	51.9	-	-
5	-	1.1	2.5	2.8	0.4	7.4	22.4	-	-
6	-	1.6	2.3	3.2	0.4	6.6	13.8	-	-
7	-	2.0	3.3	3.8	0.4	6.2	31.1	-	-
9	-	1.7	3.7	4.4	0.4	5.8	41.7	-	-
11	-	1.2	3.6	3.0	0.4	6.2	48.0	-	-
12 & 13	-	2.2	3.2	5.0	0.4	5.4	31.2	-	-
Virginia Polytechnic Institute "Boiler" Water									
3	-	2.2	19.2	24.0	5.2	72.5	31.0	3.9	7.1
4	-	6.4	27.6	39.2	4.8	70.0	33.3	8.3	6.6
5	-	0.4	30.0	40.0	9.6	118.2	25.2	0.9	11.6
6	-	1.6	20.0	28.8	13.6	160.2	11.6	102.6	21.8
7	-	0.6	27.2	35.2	6.4	93.8	31.0	0.3	11.8
9	-	3.7	34.4	50.4	6.4	80.2	40.1	1.3	11.1
11	-	0.0	27.8	36.8	2.8	58.4	47.6	1.3	4.7
12	-	5.4	20.8	34.4	4.8	58.8	28.3	27.9	6.8
13	-	6.8	28.8	49.6	11.2	126.6	18.4	152.6	7.9
New River "Raw" Water									
14-17-18	5/19/48	2.9	2.4	0.0	0.2	4.9	0.0	-	-
15-16-18-19	5/26/48	3.2	2.6	0.0	0.3	3.9	0.0	-	-
19-20	6/3/48	2.8	2.2	0.0	0.3	6.0	0.0	-	-
New River "Treated" Water									
14-17-18	-	2.5	3.1	4.0	0.3	6.2	16.3	-	-
15-16-18-19	-	1.6	2.6	2.8	0.3	6.2	21.8	-	-
19-20	-	2.5	3.4	4.8	0.3	5.8	26.2	-	-
New River "Boiler" Water									
14	-	0.0	81.2	110.4	29.4	349.0	20.2	127.0	42.0
15	-	4.9	71.6	91.2	10.4	263.0	26.1	138.0	28.4
16	-	5.2	19.6	26.4	4.8	114.0	13.3	29.0	17.1
17	-	3.6	29.2	37.6	12.8	227.0	11.5	94.0	25.6
18	-	1.2	57.2	82.4	14.0	403.0	14.0	253.0	40.1
19	-	7.6	48.8	72.8	14.0	404.0	10.4	190.0	36.6
20	-	1.2	75.6	104.8	10.0	221.0	33.8	170.0	25.2

Table VIII

Relationship between Hardness and Alkalinity of Virginia Polytechnic Institute and New River, "Raw" Waters, "Treated" Waters, and "Boiler" Waters.*

Run Number	Carbonate Hardness	Non-carbonate Hardness	Total Hardness	Total Alkalinity		
				Caustic Alkalinity	Bicarbonates	Carbonates
Virginia Polytechnic Institute "Raw" Water						
3	10.4	2.0	12.4	0.0	10.4	0.0
4	10.6	2.0	12.6	0.0	10.6	0.0
5	10.4	2.0	12.4	0.0	10.4	0.0
6	10.6	2.0	12.6	0.0	10.6	0.0
7	10.8	2.0	12.8	0.0	10.8	0.0
9	10.9	1.9	12.8	0.0	10.9	0.0
11	10.9	1.9	12.8	0.0	10.9	0.0
12-13	10.9	1.9	12.8	0.0	10.9	0.0
Virginia Polytechnic Institute "Treated" Water						
3	1.5	0.0	1.5	0.5	0.0	2.2
4	2.4	0.0	2.4	1.8	0.0	2.0
5	1.1	0.0	1.1	0.3	0.0	2.2
6	1.6	0.0	1.6	0.9	0.0	1.4
7	2.0	0.0	2.0	0.5	0.0	2.8
9	1.7	0.0	1.7	0.7	0.0	3.0
11	1.2	0.0	1.2	0.0	0.6	3.0
12-13	2.2	0.0	2.2	1.8	0.0	1.4
Virginia Polytechnic Institute "Boiler" Water						
3	2.2	0.0	2.2	4.8	0.0	14.4
4	6.4	0.0	6.4	11.6	0.0	16.0
5	0.4	0.0	0.4	10.0	0.0	20.0
6	1.6	0.0	1.6	8.8	0.0	11.2
7	0.6	0.0	0.6	8.0	0.0	19.2
9	3.7	0.0	3.7	16.0	0.0	18.4
11	0.0	0.0	0.0	9.0	0.0	18.8
12	5.4	0.0	5.4	13.6	0.0	7.2
13	6.8	0.0	6.8	20.8	0.0	8.0
New River "Raw" Water						
14-17-18	2.4	0.5	2.9	0.0	2.4	0.0
15-16-18-19	2.6	0.6	3.2	0.0	2.6	0.0
19-20	2.2	0.6	2.8	0.0	2.2	0.0
New River "Treated" Water						
14-17-18	2.5	0.0	2.5	0.9	0.0	2.2
15-16-18-19	1.6	0.0	1.6	0.2	0.0	2.4
19-20	2.5	0.0	2.5	1.4	0.0	2.0
New River "Boiler" Water						
14	0.0	0.0	0.0	29.2	0.0	52.0
15	4.9	0.0	4.9	19.6	0.0	52.0
16	5.2	0.0	5.2	6.8	0.0	12.8
17	3.6	0.0	3.6	8.4	0.0	20.8
18	1.2	0.0	1.2	25.2	0.0	32.0
19	7.6	0.0	7.6	24.0	0.0	24.8
20	1.2	0.0	1.2	29.2	0.0	46.4

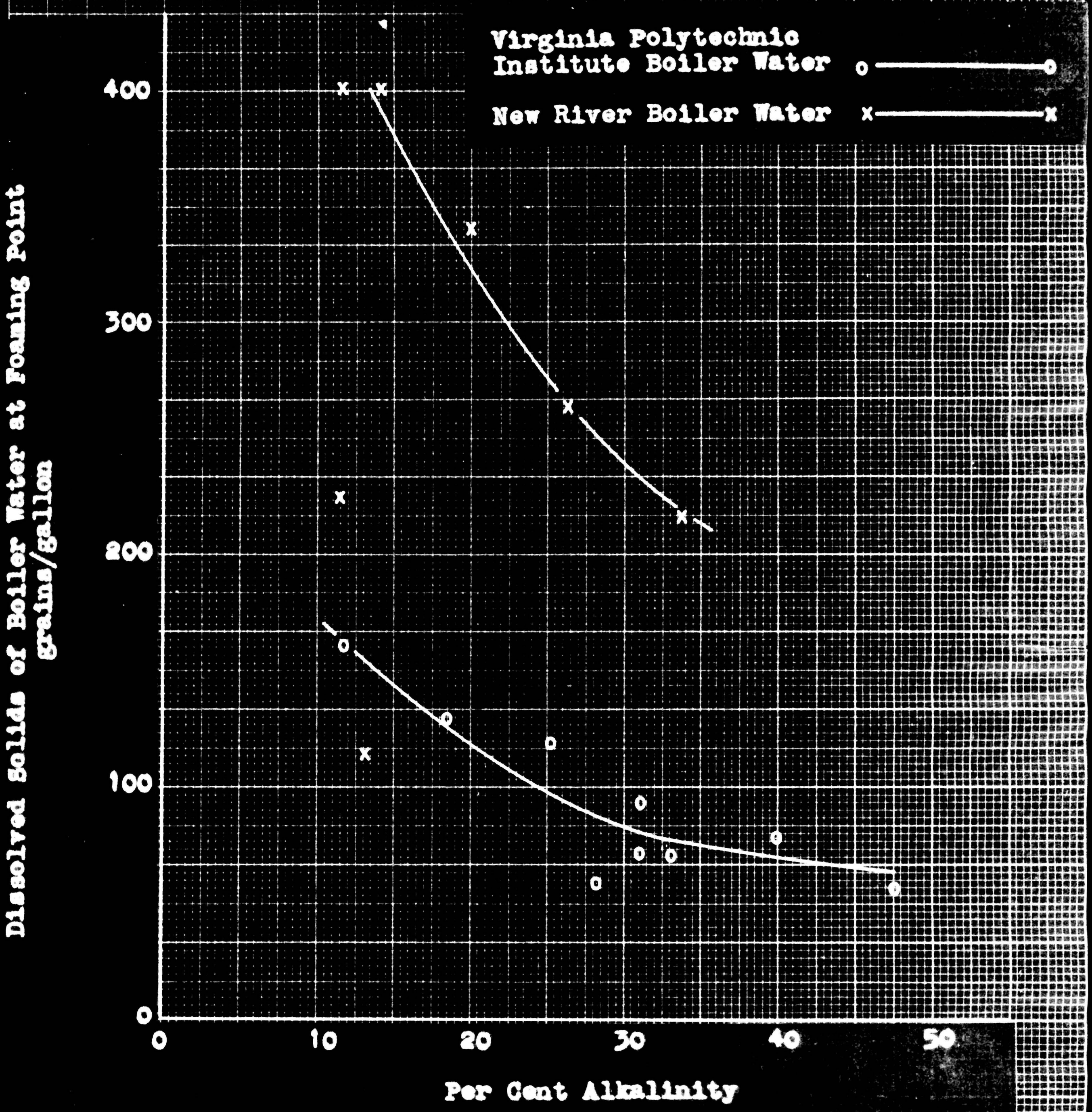
***Results expressed in grains per gallon calcium carbonate**

Table IX

Mineral Analyses Of Virginia Polytechnic Institute and New River, "Raw" Waters and "Treated" Waters.*

Run Number	Silica (SiO_2)	Iron and Aluminum (Fe_2O_3 $\not-$ Al_2O_3)	Calcium (Ca)	Magnesium (Mg)	Sodium and Potassium (Na)	Sulfate (SO_4)	Chlorides ($NaCl$)	Total Hardness ($CaCO_3$)	Total Dissolved Solids
Virginia Polytechnic Institute "Raw" Water									
3	0.45	0.20	4.50	0.76	-	0.72	0.40	12.8	13.80
4	0.66	0.24	4.26	1.43	0.46	0.32	0.40	12.6	14.10
Virginia Polytechnic Institute "Treated" Water									
3	0.08	0.73	1.03	0.07	1.06	1.26	0.40	1.5	4.90
4	0.17	0.69	0.73	0.12	0.90	1.53	0.40	2.4	5.10
5	0.08	1.10	0.70	0.25	0.83	-	0.40	1.1	7.35
6	0.26	0.09	0.57	0.16	1.02	1.47	0.40	1.6	6.65
7	0.14	1.38	0.53	0.17	0.90	1.64	0.40	2.0	6.18
9	0.28	0.48	0.85	-	-	1.37	0.40	1.7	5.80
12-13	0.44	0.38	0.68	-	0.64	1.05	0.40	2.2	5.40
New River "Raw" Water									
14-17-18	0.64	0.22	0.75	0.13	0.25	1.34	0.20	2.9	4.90
15-16-18-19	0.43	0.18	0.95	0.20	0.13	0.72	0.30	3.1	3.90
19-20	0.88	0.06	0.66	0.17	-	0.43	0.30	2.8	6.00
New River "Treated" Water									
14-17-18	0.00	0.91	0.94	0.15	0.20	2.08	0.30	2.5	6.18
15-16-18-19	0.14	0.76	0.84	0.18	0.30	1.94	0.30	1.6	6.18
19-20	0.11	0.80	0.99	0.11	0.30	2.23	0.30	2.5	5.80

*Results expressed in grains per gallon



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Effect of Treatment Variations

on Foaming Concentrations

Drawn by: PEt Approved by: RCP	Date: 6/12/48 Figure: 7

IV. DISCUSSION OF RESULTS

Raw Water, Treated Water, and Boiler Water. In this investigation, the term "raw water" referred to the water before treatment with lime and soda ash. "Treated water" referred to the water which had been treated with lime and soda ash, and was used as feed water for the simulated boiler. "Boiler water" referred to the water in the flask after carry-over due to foaming had been observed.

Apparatus for the Determination of the Foaming Concentration. It was desired to have complete visual observation of all parts of the boiler including the heating surface, body of the water, surface of the water, steam space, and steam outlet. A trial run was made using the apparatus as shown in Figure 6, page 40, except that a 500 ml. round bottom flask, containing 250 ml. of water, was used instead of a 1000 ml. round bottom flask. A second trial run was made using a 1000 ml. round bottom flask containing 500 ml. of water because the 250 ml. of boiler water was not sufficient for testing purposes. These two runs using a round bottom flask proved the following:

1. All parts of the boiling vessel were clearly visible during the entire course of the run.

2. The foam layer increased gradually in thickness with an increase in the dissolved solids content of the water.

3. A constant level could be maintained in the flask by means of a constant flow from the separatory funnel.

4. A constant evaporation rate could be maintained by adjusting the intensity of the flame of the Fisher burner.

5. The "foaming point", or instant of carry-over, could easily be detected.

Since these were the conditions desired, it was decided to use the 1000 ml. round bottom flask with the auxillary equipment, as shown in Figure 6, page 40, as the simulated boiler for this investigation.

Evaporation Rate. The evaporation rate used was 250 ml. per 12 minutes. This was equal to 20.8 ml. per minute, or 0.22 ml. per minute per sq. cm. of surface area. This rate was selected because it was approximately the maximum that could be obtained by using a Fisher burner, and it also produced vigorous boiling within the flask.

Testing of Condensate. The condensate was collected in 250 ml. samples and the phenolphthalein and methyl orange alkalinity were determined. This proved to be zero in all cases except after the foaming point had been reached. This testing of the condensate was discontinued after the first few runs, but the condensate was still collected in 250 ml. samples as a check on the evaporation rate.

Appearance of Foam Throughout Run. When boiling was begun, the bubbles formed were large and would burst immediately upon reaching the surface of the water. The disturbance caused by these few but large bubbles caused slugs of water to be thrown upward and against the sides of the flask. However, after boiling for approximately three hours, the bubbles would be more numerous, smaller in size, and a foam layer of one bubble, or approximately 1/8 inch thick would be formed on the surface. The bursting of the bubbles did not cause slugs of water to be thrown upward and against the sides of the flask, but the boiling was very smooth and the actual level of the water in the flask was more easily seen then before. The foam layer gradually increased in thickness with continued boiling until the steam space was entirely filled with foam, and foam was carried over to the condenser. The amount of feed water used before the foaming point was reached varied in the different runs from less than five liters in run 11, to forty-two liters in run 14.

Relationship between Virginia Polytechnic Institute and New River Boiler Water at their Foaming Points. Figure 7, page 74, shows the effect of treatment variation on the foaming concentrations of Virginia Polytechnic Institute and New River boiler water. The range of per cent alkalinity of primary interest was between 10% and 35%, since this is the degree of treatment that is mostly used for railroad locomotive boilers. In the case of the Virginia Polytechnic Institute water, two runs were made beyond this limit for the purpose of noting the effect of a large excess of treatment.

The data for the curves shown in Figure 7, page 74, were taken from Table VII, page 71. The scattering of the results on the curve representing the Virginia Polytechnic Institute water indicates that the accuracy of the method used for the determinations was not sufficient or that the foaming concentration varies over a range of dissolved solids at any per cent alkalinity. Only one duplicate run was made with Virginia Polytechnic Institute water. Runs 3 and 7 foamed at dissolved solids concentrations of 72.5 and 93.8 grains per gallon, respectively, with treatment of 31% alkalinity. However this difference of 21.3 grains per gallon was not concluded to be the true range because the points representing run 5, at 25.2% alkalinity and 118.2 grains per gallon, and run 12, at 28.3% alkalinity and 58.8 grains per gallon, did not correspond to that range limit. Therefore, the actual curve as drawn represents only the average of the values that might have been obtained if duplicate runs had been made.

The range limits of concentration of the New River boiler water at the same per cent alkalinity were not determined as no duplicate runs were made. Therefore, the actual curve as drawn for the New River boiler water represents only the average of the values that might have been obtained if duplicate runs had been made.

At the same per cent alkalinity, the dissolved solids concentration at the foaming point was greater for the New River boiler water. This was probably due to the fact that the amount of sodium in the feed water of runs using New River water was considerably less than in the feed water of runs using Virginia Polytechnic Institute water, as shown in Table IX, page 73. Foulk (11) stated that sodium salts apparently were the only definite chemical substances to which foaming and priming were generally attributed.

The foaming concentration of dissolved solids of New River water was found to decrease more rapidly with an increase in per cent alkalinity. From a per cent alkalinity of 15 to 35, the New River boiler water dissolved solids concentration at the foaming point dropped from approximately 370 to 215, or a decrease of 155 grains per gallon. Over this same range of per cent alkalinity, the Virginia Polytechnic Institute water dropped from approximately 150 to 75, or a decrease of 75 grains per gallon.

Inconsistent Results of New River Boiler Water. In the range between 10% and 15% alkalinity, four runs were made with New River water. Run 16, corresponding to dissolved solids of 114 and per cent alkalinity of 13.3, and run 17, corresponding to dissolved solids of 227 and per cent alkalinity of 11.5, were both far below the dissolved solids content that was expected at the foaming point. It was noted in those particular runs, 16 and 17, that the foam height did not gradually increase with concentration as in other runs, but that almost immediately the foam layer increased from only a slight layer to a height that was sufficient for carry-over. It was believed that due to the low excess of treatment of the water, the hardness had not been precipitating as new feed water was introduced. At the point just before carry-over occurred, some condition of the water caused the chemical reaction between sodium carbonate and the calcium salts, and the majority of the hardness was precipitated as calcium carbonate. During this chemical reaction, carbon dioxide was liberated and it is believed that the expelling of this excess carbon dioxide caused the foam height to increase to the point that it was carried over through the steam outlet. After allowing the water to subside, the water was reheated and again it foamed sufficiently to cause carry-over. Under normal conditions, the hardness is precipitated gradually and the small amount of carbon dioxide evolved does not duly effect the foam height. However, since the results were found as true results, New River boiler water that is treated between 10% and 15% alkalinity would be apt to foam at any dissolved solids concentration between 114 and 404 grains per gallon.

Recommended Treatment for Boiler Feed Water. New River water would be the most suitable water for use as a boiler feed water because of the greater concentration of salts that could safely be allowed to accumulate in the boiler without danger of carry-over due to foaming. The best degree of treatment would be between 15% and 20% alkalinity. Between 10% and 15% alkalinity, the boiler water would be apt to foam at a low concentration due to the inconsisent rate of removing the hardness. Above 20% alkalinity the concentration of salts that could safely be allowed to accumulate in the boiler without danger of carry-over due to foaming is reduced approximately 40 grains per gallon for each 5% increase in alkalinity.

Comparison of Results with Previous Investigations. The results found by Foulk and Miller (20) are shown in Table III, page 15. They measured the foam height produced by blowing air through a column of sodium salt solutions (Figure 1, page 12). They claim the sodium sulfocyanate solution was positively adsorbed, and the sodium sulfate and sodium chloride were negatively adsorbed. Since all of the salts commonly found in boiler waters are negatively adsorbed, it was assumed that the salts in the boiler waters of this investigation were negatively adsorbed.

Foulk and Miller found that the height of the foam layer increased with increased concentration of sodium salt in solution, and that an increase of sodium salt in solution above 0.4 molar, had little effect on the foam height produced.

In this investigation, the foaming concentration was measured instead of the foam height. It was found that the foaming concentration decreased with an increase of per cent alkalinity, and for Virginia Polytechnic Institute boiler water, there was only a slight difference between the foaming concentrations for runs with boiler water treatment above 30% alkalinity. This was not determined for New River boiler water as no runs were made with treatment above 33.8%

alkalinity (Table VII, page 71). The molar concentration of dissolved solids in the boiler waters varied from approximately 0.02 molar for 58.4 grains per gallon in run 11, to approximately 0.11 molar for 404.0 grains per gallon in run 19.

The data of Foulk and Miller were plotted on Figure 3, page 16. Although the actual values of the results found by Foulk and Miller, and the results found in this investigation, could not be compared, the general pattern of the curves (Figure 3, page 15, and Figure 7, page 74) showed similar characteristics.

There was no relationship between the foaming concentrations found in this investigation and those found by Foulk and Brill (17), as shown in Table I, page 8, and by Foulk and Ulmer (22), as shown in Table II, page 10. Both of those investigations were made with a laboratory size water tube boiler, and they experimented with only one salt in solution at a time. Since the effect on foaming of different mixtures of salts has never been satisfactorily explained, it was impossible to draw any relationship between the results of this investigation and the results found by Foulk and Brill, and Foulk and Ulmer.

Relationship to Railroad Locomotive Boilers. The actual foaming concentrations found in this investigation should probably differ for a locomotive boiler due to the difference in type of boiler, pressure, and rate of evaporation. However, the relationship between the results would probably be in agreement with this investigation.

Effect of Undissolved Solids on Foaming Concentration. No relationship between the amount of undissolved solids and the amount of dissolved solids at the foaming concentration, as shown in Table VII, page 71, was found in this investigation. In most cases, the runs containing the greatest amounts of dissolved solids usually contained large amounts of undissolved solids, but this was attributed to the fact that more feed water was evaporated in those runs, thereby increasing the amount of both dissolved solids and undissolved solids.

Method of Treatment. The lime soda-ash method of treatment was selected for use in this investigation because this method is widely used, especially for treating water for railroad locomotives and large industrial plants where there is no condensate return and a large quantity of feed water is used.

In railroad treating plants, the usual method of treatment is to form a slurry of the chemical and to pump this slurry directly into the inlet stream of raw water at the top of the treating tank. This mixture then falls down the center tube, or "Down-comer", of the tank over a series of baffles to insure proper mixing. This newly treated water is at the bottom of the tank and it rises only when more water is treated , which forces up the water level in the tank. The draw-off pipe is usually of the floating type with the outlet located about two feet below the surface of the water. The size of the tank is such that water will have approximately 12 hours in the tank before being drawn off and used as feed water.

Since the main purpose of this investigation was not a study of water treatment, and since a maximum of only 25 gallons of water were treated at one time, the system of adding the chemicals directly to the tank with intermittent stirring was used.

Results of Treatment. In all cases of treatment, the object was to remove all of the non-carbonate (permanent) hardness, reduce the carbonate (temporary) hardness to a minimum, reduce the dissolved solids to a minimum, and to keep the causticity less than the carbonates.

As shown in Table VIII, page 72, the treated water for runs 12-13 was the only one in which all the above conditions were not satisfied. The treated water for runs 12 and 13 had more causticity than carbonates, and the same condition existed in the boiler waters for those runs. This was the result of using an excess of lime for treatment of the raw water. This type of condition is undesired for boiler waters because embrittlement cracking of boiler plates is usually the result of excess causticity in the feed water which accumulates in the boiler water.

Foulk (12) stated that under the best conditions, some of the hardness will be left in the water when using the lime-soda ash method of treatment. The Virginia Polytechnic Institute water was reduced in hardness from an average of 12.7 grains per gallon to 1.7 grains per gallon calcium carbonate. The New River water, however, was reduced only from an average of 3.0 grains per gallon to 2.2 grains per gallon calcium carbonate. The final hardness in each case is approximately the limit of softening that was expected under the conditions of treatment that were used.

Differences in Raw Waters. As shown in Table VIII, page 72, the Virginia Polytechnic Institute raw water contained 10.8 grains per gallon of carbonate (temporary) hardness, and 2.0 grains per gallon of non-carbonate (permanent) hardness. The New River raw water contained 2.4 grains per gallon of carbonate (temporary) hardness, and 0.6 grains per gallon of non-carbonate (permanent) hardness. The mineral analysis of the Virginia Polytechnic Institute raw water and the New River raw water, as shown in Table IX, page 73, were approximately the same except the Virginia Polytechnic Institute water contained a greater amount of calcium and magnesium, which accounted for the greater hardness.

Amount of Lime and Soda Ash Needed for Treatment. The formulas used for the determination of the amounts of lime and soda ash needed for treatment are outlined on pages 54 and 55. If an alkalinity of ten per cent was desired for the treated water, ten per cent additional lime and ten per cent additional soda ash were added to the raw water. It was found that the theoretical amount of chemicals did not always produce the desired alkalinity for the treated water. In most cases, the actual per cent alkalinity was lower than the amount theoretically calculated. If the treatment was below 10% alkalinity, additional amounts of lime and soda ash were added. In only one case was the water excessively over-treated after the first addition of chemicals, and in this case additional raw water was added in order to reduce the degree of treatment.

Dissolved Solids Determination by Use of the Nalcometer. The accuracy of the Nalcometer for determination of dissolved solids depends upon the kind of dissolved solids that are in the water. The standard solution prepared for standardizing the Nalcometer was composed of sodium carbonate and sodium chloride in a ratio of 1 to 1. Since the electrical conductivity of salt solutions will differ with different salts, the accuracy of the Nalcometer was not exact, but was found to be within 2% of the actual value in the range above 30 grains per gallon dissolved solids. Below 30 grains per gallon the degree of accuracy was decreased because of the difficulty in interpolating between the graduations on the scale. For water containing less than 10 grains per gallon dissolved solids, the difficulty in interpolation often caused errors up to 40%. In all cases of dissolved solids determinations reported in this investigation, the values used were those obtained by evaporating a sample to dryness in the drying oven at 105° C. and weighing the residue on the balance.

Mineral Analysis. The procedure followed in this investigation for the mineral analysis was the approved method of the American Public Health Association.(4). The method of procedure was easily followed and the analysis was simple to perform. The major difficulty was the evaporation to dryness of approximately a 250 ml. sample of solution in the sodium determination. The salts would crystallize and spattering would occur, thus losing a portion of the sample.

Results of the mineral analysis are shown in Table IX, page 73.

Only two analyses were made on the Virginia Polytechnic Institute raw water as the water tested approximately the same in every case as shown in table VII, page 71.

The silica content of the treated water was less than the raw water because some of the silica is precipitated out by this method of treatment and settles to the bottom due to the coagulant. The amount of iron and aluminum was greater in the treated water due to the aluminum in the coagulant and also because the water was treated in an iron treating tank that had been painted with aluminum paint. The amount of calcium and magnesium decreased in the treated water due to the precipitation of calcium carbonate and magnesium hydroxide. However, in two cases of the New River treated water, the

the amount of calcium and magnesium in the treated water was the same or slightly more than in the corresponding raw water. This is accounted for by the fact that lime (CaO) was added for treatment and maximum softening had not been completed.

The sodium content of the treated water increased over that of the corresponding raw water due to the addition of sodium carbonate. The increase in the sulfate content of the treated water was due to the sulfate in the coagulant. The amount of chlorides remained the same as the treatment does not affect the chloride content of the water. The total hardness and total dissolved solids varied with each individual water.

Hardness Determination by Soap Method. The determination of the total hardness of water by the soap method is not a precise test on account of the different relative amounts of calcium and magnesium found in different waters.(2). The limit of accuracy which was less than 0.3 grains per gallon, was within the limits required for this investigation.

If the hardness of the water to be tested was more than six grains per gallon calcium carbonate, a half sample was used and made up to 58.3 ml. with distilled water. After subtracting the lather factor, the difference in the burette readings was multiplied by 2 in order to get the total hardness.

Magnesium Determination by Soap Method. The false end point, or "Ghost Point", which shows the dividing line between the calcium and magnesium was very difficult to determine unless great care in technique was followed. If the soap solution was added either too slow or too fast, the "Ghost point" did not appear. Quite often, more than one "Ghost point" would seem to appear during the hardness determination. In this investigation, the "Ghost point" was found only when testing Virginia Polytechnic Institute raw water. It never appeared with Virginia Polytechnic Institute treated water, or with New River raw or treated water.

Method of Testing for Alkalinity. The alkalinity of natural waters represents its content of carbonates, bicarbonates and hydroxides. The method of determination used in this investigation was the approved method of the American Public Health Association (2).

The phenolphthalein end point was easily seen when the color changed from pink to colorless. However, the methyl orange end point was harder to distinguish, especially in the case of New River raw water which in every case had a muddy appearance.

Recommendations

The following recommendations are made for future work on this subject:

1. The effect of a mixture of salts on the foaming concentration of boiler water should be determined. Foulk and Brill (17) and Foulk and Ulmer (22) found foaming values of individual salt solutions, but no data is available on solutions containing a mixture of salts.

2. The effect of increased pressure on the foaming concentration should be determined. Foulk (13) stated that high pressure boilers are less likely to foam than low pressure ones. However, the American Boiler Manufacturers Association (33), based on experience, has decreased the permissible concentration of dissolved solids with increased pressure.

3. The relationship between surface tension and foaming concentration should be determined. Foulk and Miller (20) found that the surface tension of salt solutions, most common in boiler waters, increased with concentration. Jacoby and Thompson (28) stated that, "although foaming is usually associated with a lowering of surface tension, foaming is not actually dependent upon surface tension".

4. If an accurate and quick determination of dissolved solids is desired on water containing less than 30 grains

per gallon, a Nalcometer with a range of from 0 to 50 grains per gallon dissolved solids should be used.

5. The same apparatus as used in this investigation for the determination of the foaming point should be used by future investigators on foaming of boiler waters so as the results may be compared.

6. Duplicate or triplicate runs should be made for each condition of feed water in order to have a positive check of the results.

Limitations

The experimental part of this investigation was conducted under the following limiting conditions.

1. The foaming concentrations were determined for only two waters, Virginia Polytechnic Institute water and New River water.

2. A laboratory boiler was simulated by using only a 1000 ml. round bottom flask.

3. The range limit of per cent alkalinity of the boiler water was from 10% to 35%, because treatment of industrial boiler waters is usually maintained within these limits.

4. Each run was made at atmospheric pressure -- 760 mm. of mercury.

5. The accuracy of the method used for determination of the foaming concentration was not checked by duplicate runs.

6. No anti-foam agents were used to reduce the foaming tendencies.

7. The surface tension of the boiler water was not measured.

8. The mineral analysis of the boiler water was not determined.

9. The evaporation rate for each run was maintained at 20.8 ml./min.

V. CONCLUSIONS

On the basis of the results obtained in this investigation, the following conclusions were made:

1. At atmospheric pressure and at a constant evaporation rate of 20.8 ml./min., Virginia Polytechnic Institute boiler water with treatments from 11.6 to 47.6 per cent alkalinity foamed at dissolved solids concentrations from 160.2 to 58.4 grains per gallon, respectively.

2. At atmospheric pressure and at a constant evaporation rate of 20.8 ml./min., New River boiler water with treatments from 20.2 to 33.8 per cent alkalinity foamed at dissolved solids concentrations from 349.0 to 170.0 grains per gallon, respectively.

3. Above 15 per cent alkalinity, the dissolved solids at the foaming point of the New River boiler waters were greater than the dissolved solids at the foaming point of the Virginia Polytechnic Institute boiler waters by an average of 200 grains per gallon.

4. On the basis of the literature, the dissolved solids at the foaming point of the New River boiler waters were greater than the dissolved solids at the foaming point of the Virginia Polytechnic Institute boiler waters by an average of 200 grains per gallon due to the smaller amount of sodium salts in the New River water.

VI. SUMMARY

The purpose of this investigation was to determine the effect of various degrees of lime and soda ash treatment on the foaming characteristics of Virginia Polytechnic Institute boiler water and New River boiler water, at atmospheric pressure and at a constant evaporation rate.

The range of treatment was between 10% and 35% alkalinity because feed waters for railroad locomotives are usually maintained between these limits. A 1000 ml. round bottom flask was used to simulate the boiler used for the determination of the foaming point concentration. A constant volume of 500 ml. of water was maintained in the flask throughout each determination. Atmospheric pressure was used throughout and a constant evaporation rate of 20.8 ml./min. was maintained.

Before treatment, the Virginia Polytechnic Institute water contained 10.8 grains per gallon of carbonate (temporary) hardness and 2.0 grains per gallon of non-carbonate (permanent) hardness. The New River water contained 2.4 grains per gallon of carbonate hardness and 0.6 grains per gallon of non-carbonate hardness. Treatment removed all of the non-carbonate hardness and reduced the carbonate hardness to an average of less than 2.0 grains per gallon in terms of calcium carbonate.

On the basis of the results obtained in this investigation, the following conclusions were made:

1. At atmospheric pressure and at a constant evaporation rate of 20.8 ml./min., Virginia Polytechnic Institute boiler water with treatments from 11.6 to 47.6 per cent alkalinity foamed at dissolved solids concentrations from 160.2 to 58.4 grains per gallon, respectively.

2. At atmospheric pressure and at a constant evaporation rate of 20.8 ml./min., New River boiler water with treatments from 20.2 to 33.8 per cent alkalinity foamed at dissolved solids concentrations from 349.0 to 170.0 grains per gallon, respectively.

3. Above 15 per cent alkalinity, the dissolved solids at the foaming point of the New River boiler waters were greater than the dissolved solids at the foaming point of the Virginia Polytechnic Institute boiler waters by an average of 200 grains per gallon.

4. On the basis of the literature, the dissolved solids at the foaming point of the New River boiler waters were greater than the dissolved solids at the foaming point of the Virginia Polytechnic Institute boiler waters by an average of 200 grains per gallon due to the smaller amount of sodium salts in the New River water.

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