T H E S I S

on

BOILER-WATER CONDITIONING

IN WESTERN OREGON

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SUMMARY

Boiler problems peculiar to the water conditions in western Oregon are formulated and described.

The somewhat unique and not universally recognized situation of the entrance of silicon, silica, or the silicates into boiler scales as principal constituents is examined as peculiarly the situation in western Oregon. The possibility of a sodium salt content of siliceous scales is noted. The entire problem of siliceous boiler scale is considered at length. Specific remedies are suggested for the prevention of that scale. Dangers of certain partial remedies are shown.

The facts about which center any scientific and fruitful program of boiler-water conditioning in western Oregon are enunciated.

Data are given from a successful program of boiler-water control established to good economic advantage in a typical western Oregon boiler plant.

The boiler ills commonly attributed to water or to the impurity content of water are outlined, and remedies for those ills are critically examined in the light of recent findings.

A bibliography is included as a guide to the more important literature on the subject.

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CONTENTS

BOILER-WATER CONDITIONING
IN WESTERN OREGON

I. INTRODUCTION

Only within the last decade has science been defi-
nitely applied to the solution of problems in boiler
operation traceable to the water supplied to or contained
in steam boilers. All that was traditional to the pre-
paration or control of boiler water has been modified.
Remedies for difficulty have engendered new difficulty.
Every apparent palliative for a specific trouble has re-
flected other troubles until it becomes apparent that
system should underlie any action that is taken. Boiler-
water problems need to be considered in their entirety.

In sections of the Pacific Northwest, especially
west of the Cascade Mountains, and for the purpose of the
present discussion in western Oregon, water conditions
have been described as ideal and excellent. Not even as
late as 1926, and not generally by the time of this
writing, was it recognized in that area that there were
even to be found serious difficulties in boiler operation
blamable to the working substance of boilers. Natural
water available was considered exactly suited to the
demands made of it.

Troubles encountered were not recognized, were tol-

erated because of the prevalent apathy to their recognition, or crude treatments of the previous seventy-five years were applied (1) without apparent consideration of conditions truly peculiar to the region. An awakening of interest and a growing need of the last few years have appeared in a setting devoid of a substantial background of experience. Chemical supply houses are chiefly in the Middle West and East. Water treating agencies are established where water problems have long been felt serious. Outside commercial interests are able to solve the problems of perhaps any section of the United States better than the problems of western Oregon.

II. PURPOSE

It is the purpose of this paper to deal with the problems of boiler water as they are encountered in western Oregon and to present methods suitable for the solution of those problems. The attitude is taken that the aim of research is to leave the field clearer than when found (2). No wealth of experimental data is offered, therefore, but it is the intent to give a critical review of what is now established in the field that that may dispel the prevailing ignorance, confusion, and misinformation. It is not the intention to set down definite courses of procedure that apply with certainty only to specific cases. It is the desire to put what is at present regarded as fact in a clear, useful form for reference and to present a basis for further work. An extensive bibliography is included as a guide to the important literature of the subject and that the reader may pursue statements to their first sources. Detailed explanations of equipment, and even of some processes are left to the references. The siliceous scale problem is treated at length because of its peculiar importance in the region considered.

Western Oregon is regarded as that portion of Oregon lying west of the Cascade Mountains. Definition of the region is made on the basis of a rough consistency therein

of conditions of rainfall, geological structure, vegeta-
tion, and impurity content of natural waters, as con-
trasted with the great variance of such conditions
throughout the state as a whole. The name "boiler" is
used throughout this paper in its generic sense as a term
of description rather than as a term of limitation.

III. THE PROBLEM

GENESIS OF THE PROBLEM

It is apparent that water available for boiler use
in western Oregon is such that boiler water presents in
that region unique problems distinct from those of boiler
waters encountered generally throughout the United States.
Especially significant are these observations:

(1) There is low total hardness. The figure is
below the lower limits of operation of most common
treatments for feedwater. The hardness consistently
encountered is decidedly lower than the average for
the United States.

(2) There is, in many cases, a high dissolved oxygen
concentration.

(3) There are peculiar scale forming materials,
combinations of matter, or proportions of materials.
There is a decided lack of the sulphate of the East.
There is an unusual proportion of siliceous impurity.

Additional considerations grow out of the natural
facts presented foregoing, and out of human tendencies
and shortcomings related to those facts:

(4) There is a tendency toward misapplication of
treatments successful elsewhere, with resultant
lack of success and often with the promotion of
deleterious results.

(5) There is almost universal nonobservance of
certain chemical ratios prescribed by the American
Society of Mechanical Engineers for the promotion
of safety and economy in boiler operation. Where
those ratios are properly disregarded, assurance
of operators is almost as great a problem as en-
forcement of the regulation when and where it is
needed.

(6) There is present more than usual the tendency,
current in small plants without adequate chemical
supervision, to assist the promotion of graft and
the operation of vendors of every false panacea.
There is an awakening unprepared clientele in
boiler-water treatment, hence a clientele much
subject to commercial racketeering.

LOW HARDNESS OF NATURAL WATER

IS NOT A GUARANTEE OF FREEDOM FROM BOILER SCALE

Analyses of natural waters from the region under consideration present an interesting feature of the treatment problem. Tables I and III give data regarding typical water conditions encountered in a random sampling from situations under the most of which boiler water difficulties have been encountered. Tables II and IV present data for comparison of conditions in western Oregon with those of the entire United States. It is interesting to note that the western Oregon waters described excel the product of some modern treating plants (3) through both low hardness and small impurity content. Total hardness of the waters is in no instance more than a few grains to the gallon. Even well waters are softer than usual surface supplies elsewhere. Very little "permanent" hardness is evident. Sulphates naturally present in the surface supplies are less than one grain to the gallon, expressed as calcium sulphate. Comparison of Tables I and II shows that western Oregon waters cannot be properly classified as carbonate, sulphate, chloride, or nitrate, as other natural waters of the United States are often designated. The unusual proportion of SiO_2 in the analyses, roughly 25 to 40 per cent, characterizes the waters as siliceous in nature.

TABLE I

AVERAGE CHEMICAL COMPOSITION OF THE WATER OF SOME WESTERN OREGON RIVERS
(From U.S. Geological Survey, Water-Supply Paper 363, 1911-12 Aug.)

River and Sampling Station	Mineral Content as Parts per Million										
	SiO_2	Fe	Ca	Mg	Na	K	CO_3	HCO_3	SO_4	NO_3	Cl
Bull Run, Bull Run	9.0	0.03	2.7	0.53	3.1	0.5	0.0	12	3.1	0.31	1.3
Clackamas, Cazadero	17	0.05	5.3	1.4	4.2	0.8	0.0	26	3.9	0.23	1.7
McKenzie, Springfield	17	0.06	4.4	1.1	4.1	1.2	0.0	24	3.8	0.18	1.3
Rogue, Tolo	24	0.07	7.2	1.7	6.1	1.3	0.0	38	4.1	0.26	1.4
Sandy, Brightwood	16	0.07	4.6	1.3	4.2	0.8	0.0	18	7.2	0.23	1.7
Santiam, Mehama	17	0.04	5.2	1.3	3.7	1.1	0.0	23	4.5	0.25	1.0
Siletz, Siletz	9.4	0.03	4.5	0.9	5.5	0.7	0.0	17	4.6	1.6	4.2
Umqua, Elkton	18	0.10	7.9	2.2	5.7	1.6	0.0	36	5.2	0.30	3.0
Willamette, Salem	15	0.10	5.3	1.4	3.8	0.8	0.0	26	3.7	0.36	1.9

TABLE II

TYPICAL MINERAL CONTENTS OF NATURAL WATERS OF THE UNITED STATES

Designation and Type of Water	SiO_2	Fe	Ca	Mg	Na	K	HCO_3	SO_4	NO_3	Cl
1. Carbonate	7.9	0.07	52.0	5.0	2.4	1.7	178	3.9	0.20	1.8
2. Carbonate	9.0	0.02	32.0	15.0	2.6	1.3	171	2.7	0.53	2.6
3. Carbonate	16.0	0.07	5.3	3.9	141.0	3.2	388	5.0	1.1	12.0
4. Sulphate	13.0	0.08	113.0	29.0	97.0	3.9	186	407.0	7.3	23.0
5. Chloride	30.0	0.12	184.0	29.0	127		214	48.0	1.0	454.0
6. Nitrate	17.0	0.03	68.0	19.0	19.0	4.7	239	19.0	50.0	29.0
	Average Percentage Mineral Content of North American Waters									
7.	8.6	0.60	19.0	5.0	7.4	1.5	(67.9)	16.0	1.1	7.4

Analyses 1-6 were selected from more than 5000 made by the U.S.G.S. (See report by
C.S. Howard in Ind, and Engr. Chem., Anal. Ed., vol. 5, p. 4, Jan. 15, '33)
The water sources were as follows:
1. Allan Springs at Price, Ala., 1928
2. Springs at Valley Springs, Ala., 1928
3. Well, 28 feet deep, at Hendersonville, Pa., 1926
4. San Juan River near Bluff, Utah, average, 1931
5. Well, 162 feet deep, at St. Petersburg, Fla., 1923
6. Well, 24 feet deep, at Bartonsville, Fla., 1931
Entry 7 shows the relative quantities in which the mineral impurities appear. (See
U.S.G.S. Professional Paper 135, p. 5). Values listed are adjusted
slightly from the original to make them conform to the significant fig-
ures reported for other entries. Bicarbonate is calculated to equivalent
carbonate, 33.4, in the summation of the percentages.

TABLE III

HARDNESS ANALYSES OF SOME NATURAL WATERS OF WESTERN OREGON
(From various tests by the author)

Water Source and Location	Hardness as Grains per Gallon		
	Temporary as $CaCO_3$	Permanent as $CaSO_4$	Total U.S. Deg.
1. Buckley well near Corvallis	2.91	2.47	4.73
2. Corvallis City Water Avg. of 5 tests	2.80	0.00	2.80
3. Doyle well 12 miles east of Eugene	2.00	0.00	2.00
4. Hamilton well 4 miles east of Corvallis	7.15	4.50	10.46
5. North Fork Santiam River at Mill City	1.85	0.00	1.85
6. Patty well 3 miles south of Amity	10.47	0.00	10.47
7. Willamette river at St. Johns	1.53	0.00	1.53

TABLE IV

AVERAGE HARDNESS
OF WATER FROM LARGE PUBLIC SUPPLIES
IN THE VARIOUS STATES

(From U.S. Geological Survey, Water Supply paper 496)

Region, State or States	Average Hardness as ppm of $CaCO_3$		
	Surface supplies	Ground supplies	All supplies
Oregon	9.0	19	9.6
Avg. U.S.	85	225	99
No. lower than Oregon	One	None	None

In spite of the lack of interest in boiler-water difficulties in western Oregon and notwithstanding the good water resources there apparent, there has recently been borne by boiler operators of that region too great a cost in trouble and expense. A few specific cases can be cited:

1. From one plant it was reported that cleaning of boilers was necessary monthly when raw water contained only a few grains of hardness per gallon.

2. In another plant using little make-up water the yearly cost of boiler cleaning was found to approximate five hundred dollars for every boiler, and with the best efforts clean tubes could not be maintained.

3. In a high pressure plant supplied with evaporated make-up water, burning out of water wall tubes was encountered.

4. The cleaning of evaporators in the plant referred to in (3) was found to be difficult even with an unusually brief operating cycle.

5. In plants in general the blow-down practices followed resulted in large losses of heat and water.

Such difficulties as those of the illustrations given are not consistent with description of the water used as perfect (4) for boiler purposes.

DISSOLVED AND ENTRAINED GASES

PROMOTE BOILER CORROSION

Surface water in a natural state tends to dissolve
and entrain fixed gases that make contact with it. Be-
cause they are apparently factors in the destruction of
boiler metal, the gases carbon dioxide and oxygen warrent
special consideration. (See the discussion of corrosion
presented in the Appendix). Carbon dioxide, as pointed
out in the discussion of siliceous matter, is a common
water impurity in regions of the rainfall and vegetation
of western Oregon. (Note the prevalence of bicarbonates
rather than carbonates shown for the waters of Table I).

Oxygen, readily derived from the air, is both dis-
solved and entrained in turbulent, fast flowing streams.
Tending to counteract the concentration of total oxygen
in natural water is the consumption of that gas by ox-
idizable impurities in the water. At headward positions
in streams flowing through sparsely populated and little
industrialized country the removal of oxygen from water
does not proceed at a high rate. All but the larger and
longer streams of western Oregon are likely to average
high in oxygen content of water. The oxygen content of
the upper Willamette River or its tributaries has been
reported (5) as high as 8 to 10 parts per million, even
in the summer season. Concentrations over 12 parts per

million were measured during cool weather. Those re-

sults, found for turbulent natural water, often corres-

ponded to percentages of saturation of from 90 to 100

or more, even at the low water temperatures encountered.

SILICEOUS MATTER

IS A LITTLE KNOWN SOURCE OF MUCH TROUBLE

GENERAL OBSERVATIONS

The formation of siliceous deposits of deleterious nature in steam power plant equipment is attested to by constantly recurring, although often fragmentary, evidence. Literature on steam power production and boiler operation is filled with facts having bearing on the harmful effects of silicon compounds. So deeply ingrained is the conception of hardness as a complete and accurate measure of the tendency of impure water to form encrustations and boiler scales that estimation of the action of silicates must often be read from between the lines in accounts of troubles and in reports of investigations. Some direct recognition is given, however, to silicates both as a constituent of boiler scales and as a component in turbine blade deposits. A few illustrative quotations are in order:

W. D. Collins in discussing the industrial utility of public water supplies (6) says "As an insoluble constituent the silica in water contributes to the formation of boiler scale, and it sometimes helps to cement the other material into a hard scale."

Findings of the Cochrane Corporation, manufacturers of boiler plant equipment, are indicated by C. E. Joos,

chemical engineer for the Corporation, as follows (3):
"With certain water supplies, difficulty has arisen from
the formation of silicate scale, even at moderate
pressures. Silicate scale is perhaps the most difficult
to overcome...."

From the voluminous writings of Dr. R. E. Hall in
the realm of boiler chemistry reference (7) is made to
"the prevention of silica deposits" in boilers and such
statements as (8) "The maintenance in the boiler water
of this relation....will also prevent the formation of
calcium-silicate scale," and "The control of the deposi-
tion of the hydrous magnesium silicate as adherent
scale...." suggest the consideration of remedies for the
trouble.

In the description of thin, tenacious scales of high
insulating value the statement was made by H. E. Jones
before the Manchester, England, Section of the Society of
Chemical Industry (9) that such peculiar scale might "con-
sist of calcium silicate. Very often it was due to
sodium silicate in the water."

A recent publication of the National Electric Light
Association (10) comments on the "Deposition of calcium
silicate in tubes and drums, very thin, but hard to re-
move...." [deposits].

C. J. Block, writing of the difficulties encountered

with silicate scale in Dutch steamers operating along the
coast of Sumatra (11) decries the lack of attention to
silicic acid in treatises on boiler-water chemistry. He
says, "it is absolutely necessary to determine the silic-
ic acid content of the [feed-] water, especially for soft
water." He points out that the silicic acid content of
soft water can amount to more than ten to twenty per cent
of the evaporation residue.

The German publication "Chemiker-Zeitung" recently
carried a discussion (12) of the test methods for silicic
acid that was prefaced by the statement that "Especially
for the critical examination of waters which are intended
for boiler feeding the quantitative analysis of the
silicic acid content is not to be underestimated."

K. Braungard, chemist in Berlin, has written a gen-
eral discussion of the subject "Silicic Acid in Boiler
Feed-water" (13) in which he shows that in spite of the
success of the German Union of Large Boiler Owners in
prescribing remedies and in offering explanations for the
usual boiler ills, there yet remains some work to be done
in the prevention of the deposition of silicates as
boiler scale.

Once the narrow limitation of the blame for the
deposit of scale and encrustations from water to carbon-
ate and sulphate hardness is discarded the importance of

the possible place of silicates in boiler-water chemistry
is seen.

ORIGIN OF SILICEOUS MATTER FOUND IN NATURAL WATERS

Silicon, surpassed in its activity by the somewhat
related element, carbon, is next to oxygen, the most
abundant element of the earth. It is (14) "the character-
istic element of all important rocks except the carbon-
ates. Silica also exists in probably all river, well,
and spring waters." It is the universal occurrence of
silica in natural waters (15) that surprises the in-
vestigator and the multiform appearance of it that often
confuses the analyst.

Small streams, near their sources, in new regions of
the earth recently subjected to volcanism are likely to
carry a large relative proportion of silicate impurity
even when their total impurity content is low. This is
particularly the case where rainfall is abundant and
vegetation is present in profusion. "This silica (14)
is directly derived from the rocks at the time of their
decomposition by carbonated water, and forms a large part
of the material which is at first taken into solution.
The seepage or ground water which afterward enters the
streams is much poorer in silica, and so the proportion
of the latter tends to diminish as a river flows toward
the sea."

The situation described is typically the one found in western Oregon. Water analysis data, inadequate as are the customary determinations of silicon compounds, are presented in Table V to complete the picture. The silicon content, as SiO_2, is from 30 to 35 per cent of the anhydrous residue. That amount is four times the usual percentage for the United States (See Table II).

TABLE V

AVERAGE PROPORTION OF SILICON IN THE WATER OF SOME WESTERN OREGON RIVERS
(From U. S. Geological Survey, Water-Supply Paper 363, 1911-12 Aug.)

River and Sampling Station	Silicon as Silica, ppm, (SiO_2)	Percentage Silica in Anhydrous Residue	Ca, Mg, and SO_4, Sum in ppm.
Bull Run, Bull Run	9	34.0	6.3
Clackamas, Cazadero	17	35.7	10.6
McKenzie, Springfield	17	37.6	9.3
Rogue, Tolo	24	36.8	13.0
Sandy, Brightwood	16	35.5	13.1
Santiam, Mehama	17	37.7	11.0
Siletz, Siletz	9	23.6	10.0
Umqua, Elkton	18	29.0	15.3
Willamette, Salem	15	33.0	10.4

FORM OF OCCURRENCE OF SILICA IN WATER

Some doubt exists as to the form in which silicates
appear in natural waters. The tendency in analysis has
been to report all siliceous matter as SiO_2, pure silica.
Such a measure could apply strictly to only sizable
particles of silica in suspension or to colloidal dis-
persions in the realm of usual suspensoid colloids. That
silica would be chemically inactive and would perhaps be
expected to enter into boiler incrustments only through
being trapped as an aggregate by other cementing material.
The simple silicic ion SiO_3^{--} is indicated as possible by
chemical equations but there is a dearth of proof that
any considerable concentration of that ion ever exists
in water. Yet siliceous material can exist in water in
a considerable concentration and still resist removal by
filtration (15). Such dispersed silicate can cause
freezing point lowering, changes in electrical conduct-
ivity, and high ionic mobility (16) in transport number
experiments. There is a realm of silicate aggregation
that partakes of the true solution while having some of
the properties of the colloidal state. Vail says (15)
of industrial silicate solutions that they are "systems
in which solloidal silica plays an important role. To
attempt to interpret their behavior without taking this
into account is to miss the meaning of some of the most

important phenomena." Even Stabler, whose writings are often quoted in proof of the stand that siliceous matter occurs in water only in colloidal form, recognized (17) the possibility of the silicate ion in natural water.

Silicates of the alkali metals, particularly sodium, unquestionably predominate in the majority of cases of apparent true solution. The soluble glasses can be thought of, for the present purpose, as $Na_2O \cdot xSiO_2$ in the formula for which x is a coefficient indicating the proportion (or ratio of SiO_2 to Na_2O) of siliceous matter in the silicate. The coefficient is not intended to describe an exact ratio of chemical combination but rather an average overall proportion of association of the components that may form definite molecules. The formula is to be used with reservations that have regard for gelation of the silicate molecules with large quantities of water, the clustering together of true molecules or particles into micelles, and the adsorption of siliceous matter on silica or of sodium on silica. A summary of information concerning siliceous dispersions in water is due to Harman (18): "Silica exists in solutions of these ratios not wholly colloidal as heretofore supposed, but wholly or partly as crystalloidal silica depending upon the ratio $Na_2O \cdot SiO_2$, and upon the concentration. This crystalloidal silica exists in equilibrium with silicate ions,

or electrically charged aggregates, of silicate ions and
silica, i.e., ionic micelles, or pure colloidal aggregates,
as the case may be, depending upon the ratio and concen-
tration.

"In aqueous solution at 25°C. two and only two salts,
viz., Na_2SiO_3, i.e., ratio 1:1, and $NaHSiO_3$, i.e., ratio
1:2, appear to exist as such, the behavior and nature of
which are now elucidated.

"Ratios other than 1:1 and 1:2 are not definite salts
but are typical examples of colloidal electrolytes.

"The fundamental nature of silica in solution appears
to depend upon the existence, at least in the range here
investigated, of only one acid, metasilicic acid, in which
the equilibrium between the crystalloidal and the colloidal
constituents depends upon the concentration, the crystal-
loidal content at ordinary concentrations being much
greater and the acid, therefore, much stronger, than
generally supposed."

Consideration of the total silicon in water as con-
tained in silica, SiO_2, appears to assume an improbable
situation and to involve evident error when there are high
absolute and relative values of that element in the solids
from evaporation of the water. Inclusion of silicon in
the ionic form, as a negative silicate ion such as SiO_3,
often results in better balancing of positive and negative

ions (19), and makes the sum of all ions approach closer to the residue by evaporation. Thresh and Beale (20) who have been concerned with water surveys throughout the British Isles have this to say regarding the form of occurrence of silica: "In 99 per cent of potable waters the silica appears to be in actual solution, and not in a colloid state, but in what condition it is impossible to say, since it may be in combination with any of the bases usually found in water. It occurs in the largest quantities in chalk waters and in waters containing sodium bicarbonate." The same authors say further, "In an alkaline water the SiO_2 may be present as Na_4SiO_4, in which case 1 part of SiO_2 represents 3.05 parts of Na_4SiO_4; in a neutral solution the silicate may be Na_2SiO_3, when 1 part SiO_2 equals 2.03 parts of silicate; in an acid solution the silicate present may be $Na_2Si_2O_5$, in which 1 part of SiO_2 equals 1.5 of the silicate.

"Where a water contains free carbonic acid, $Na_2Si_2O_5$ or $CaSi_2O_5$ is the most probable constituent, and the study or analyses of numerous waters shows that this is most likely, since the other silicates would in nearly all cases make the total solids by addition more than the total solids by direct estimation."

PRESENCE OF SILICEOUS MATTER IN BOILER SCALES

That siliceous matter is a major constituent of

resistant boiler scales formed in the region with which this paper is concerned can be shown by analyses of a random selection of scale deposits from western Oregon boilers as presented in Table VI.

It is desirable to recognize here that all isolated results of scale analysis are properly regarded as having only rough quantitative value. It is known by persons familiar with boiler chemistry that scale composition is seldom uniform throughout any given boiler. It is less well known that comparisons between amounts of one specific component of two different scale deposits are properly made only in terms of the total absolute quantity of the component in the total amount of each deposit. The comparative rates of component deposition should also be known (21).

An interesting feature of scale composition is indicated by the analyses given herewith. Reference to the Table brings to light the hitherto largely unrecognized situation of scale formation from sodium salts as well as from compounds of calcium and magnesium. Doctor Hall (22) has verified the writer's experience by comment on a similar observation.

TABLE VI

COMPOSITION OF TYPICAL BOILER SCALES OF WESTERN OREGON
(Percentages by weight)

Sample Designation	1	2	3	4	5	6
SiO_2	47.70	38.36	45.10	29.46	58.6	27.68
Fe_2O_3 and Al_2O_3	10.48	17.52	5.94	18.90	12.5	40.31
CaO	19.44	21.75	22.65	39.88	21.9	16.61
MgO	15.18	11.97	7.21	0.58	2.2	1.23
Na_2O	1.94	2.41	7.81	...	...	...
SO_3	None	Trace	None	0.80	...	2.46
Drying and Ignition Loss	4.63	7.98	11.00	5.92	...	4.60
Undermined, Etc.	0.63	0.21	0.29	4.46	4.8	7.11

Analyses 1-3 by the author. Sources of the scales and the waters from which they were
generated were:
1. Boilers in Oregon State Agricultural College central heating plant using
Corvallis city water for makeuup.
2. Source and conditions the same as for sample 1 except that a part of the
sample was of later origin subsequent to filtration of the water.
3. Boilers at Oregon State Hospital in Salem. Water taken from the North
Fork of the Santiam River.
Analyses 4-6 by courtesy of the Portland General Electric Company.
4. Four hundred pound pressure boiler supplied with make up evaporated from
the Willamette River at Portland.
5. Feedwater evaporator used to purify Willamette River water at Portland.
6. Mud drum of high pressure boiler served by the evaporator from which sample
5 was obtained.

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CEMENTING ACTION OF SILICA AND THE SILICATES IN BOILER
SCALES

Aggregation of silica or the silicates from boiler
water to form a solid or the formation of boiler scale
containing siliceous matter as a cementing or binding con-
stituent can conceivably take place in one or more ways.
The probability is that a variety of actions account for
any one extensive scale deposit.

The formation of boiler scale as a deposit of essen-
tially silica or quartz appears unlikely and has never
come to the writer's attention. The weight of authority,
furthermore, inclines toward the view expressed. There
must be excepted, of course, the appearance of solid silica
in boiler water as material introduced not unlike fine
sand suspended in feedwater, especially in turbid natural
water. That suspended silica can become entrapped as a
filler or aggregate by other scale forming matter there-
by augmenting the scale yield and enriching the deposit
in silicon (13). Deposits formed from such foul water are
likely to appear as mud or sludge, amorphous rather than
crystalline. The normal alkaline concentration in steam
boilers tends to bring suspended silica into solution so
that it appears the concentration of such suspended solid
matter in a boiler should not be as high as indicated by
the concentration ratio existing between boiler water and

feedwater. The appearance of crystalline silica as an
adherent surface layer over a thin calcium scale has been
reported by F. Hundeshagen (23) who, however, inclines to
the views expressed foregoing. It is interesting to note
that at the high boiler temperatures now in use there is a
not remote possibility of the precipitation of silicic acid
as quartz. The formation of true rock crystal from acid
silicate solution is reported to have been observed (24)
at various temperatures in the range from 400 to 750 de-
grees F. Furthermore, silica might be set free by a re-
action such as those illustrated by the equations (23):

$$Na_2SiO_3 + H_2O = SiO_2 + 2NaOH, \text{ and}$$
$$4Na_2SiO_3 = 2SiO_2 + 2Na_4SiO_4.$$
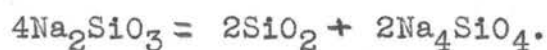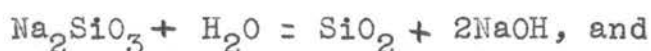
The usual form of entry of silicon into boiler scales
appears to be that of a silicate of an alkaline-earth or
of iron or aluminum. In that form it often constitutes
from forty to fifty per cent of the scale, measured as
SiO_2. Braungard (13) gives the opinion that calcium sili-
cate never enters scale in other than an amorphous form
while magnesium silicate, he believes, is often crystal-
line. He observes, further, a preferential combination of
siliceous matter with magnesium rather than with calcium.
The occurrence of sodium in siliceous scales might appear
to be as a sodium silicate. It is more likely present as
occluded alkali (15).

PREVENTION OF SILICEOUS DEPOSITS IN BOILERS

When water of a considerable silicon content must be used for make-up water in a boiler plant, the prevention of siliceous scale deposit depends on (a) elimination of siliceous matter from the water before it is used for boiler feeding, (b) extraction of siliceous matter from the boiler water as a non-adherent sludge, or (c) maintenance of siliceous matter in the boiler in a soluble and non scale-forming form.

While suspended silica can be largely eliminated by pretreatment (for example, filtration) of boiler feedwater, little success has attended a corresponding removal of dissolved siliceous matter. From the very nature of the usual situation, efforts directed toward preprecipitation of silicate ion may be expected to be inadequate. The softer waters tend to be the more silicate bearing (see (23) the rule of Goldberg). With very soft water chemical pretreatment in any form appears superfluous and equipment is seldom provided.

The methods for the removal of silicate from water are none too sure. Where basic facts have not been established, definite results of a treatment cannot be forecast for specific cases. In this country success has been ascribed to the use of a commercial sodium aluminate preparation (25) consisting of sodium aluminate in a strong sodium hy-

droxide base. The present writer often feels inclined to
attribute the results that are obtained to conditions at-
tending the treatment rather than to the expected primary
reactions. In Germany several treatments are given con-
sideration. Flocculating material, such as aluminum sul-
phate, has been of little use in removing silica evidently
in solution. In laboratory tests, colloidal magnesium hy-
droxide has shown promise as an effective precipitating
agent in several instances. The question may naturally be
asked concerning the use of added magnesium as a supposed
adjunct to the operation of certain commercial reagents
tried in this country whether it is not perhaps the magnes-
ium that ultimately accounts for the silicon removal that
is effected. It appears that silicate removal by lime or
lime-soda water treatment can take place in waters natural-
ly high in magnesium. A much disputed action of the lime-
soda process is perhaps thus clarified. In many careful
German experiments there was observed a much greater af-
finity of silica for magnesium rather than for calcium.
It is interesting to recall in this connection the obser-
vation often made in metallography of the tendency toward
the combination of silicon and magnesium present as im-
purities in non-ferrous metals and alloys. A recent Brit-
ish patent (26) proposes the removal of silicic acid from
water by difficultly soluble hydroxides, such as those of

zinc and iron, applied to the water at pH values in the
alkaline range.

Precipitation of silicates in a non scale-forming
sludge within a boiler has been attempted as in the several
external treatments. The possibilities of success are
less than those of external treatment because of limita-
tions imposed by the dangers of foaming, priming, and
boiler-metal destruction. Organic colloidal substances,
intended to interfere with the building of firm scale,
have proven of little value.

Retention of siliceous matter in soluble and non
scale-forming state in boiler water appears to offer the
best possibilities at present.

By the addition of sufficient sodium and with the
maintenance of pH values in the range from 10 to 12 (a
range suited to boilers for other reasons) it is possible
to render silica soluble in boiler water to concentrations
far greater than those of the permissible or desired
boiler-water densities. The curves of Fig. 1 present
proof of the contention. Various German organizations of
boiler operators have set alkali-silicate concentration
limits of from 1 to 2 degrees Baumé as satisfactory in
every respect for boiler water.

It is unavoidable that alkali-silicate solutions con-
centrated in boilers be loaded with a multiplicity of
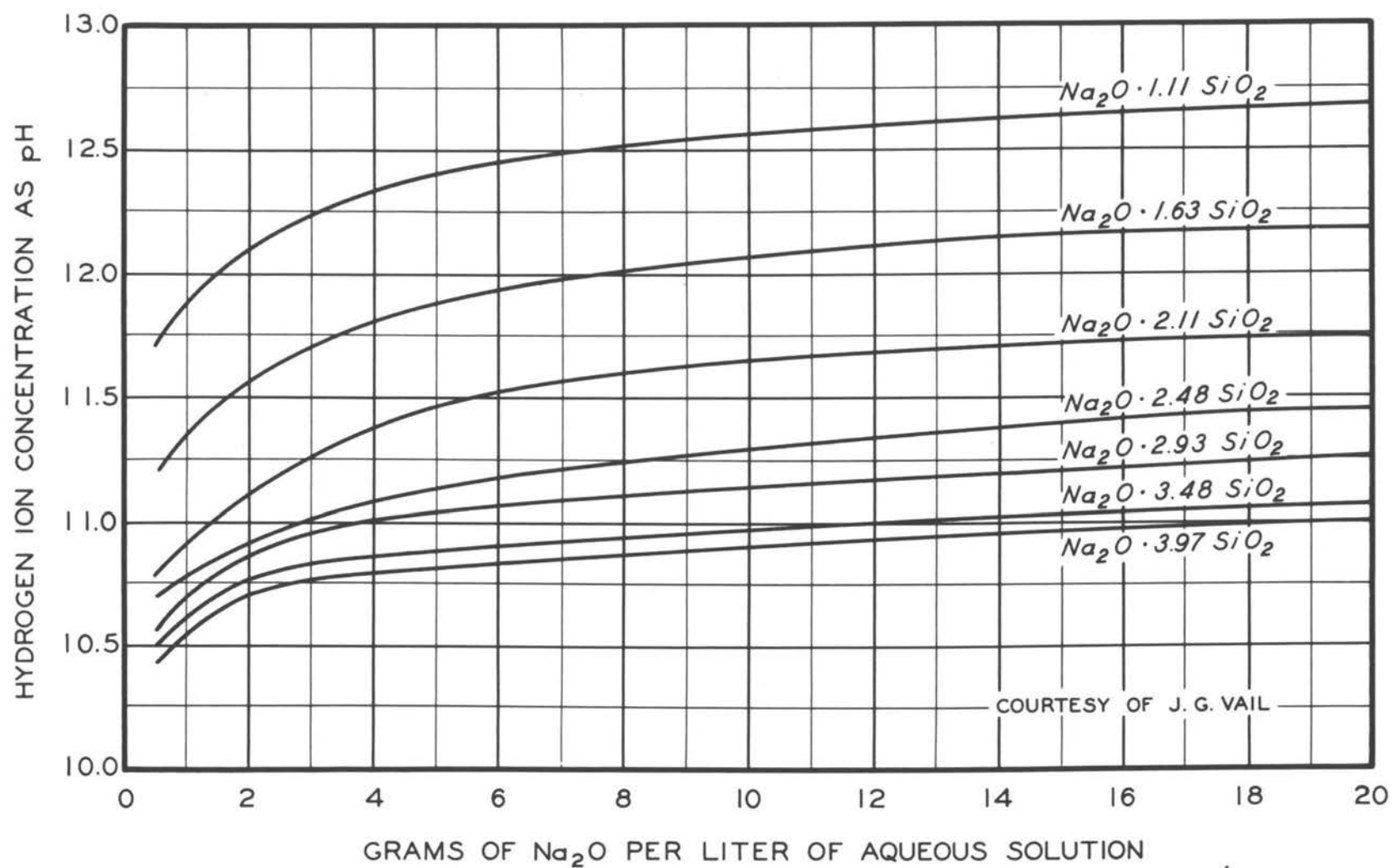
FIG. I. SOLUBILITIES OF SODIUM SILICATES.

other salts such as chlorides, nitrates, sulphates, carbon-
ates, and with positive radicals of any residual calcium
or magnesium hardness. Opportunity is always at hand,
therefore, for siliceous matter to unite with calcium or
magnesium thus escaping from solution as boiler scale.
A very high degree of freedom from the hardness-forming
agents is therefore necessary if siliceous matter is to
be concentrated in boiler water. Even then siliceous de-
posits might occur as a gel formed from high concentra-
tions of solute at evaporating surfaces where water cir-
culation is sluggish. Free silica might be liberated ac-
cording to the reactions suggested foregoing. Any pos-
sible degree of silicon elimination is apparently desir-
able.

Sodium phosphate treatment of boiler water has sever-
al features to recommend it. The phosphate salts of cal-
cium and magnesium are highly insoluble in alkaline solu-
tion in the presence of excess phosphate. A small initial
or residual hardness of water can therefore be removed to
a considerable degree of completeness, as phosphate.
Sodium from the original reagent contributes to the forma-
tion of soluble alkali-silicates (27). The normal high
pH values of solutions of the less acid alkali-phosphates,
for example, trisodium phosphate with a solution pH rang-
ing around 12, insure a maximum solubility of siliceous

matter. Magnesium and calcium precipitates formed with
phosphate have the added advantage of carrying with them
from the water a considerable amount of silica. Hunde-
shagen (23) observed tests in which those precipitates
removed 40 to 80 per cent of the silicon from weak silic-
ic acid solutions. Magnesium precipitates were nearly
twice as effective as like calcium precipitates. The
present writer has found fifteen per cent SiO_2 in the
dried precipitate recovered from the waters of boilers
subjected to internal phosphate treatment. In that in-
stance the boiler make-up water was a soft natural water
in which magnesium made up a part of the little hardness
present. The cold, raw water was passed through a pres-
sure sand filter and was deaerated in an open heater be-
fore being fed. The silica recovered in the determination
was observed to be surprisingly light and fluffy.

It is interesting to note that some difference of
opinion exists concerning the effect of alkali on the
formation of siliceous scales. The preponderance of o-
pinion is in accord with that expressed herein, that in-
crease in sodium concentration in boiler water increases
the solubility of the siliceous matter, thus reducing the
tendency of it to form scale. It is the recommendation of
some European boiler users associations that limitation of
the alkali content of boiler water be depended on to pre-

vent siliceous scales.   It is not impossible that with

turbid water containing SiO_2 in suspension and little

siliceous matter or alkali in solution the restriction

of sodium in boilers using that water would prevent the

bringing of the silica into solution in the boiler, where

concentration of its solutions under unfavorable condi-

tions would result in scale formation.

IV. POSSIBILITIES OF RATIONAL

BOILER-WATER TREATMENT IN WESTERN OREGON

Consideration of the problems of boiler water unique
to western Oregon in relation to the usual possibilities
of their solution brings to light these facts:

(1) Scale problems arise from combination of material
with hardness less than the lower limit of operation of
several of the most common external water treatments.
Evaporation as a treatment is usually justified in only
high pressure or high capacity power plants, and there it
is inadequate because of impurity carryover in the vapor,
steam condenser cooling water leakage, etc. Thermal de-
gasification, as in open heaters, can be expected to re-
move practically no scale-forming matter in the region in
question. The lime-soda process of water softening is
useless in most instances and is hazardous in the majority
of cases in which it is effective in lowering hardness (28)
because the carbonate hardness tends to exceed the perma--
nent hardness in the waters encountered. Base-exchange
treatment gives only a small percentage removal of the
very low hardness, may actually contribute to the sili-
cate content of the water treated (9, 29), and leaves the
way open for embrittlement of boiler metal, except under
close and intelligent supervision, because of the low sul-
phate content of natural waters. Properly chosen and pro-

perly administered internal treatments are economically
justified and **practically** necessary as in the after-
treatment of softened water. The stable, sparingly soluble
radicals, such as the phosphate radical, are indicated.
Specifics, if any, for silicate deposition are necessary.
Either silicate should be removed from boiler water, it
should be held in solution so it cannot accrete as scale,
or hardness that aids it in scale formation must be pre-
vented from combining with it.

(2) Foaming and priming have not yet developed as
serious problems with the boiler operating rates demanded,
the general purity of natural water, and the small use of
water treatments. It is apparent that resort to water
treatments, suitable or improper, will develop these ten-
dencies and all programs of water betterment should regard
them with caution. The very freedom from foaming and
priming indicates the need for blow down schedules scien-
tifically evolved, that there can be a full realization
of the benefits of good water.

(3) Corrosion is a hazard of more than usual ser-
iousness. The dissolved oxygen content of surface water
likely to be used in boiler plants may actually exceed
saturation value of oxygen in water. In the centers of
population where dissolved oxygen is least in streams the
best control of corrosion is exercised in the central

power stations there located. In the rural sections, the camps, and the mountains, laying claim to many mills, the potential corrosive capacity of water is found at its maximum, less thorough supervision is the rule in isolated plants there encountered, and treatments that might minimize the effect of dissolved oxygen are less common. Various influences that tend to raise the effective alkalinity of boiler water, such as feedwater softening and the minimizing of blowdown, are not generally at work. When the carbonate content of waters is low, hydroxide is but slowly developed from carbonate breakdown. Low pH values and high dissolved oxygen concentrations tend to occur simultaneously in those plants where operators are least prepared to understand and effectively combat corrosion. The price paid for boiler metal corrosion in western Oregon is not well known. It is sure to be a price all out of proportion to that suffered in regions where corrosion is now seriously regarded.

Thermal and vacuum degasification should be rigorously applied to raw feedwater, but in addition to all attempts at oxygen removal the corrosion rate of residual oxygen should be made low by maintenance of sufficient effective alkalinity. Boiler water should have a pH value of more than 10 or 11 even if the feeding of caustic must be undertaken with proper precautions, of course. Steam

should be slightly alkaline rather than acid as it tends to become when no treatment is used. Feedwater, degasified even to the point of introduction into the boiler, should be maintained alkaline by the addition to it of chemicals required by the boiler water or by recirculation of a small amount of boiler saline in the feedwater system.

(4) Embrittlement is a danger in all boiler installations. It is a constant threat of property damage and destruction of human life the only escape from which is found in a record of boiler operation showing water conditions at all times unfavorable to embrittlement. That embrittlement has not been identified in the region is no proof of its nonoccurrence there. With the advent of high pressure boiler installations and with the extension of water treatment, good or bad, this type of boiler failure must surely put in an appearance. The natural waters are singularly free of protecting sulphates. The difficulty with silicates tends to promote caustic treatments that in turn promote boiler metal failure. The A.S.M.E. embrittlement protection ratios should unquestionably be maintained in all those plants where the most precise water control is not the rule. In central stations where chemists are in charge the newer inhibitors and the more abstruse control methods might be tried. Straub has expressed the opinion to the writer (30) that "as soon as

chemical treatment is resorted to and the sodium alkalin-
ity becomes appreciable, it would be advisable to make
certain that the proper ratios are being maintained."

V. SPECIFIC RESULTS

BOILER-WATER STUDIES---

OREGON STATE AGRICULTURAL COLLEGE HEATING PLANT

A study of boiler water conditions was undertaken
at the central heating plant of Oregon State Agricultural
College during the late summer of 1932. That work was
continued through the winter of 1932-33 and a program of
control that was evolved and tried has been carried out
without interruption and with no essential change to the
present writing (April, 1933). An apparently satisfactory
solution of boiler water problems has been achieved at the
college heating plant, and it is the intention of the
Superintendent of Heating, Mr. M. C. Phillips, to continue
the control as herein devised and developed.

The development, findings, and application of the
study are given here to illustrate the general principles
that have been found satisfactory and effective in boiler-
water conditioning under the distinctive conditions of
western Oregon.

Just prior to initiation of the study the heating
plant boilers had received their annual inspection and
cleaning. The thin scale deposit accumulated in the tubes
was found to be exceedingly adherent and very hard. Tur-
bine type tube cleaners penetrated the deposits with the
greatest difficulty, such that an allowed cleaning time

of two to three hours a tube did not remove all scale. For
the protracted cleaning periods required, the cost of
labor and of water for tube cleaner operation was regard-
ed as the equivalent of a large possible saving, could
such cost be eliminated. Other benefits expected of a
truly successful chemical treatment were reduced wear and
tear on cleaning equipment and on boiler tubes and the
possibility of always having the boilers cleaner than they
could be made even at the time of mechanical scale re-
moval. Some dissatisfaction had grown up with regard to
the common commercial treatments previously used due to
lack of assured embrittlement protection and because of
the large blow down rates that they tolerated.

Rough qualitative tests of scale removed from the most
used boilers showed it to consist in large part of sili-
ceous matter (See also Table VI). Lack of water treatment
or the nature of some treatments used presaged a small
sodium concentration in the boiler water. A considerable
blow down (concentration not more than four or five times)
with a pure, relatively very soft make-up water from Cor-
vallis city mains, (hardness not more than about 2.5 grams
per gallon expressed as $CaCO_3$, all bicarbonate), indicated
low total and effective boiler-water alkalinities. The
siliceous matter content of filtered raw water was ob-
served to be as high as 20 parts per million as SiO_2.

It was decided to precipitate calcium and magnesium from
the boiler water as a phosphate applied within the boil-
ers, thus eliminating certain components of the scale
building material to a high degree of completeness. Pro-
tection against boiler metal embrittlement was to be made
certain through continuous adherence to the A.S.M.E. sul-
phate-alkalinity specification. A preliminary control
test was made on one boiler, number 3, as shown in the
data for that boiler in the period, September 2 to October
2, 1932. (See Appendix A).

From the findings of the preliminary test on boiler
number 3, two useful results were obtained:

(1) A phosphate demand curve, Fig. 2, was prepared
for use in forecasting the phosphate requirements of the
make-up water, should the impurity content of that water
continue to be substantially that encountered during the
test. It has often been recognized by those persons en-
gaged in boiler water treatment, and the statement has
been published (31) subsequent to this work, that depend-
ence is seldom to be placed on water treatment dosages
calculated from one or even from several mineral analyses
of the water used. One leader in the field depends solely
on obtained soluble phosphate shown by actual analysis of
water from the boiler treated. Phosphate concentration is
built up in the boiler as boiler-water analyses show need
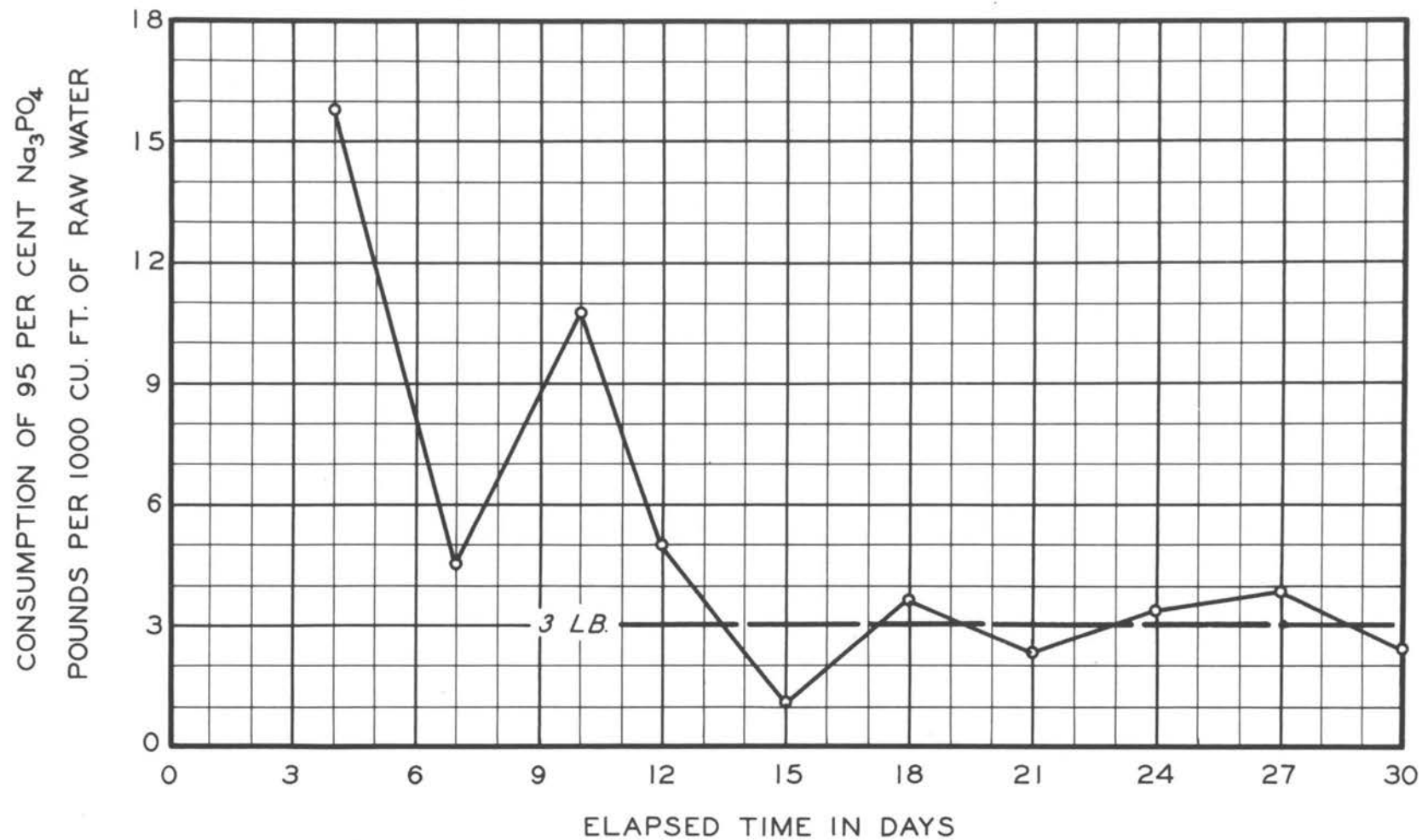
FIG. 2. PHOSPHATE DEMAND – O.S.A.C. HEATING PLANT.

for it is required. The discordancy is particularly great
at the outset of treatment when interaction between treat-
ment chemical and scale residue in the boiler is likely to
be most rapid. The rate and extent of action of phosphate
on scale-forming matter already deposited, probably cannot
be forecast. The diagram obtained was prepared from a
phosphate account included with the test results. Items in
the phosphate account were calculated as illustrated in
Appendix A. From the diagram it was determined that the
phosphate demand tended, after some days of treatment, to
approach three pounds of commercial trisodium phosphate
for every thousand cubic feet of make-up water. Since the
PO_4 content of a pound of commercial disodium phosphate
differs but little from that of a pound of the tribasic
salt, it was reasoned that the two salts could be used more
or less interchangeably on the practical basis of three
pounds per thousand cubic feet of water. A convenient
practical means of alkalinity control was thus made avail-
able without introducing confusion of the boiler operators
in the change of dosage rate with change of the phosphate
form. Periodic adjustment of the actual phosphate content
of the boiler water was planned on the basis of weekly
routine analyses of the water.

(2) As an application of the facts observed and the
fundamental principles presented in the work, a schedule

or control program was established for subsequent use. Some items in that schedule perhaps cannot be precisely justified, representing the writer's judgment in the light of facts available. The schedule is given to indicate the type of information that a plant superintendent has use for.

In the application of the control program, volumetric measurement of sodium phosphate was provided for. The boiler operating crew was supplied with a pan that would just contain the three pound portion of chemical indicated for every thousand cubic feet of raw water. Instructions for the replacement of phosphate and sulphate lost in blow down were reduced to simple form. Adjustments of chemical concentrations, other than those cared for by the routine work of the boiler operators, have been necessary on relatively few occasions in six months of plant control. Several of the adjustments that have been made were related to anticipated changes in natural water conditions due to winter storms. No lack of flexibility of operation of the several units of the boiler plant has resulted from the control program.

Records that depict the operation of the control program proper are given in Appendix B. The economic gain from the control program is greater than that at first apparent. The saving in boiler cleaning costs can be estimated when usual cleaning costs and the percentage

reduction in cleaning time are known. (See Appendix B).
The fuel saving due to better heat transmission through
boiler surfaces kept constantly clean can be considered
appreciable. The saving due to reduction in water dis-
carded in blowdown, not counting the heat lost in that
water, represents a cash saving of at least twenty cents
a day or roughly sixty dollars a year. That amount is
approximately sufficient to pay for all chemicals, includ-
ing even the sodium sulphate necessary in any event for
metal embrittlement control.

See page 48 for Schedule for Control Program.

SCHEDULE FOR CONTROL PROGRAM

BOILER-WATER STUDIES

O.S.A.C. HEATING PLANT

1932 - 1933

PHOSPHATE

Hold to approximately 50 p.p.m. of PO_4 in solution.

(a) To give reserve capacity for hardness pre-
cipitation

(b) To promote thorough precipitation of calcium
and magnesium

(c) To realize any embrittlement protection due
to phosphate

ALKALINITY

Hold the total methyl orange alkalinity above about
150 to 200 and below, about 350 p,p.m. as Na_2CO_3.

(a) To give a high enough pH value

(b) To keep silicate in solution

(c) To make possible infrequent blow down

(d) To obviate very high sulphate concentrations
necessary for embrittlement protection

(e) To minimize carry-over in the steam

HYDROGEN ION CONCENTRATION, pH

Maintain from 10.0 to 11.5.

(a) To minimize the corrosion rate

(b) To promote silicate solubility

SCHEDULE FOR CONTROL PROGRAM (Concluded)

(c) To insure the formation of tribasic, or at

least dibasic, phosphate precipitates

SULPHATE

Maintain the Na_2SO_4 - Na_2CO_3 ratio well above 1 and

preferably nearly 2, to give positive adherence to

the best practice in embrittlement control.

BLOW DOWN

Limit to one blow down of 1000 gallons for every

boiler once each week.

(a) To insure sufficient alkalinity and sodium

content of the boiler water

(b) To save water and chemicals

DISSOLVED SOLIDS

Limit tentatively to 100 grains per gallon.

(a) To minimize carryover and guard against ex-

cessive priming

(b) To limit the sulphate

VI. CONCLUSIONS

The general conclusions to be drawn from this investigation may be stated as follows:

1. The practice of boiler-water conditioning has advanced to such a position that any ordinary difficulty can be eliminated or mitigated. Attention is now being turned to a refinement of methods and toward a complete solution of the unique chemical and economic problems involved.

2. It is apparent that no natural water, regardless of its freedom from hardness, is entirely satisfactory for boiler use without at least some treatment or chemical control.

3. The highly soft natural waters of western Oregon, and perhaps other waters from diverse localities softened to a like degree, are inclined, under the prevailing high boiler temperatures, minimum blow down rates, and limited boiler-water alkalinities (demanded by metal embrittlement control), to the deposition of very hard, heat resistant siliceous boiler scale of the most objectionable and dangerous type.

4. The now somewhat traditional practices in blowing down boilers can be largely eliminated where soft water is available. Reduction in blow down should result in the saving of heat and of water and in some cases may actually

retard scale deposition.

5. Reference to and discussion of the causes, possibilities of formation, objectionable features, and preventives of siliceous boiler scale are most casual and incidental, if not wholly omitted, in water treating literature. The entire subject merits more attention than it has heretofore received in this country. In western Oregon it is properly given first consideration in treating water for boiler use. The author has encountered natural waters that contained 45 parts per million of siliceous matter (expressed as SiO_2) apparently in solution, an amount not much less than the accompanying calcium and magnesium hardness.

6. For the prevention of siliceous boiler scale deposition from feedwater bearing silicates apparently dissolved, some practices are to be observed as working rules:

(a) Hardness-forming matter is to be removed to a high degree of completeness. Terminal or internal water treatment is to be resorted to, when necessary.

(b) Siliceous matter is to be maintained in a highly soluble form in the boiler water. This requires high boiler-water pH values and sodium concentrations, both of which are to be tolerated only

when metal embrittlement protection is sure.

(c) Even partial elimination of siliceous matter
from the concentrated boiler water is highly
desirable. Precipitates formed in hardness
treatment, especially the phosphate precipitates,
appear to bring down some silicon.

7. In western Oregon the conventional feedwater and
boiler-water treatments for hardness removal should be
used with reservation and with a knowledge of their limita-
tions. Internal treatments are often necessary and are
usually economically justified. When phosphates are used
they should be the more alkaline-forming sodium salts
rather than the alkali-neutralizing salts used to advan-
tage elsewhere. In the use of special phosphates de-
veloped for the Hall system of water treatment, the feeding
of sodium hydroxide to treated boilers is desirable, as-
suming adequate chemical control.

8. The situation in boiler chemistry favors procedures
that are systematic and specific with respect to the needs.
No one problem is to be considered apart from all possible
problems. This is especially true in western Oregon where
treatment for the peculiar troubles will certainly result
in the appearance of difficulties, such as boiler metal
embrittlement, common elsewhere but little known there.
The practice employed and the care and control exercised,

rather than the special chemical or reagent used, measure the success of the work. Emphasis is properly placed on chemical conditions consistently maintained in the boiler water rather than on the impurity content of any natural water used as a primary source of water supply.

APPENDIX A

BOILER-WATER STUDIES

O.S.A.C. HEATING PLANT

PRELIMINARY TESTS, BOILER NO. 3   SUMMER OF 1932

TABLE VII

TOTAL ALKALINITY

Date	Burette Reading, cc. N/50 Acid to 100 cc.	Alkalinity, p.p.m. As $CaCO_3$	As Na_2CO_3
Sept. 2	6.2	62	66
3	11.0	110	117
4	....	...	...
5	11.5	115	122
6	11.0	110	117
7	14.5	145	154
8	24.2	242	257
9	22.0	220	233
10	24.0	240	254
11	....	...	...
12	....	...	...
13	....	...	...
14	12.0	120	127
15	....	...	...
16	17.0	170	180
17	16.5	165	175
18	....	...	...
19	17.5	175	186
20	25.0	250	265
21	25.0	250	265
22	....	...	...
23	24.5	245	259
24	....	...	...
25	....	...	...
26	27.0	270	286
27	....	...	...
28	....	...	...
29	22.0	220	233
30	....	...	...
Oct. 1	....	...	...
2	22.0	220	233

For test procedure see American Public Health Association, "Standard Methods", Ed. 7, p. 33, 1933

TABLE VIII

PHOSPHATE

Date	Time of Day	Concentration, p.p.m. PO_4	Remarks
Sept. 2	....	...	Phosphate first introduced
3	....	...	Blow down
4	....	...	Off line, Plant closed
5	....	...	Blow down
6	9:00 A.M.	5	Blow down
	3:00 P.M.	25	....
	4:50 P.M.	50	....
	6:45 P.M.	60	....
7	6:50 A.M.	35	Blow down only 500 gallons*
	11:25 A.M.	100	....
	6:30 P.M.	90	....
8	7:00 A.M.	85	No blow down
	12:00 M	70	....
	6:00 P.M.	65	....
9	6:00 A.M.	65	No blow down
	4:15 P.M.	65+	....
	6:30 P.M.	90+	....
10	6:00 A.M.	85+	No blow down
11	....	...	Off line. No blow down
12	7:00 A.M.	60	Boiler cooled and opened*

*After test

TABLE VIII--Continued

PHOSPHATE

Date	Time of Day	Concentration, p.p.m. PO_4	Remarks
Sept. 13	....	...	Boiler refilled with city
14	7:30 A.M.	50	No blow down water
15	....	...	No blow down
16	....	...	Blow down 1000 gallons
17	7:00 A.M.	70	No blow down
18	....	...	Blow down 1000 gallons
19	7:00 A.M.	15	No blow down
20	8:00 A.M.	85	Blow down 1000 gallons
21	7:00 A.M.	90	Blow down 1000 gallons
22	....	...	No blow down
23	7:00 A.M.	60	No blow down
24	....	...	No blow down
25	....	...	No blow down
26	7:00 A.M.	60	No blow down
27	....	...	Blow down 1000 gallons
28	....	...	No blow down
29	9:00 A.M.	20	No blow down; off line P.M.
30	....	...	No blow down; off line
Oct. 1	....	...	No blow down P.M.
2	8:00 A.M.	35	No blow down
3	....	...	Blow down 1000 gallons

For test procedure see Straub, F.G., "Control of Boiler-Water Treatment to Prevent Embrittlement," Mechanical Engineering, v. 51, p. 366, 1929.
Interference due to silica was found to be little.

TABLE X

pH VALUE

Date	Approximate Reading[*]	Method of Test
Sept. 2	10	By universal indicator
3	10+	By Sofnol indicator
4	..	....
5	10+	By Sofnol indicator
6	..	....
7	10+	By Sofnol indicator
8	10+	By universal indicator
9	10+	By Sofnol indicator
10	10+	By Sofnol indicator
11	..	....
12	..	....
13	..	....
14	10+	By Sofnol indicator
15	..	....
16	..	....
17	..	....
18	..	....
19	10+	By Sofnol indicator
20	..	....
21	11	By universal indicator
22	..	....
23	10+	....

[*]The testing facilities were such that readings in excess of 10 were estimates only.

TABLE IX

SULPHATE

Date	As read[*]	Concentration as Na_2SO_4 g.p.g.	p.p.m.	Na_2SO_4/Na_2CO_3
	Application deferred until September 19 due to an inadequate supply of chemical			
Sept. 19	1.7	17	288	1.50
20	1.6	16	272	1.03
21	1.8	18	306	1.15
22	...	..	...	....
23	1.7	17	288	1.11
24	...	..	...	....
25	...	..	...	....
26	2.1	21	357	1.25
27	...	..	...	....
28	...	..	...	....
29	1.7	17	288	1.23
30	...	..	...	....
Oct. 1	...	..	...	....
2	1.9	19	323	1.39

[*]Results are cc. of N/7 sodium hydroxide required by 58.3 cc. of boiler water in the benzidine test for sulphates.

For test procedure see National Electric Light Association, "Treatment of Feedwater," Publication No. 235, p. 9, July 1932.

TABLE XI

TOTAL DISSOLVED SOLIDS

BY SPECIAL HYDROMETER

Date	Determination, Grains per gallon
Sept. 16	Less than 20
17	. . . .
18	. . . .
19	20
20	20
21	Less than 20
22	. . . .
23	Less than 20
24	. . . .
25	. . . .
26	40
27	. . . .
28	. . . .
29	40
30	. . . .
Oct. 1	. . . .
2	60

TABLE XII

RAW WATER

Date		Time of Day	Meter Reading, Cumulative cu. ft.
Sept.	2	4:00 P.M.	0876650
	3	9:00 A.M.	0876970
	4	....	....
	5	9:00 A.M.	0877510
	6	9:00 A.M.	0877910
	7	9:00 A.M.	0878330
	8	9:00 A.M.	0878850
	9	9:00 A.M.	0879590
	10	....	....
	11	....	....
	12	....	....
	13	....	....
	14	....	....
	15	....	....
	16	9:00 A.M.	0883270
	17	....	....
	18	....	....
	19	8:00 P.M.	0886450
	20	6:30 A.M.	0886980
	21	6:00 A.M.	0888330*
	22	7:00 A.M.	0889470
	23	7:00 A.M.	0890500
	24	....	....
	25	....	....
	26	7:00 A.M.	0893530
	27	....	....
	28	....	....
	29	7:00 A.M.	0896190
	30	....	....
Oct.	1	8:20 A.M.	0899760
	2	....	....

*Divide the water between two boilers after the reading of Wednesday morning, September 21.

TABLE XIII

CHEMICALS USED

(Phosphate in terms of 95 per cent $Na_3PO_4 \cdot 12 H_2O$;
sulphate as approximately $Na_2SO_4 \cdot 10 H_2O$)

Date	Time of Day	Material to Boiler
Sept. 2	4:00 P.M.	10.0 lb. phosphate; 1.0 lb. sulphate
3	7:00 P.M.	5.4 lb. phosphate; 4.0 lb. sulphate
4	....	....
5	....	....
6	7:00 A.M.	5.4 lb. phosphate
	1:00 P.M.	9.0 lb. phosphate
7	10:30 A.M.	10.0 lb. phosphate
8	....	....
9	4:25 P.M.	4.5 lb. phosphate
10	....	....
11	....	....
12	(During shut down September 12 there was added
13	12.5 lb. phosphate to city water fed for oper-
14	ation beginning September 14)
15		
16	6:00 A.M.	7.0 lb. phosphate
17	....	....
18	....	20.0 lb. sulphate
19	7:00 A.M.	3.5 lb. phosphate for blow down
20	6:00 A.M.	12.5 lb. phosphate
21	6:00 A.M.	4.3 lb. phosphate; 5.0 lb. sulphate
22	....	....
23	6:00 P.M.	5.0 lb. phosphate; 5.0 lb. sulphate
24	....	....
25	....	....
26	....	....
27	....	....
28	....	....
29	....	....
30	8:00 A.M.	7.0 lb. phosphate; 5.0 lb. sulphate
Oct. 1	....	....
2	....	....
3*	5:00 P.M.	4.0 lb. phosphate; 5.0 lb. sulphate

*Control program in operation

TABLE XIV

PHOSPHATE ACCOUNT

(In terms of 95 per cent $Na_3PO_4 \cdot 12\ H_2O$)

Date	Time of Day	Gross Supplied, Lb.		Amount in Solution, Lb.
		Increment	Total	
Sept. 2	....	10.0	10.0	....
3	7:00 P.M.	5.4	15.4	....
4	....	....	....	....
5	....	....	....	....
6	9:00 A.M.	5.4	20.8	0.9
7	....	....	....	....
8	....	....	....	....
9	6:00 A.M.	19.0	39.8	11.7
10	....	....	....	....
11	....	....	....	....
12	7:00 A.M.	4.5	44.3	10.8
13	Boiler inspected and treatment resumed.			
14	7:30 A.M.	12.5	12.5	9.0
15	....	....	....	....
16	....	....	....	....
17	7:00 A.M.	7.0	19.5	12.6
18	....	....	....	....
19	....	....	....	....
20	8:00 A.M.	16.0	35.5	15.3
21	....	....	....	....
22	....	....	....	....
23	7:00 A.M.	4.3	39.8	10.8
24	....	....	....	....
25	....	....	....	....
26	7:00 A.M.	5.0	44.8	10.8
27	....	....	....	....
28	....	....	....	....
29	9:00 A.M.	0.0	44.8	3.6
30	....	....	....	....
Oct. 1	....	....	....	....
2	8:00 A.M.	7.0	51.8	6.3

TABLE XIV--CONTINUED

PHOSPHATE ACCOUNT

(In terms of 95 per cent $Na_3PO_4 \cdot 12\ H_2O$)

Date		Time of Day	Days Elapsed	Blow Down Loss, Lb. Increment	Total	Raw Water, Cu. Ft.
Sept.	2	....	0	0.0	0.0	....
	3	7:00 P.M.	1	Neglected	0.0	....
	4	....	2	0.0	0.0	....
	5	....	3	Neglected	0.0	....
	6	9:00 A.M.	4	Neglected	0.0	1260
	7	....	5	...	...	....
	8	....	6	...	...	....
	9	6:00 A.M.	7	0.6	0.6	1680*
	10	....	8	...	...	....
	11	....	9	...	...	....*
	12	7:00 A.M.	10	0.0	0.6	500*
	13	Boiler inspected and treatment resumed.				
	14	7:30 A.M.	12	0.0	0.0	700*
	15	....	13	...	...	....
	16	....	14	...	...	....*
	17	7:00 A.M.	15	1.8	1.8	1500*
	18	....	16	...	...	....
	19	....	17	...	...	....
	20	8:00 A.M.	18	1.8*	3.6	2980
	21	....	19	...	...	....
	22	....	20	...	...	....d
	23	7:00 A.M.	21	3.2	6.8	2435d
	24	....	22	...	...	....
	25	....	23	...	...	....d
	26	7:00 A.M.	24	0.0	6.8	1515d
	27	....	25	...	...	....
	28	....	26	...	...	....d
	29	9:00 A.M.	27	2.0	8.8	1330d
	30	....	28	...	...	....
Oct.	1	....	29	...	...	....d
	2	8:00 A.M.	30	0.0	8.8	1785d

*Approximate or involves estimate of some quantity. The long time totals are necessarily exact.

dBased on an assumed equal division between two boilers operated simultaneously.

TABLE XIV--Concluded

PHOSPHATE ACCOUNT

(In terms of 95 per cent $Na_3PO_4 \cdot 12\ H_2O$)

Date		Total	Increment	Net Consumption in Pounds per 1000 Cu. Ft. Water
Sept.	2	0.0	0.0	....
	3	....	....	....
	4	....	....	....
	5	....	....	....
	6	19.9	19.9	15.8
	7	....	....	....
	8	....	....	....
	9	27.5	7.6	4.5
	10	....	....	....
	11	....	....	....
	12	32.9	5.4	10.8
	13	Boiler inspected and treatment resumed		
	14	3.5	3.5	5.0
	15	....	....	....
	16	....	....	....
	17	5.1	1.6	1.1
	18	....	....	....
	19	....	....	....
	20	16.6	11.0	3.7
	21	....	....	....
	22	....	....	....
	23	22.2	5.6	2.3
	24	....	....	....
	25	....	....	....
	26	27.2	5.0	3.3
	27	....	....	....
	28	....	....	....
	29	32.4	5.2	3.9
	30	....	....	....
Oct.	1	....	....	....
	2	36.7	4.3	2.4

ILLUSTRATIVE CALCULATION OF ENTRIES

IN THE PHOSPHATE ACCOUNT

It is apparent that, at any time after treatment has
been in progress, phosphate can be accounted for by the
expression:

Phosphate Consumed = Total Supplied

- (That Present + Total Lost)

When a record is kept of the total phosphate supplied,
the amount of phosphate consumed by chemical reaction may
be readily calculated if the amount of the free phosphate
in solution is known and if losses in blow down, etc., are
likewise known, or can be estimated.

An illustrative calculation may be made from the data
of September 26 and 29. Knowing that every part per mil-
lion of PO_4 represents 0.18 pounds of the salt as measured
(See "Calculation of the Phosphate Charge), it is seen
from the phosphate concentration data that the phosphate
present September 26 was 60 x 0.18 or 10.8 pounds, while
on September 29 it was 20 x 0.18 or 3.6 pounds. The phos-
phate consumed in the entire duration of the test to Sep-
tember 26 was 44.8 - (10.8 + 6.8) = 27.2 pounds. Likewise
the amount consumed by September 29 was 44.8 - (3.6 + 8.8)=
32.4 pounds. The phosphate consumption in the time inter-
val considered was 32.4 - 27.2 = 5.2 pounds. The water
supplied in the same period was 1330 cubic feet. The phos-
phate demand indicated was Demand = $\frac{5.2}{1330}$ = 3.9 pounds.

CALCULATION OF THE PHOSPHATE CHARGE

BASED ON

50 PARTS PER MILLION OF PO_4 IN SOLUTION

Capacity of boiler 5000 gallons.

Quantity of trisodium phosphate equivalent to 50 p.p.m. of PO_4:

General data:

Nature of chemical used
$Na_3PO_4 \cdot 12H_2O$ (95 per cent pure) = 380

Active Matter
PO_4 = 95

Dosage ratio
$$\frac{380}{95} \times \frac{1}{0.95} = \frac{4}{0.95} = 4.20$$

Practical measure of 50 p.p.m.:

50 p.p.m. = nearly 3 grains per gallon

Pounds per 10000 gallons = $\frac{3}{0.7}$ = 4.30

Pounds per 5000 gallons = 2.15

Actual reagent required:

2.15 x 4.20 = 9.0 pounds, or

0.18 pounds for each p.p.m. of PO_4.

CALCULATION OF SULPHATE DOSAGE

TO PRODUCE

ANY DESIRED SOLUTION CONCENTRATION

Capacity of boiler 5000 gallons.

Quantity of sodium sulphate equivalent to any concentration:

General data:

Nature of chemical used
$Na_2SO_4 \cdot 10H_2O$ (approximately) = 322

Active Matter
Anhydrous Na_2SO_4 = 142

Practical measure of the actual reagent required:

100 p.p.m. = 5.9 grains per gallon

Pounds per 10000 gallons = $\frac{5.9}{0.7}$ = 8.4

Pounds per 5000 gallons = 4.2

$4.2 \times \frac{322}{142}$ = 9.7, or nearly 10, pounds of Na_2SO_4
$Na_2SO_4 \cdot 10H_2O$ for every 100 p.p.m.
Use 1 pound for 10 p.p.m.

APPENDIX B

BOILER WATER STUDIES

O.S.A.C. HEATING PLANT

A CONTROL PROGRAM   1932-1933

TABLE   XV

PHOSPHATE

(ALL BOILERS)

| Date | Phosphate as p.p.m. PO_4 in Solution | | |
	No. 1	No. 2	No. 3
Oct. 2	...	55	35
9	...	35	30
16	...	35	65
23	...	60	35
30	...	55	50
Nov. 2	50	50	...
6	70	...	70
13	...	70	110
20	...	60	50
27	...	50	70
Dec. 4	70	120	40
11	90	45	35
18	70	...	70
25	...	70	70
Jan. 1	...	65	70

TABLE   XVI

ALKALINITY

BOILER NO. 1

Date	Alkalinity as p.p.m. $CaCO_3$ Phenolphthalein	Methyl Orange	Total Alk. as Na_2CO_3
(Boiler was not in service until November 2)			
Nov. 2	140	185	196
6	172	230	244
13		Out of service	
20		Out of service	
27		Out of service	
Dec. 4	153	221	234
11	244	327	347
18	292	384	407
25		Out of service	
Jan. 1		Out of service	

TABLE XVII

ALKALINITY

BOILER NO. 2

Date	Alkalinity as p.p.m. $CaCO_3$		Total Alk. as Na_2CO_3
	Phenolphthalein	Methyl Orange	
Oct. 2	...	300	318
9	150	187	198
16	183	220	233
23	136	165	175
30	126	156	165
Nov. 2	125	148	157
6	Off line from November 4		
13	98	135	143
20	89	142	151
27	154	203	215
Dec. 4	178	260	276
11	203	289	306
18	Out of service		
25	113	162	172
Jan. 1	134	202	214

TABLE XVIII

ALKALINITY

BOILER NO. 3

Date	Alkalinity as p.p.m. $CaCO_3$		Total Alk. as Na_2CO_3
	Phenolphthalein	Methyl Orange	
Oct. 2	...	220	233
9	187	215	228
16	164	193	205
23	133	155	164
30	123	145	154
Nov. 2	Off line October 30 to November 4		
6	105	140	148
13	112	137	145
20	95	130	138
27	95	123	131
Dec. 4	82	122	129
11	91	125	133
18	130	205	217
25	125	167	177
Jan. 1	158	212	224

TABLE   XIX

SULPHATE

(ALL BOILERS)

Date	Sulphate as p.p.m. Na_2SO_4		
	No. 1	No. 2	No. 3
Oct. 2	...	408	323
9	...	323	407
16	...	255	205
23	...	221	205
30	...	238	205
Nov. 2	306	187	...
6	272	...	390
13	...	390	254
20	...	305	238
27	...	306	136
Dec. 4	340	459	374
11	561	459	272
18	612	...	289
25	...	408	306
Jan. 1	...	391	323

TABLE XX

A.S.M.E. EMBRITTLEMENT RATIO

(ALL BOILERS)

| Date | Ratio of Na_2SO_4 to Na_2CO_3 | | |
	No. 1	No. 2	No. 3
Oct. 2	....	1.29	1.39
9	....	1.63	1.79
16	....	1.10	1.00
23	....	1.26	1.25
30	....	1.44	1.33
Nov. 2	1.56	1.19	....
6	1.12	....	2.63
13	....	2.73	1.75
20	....	2.02	1.72
27	....	1.42	1.07
Dec. 4	1.46	1.67	2.90
11	1.61	1.50	2.05
18	1.51	....	1.33
25	....	2.38	1.72
Jan. 1	....	1.83	1.45

INSPECTION RECORD

Boiler No. 3 was opened for inspection March 20, 1933, after practically continuous operation under the control and study programs from September 1, 1932.

Scale in the boiler tubes was observed to consist of only scattering residual patches of old scale not removed by cleaning during the summer of 1932. Old scale was much softer than originally and gave the appearance of tending to flake off gradually. Tubes observed were absolutely devoid of hard scale between old deposits. Tube sheets, hand hole sheets, and staybolts were practically freed of old scale deposit left at the time of the last boiler cleaning. Very little sludge and sediment was left in the boiler after it was drained. The boiler metal showed only a normal oxide coating. No feed line deposit of mineral origin could be found. There was no evidence of solid matter carryover in steam. Indications were that old scale deposits would be almost entirely removed in a few more months of operation or the residue of them would yield readily to normal cleaning.

Experimental cleaning time per tube necessary to remove virtually all residual old scale patches was indicated by trial as ten to fifteen minutes. Cleaning time resulting in incomplete scale removal previous to treatment was two to three hours per tube.

APPENDIX C

BOILER ILLS AND THEIR CAUSES

BOILER ILLS AND THEIR CAUSES

An understanding, in general, of the boiler ills that grow out of unsatisfactory water conditions is a prerequisite to all intelligent applications of treatments for those ills. A summary of boiler troubles, chargeable in part or in whole to water and its impurities, is therefore in order.

INCRUSTATION:
THE DEPOSITION OF SCALE, SLUDGE, OR SEDIMENT

Boiler scale is a deposit formed on boiler surfaces in contact with water. It may range in physical resistance from no more than a sludge, readily removable by washing, to a flint-like solid. It varies both with the nature of the material in water from which it is formed and with conditions of formation. Factors known to influence scale formation include chemical concentration, effective alkalinity, and temperature of the boiler water and the position (21) at which the scale is formed in any given boiler. Scale is built from material carried into the boiler in suspension in water or from precipitates of matter carried in in aqueous solution. The precipitates can be the result of chemical action or interchange, of loss of the soluble power of water when it is converted from feedwater to boiler water, or of the normal concentration of impurities during the production of relatively pure steam from relatively impure feedwater.

Whatever the composition of scale it is seldom simple or composed of a single impurity. It is found as a combination of a cementing or binding agent, or agents, with a filler or aggregate (23). Scales of inorganic or mineral origin, and those are the ones of moment in modern boiler practice, are not likely to be the result of the "baking on", or coalescence due to heat alone, of solid bodies from suspension in the boiler water. The formation of adherent oil films from an excess of droplets of oil carried in the boiler water (32) is an exception to this statement. Researches of Dr. R. E. Hall and the Hagan Corporation appear to prove that scale forms where and as it is found, or as Doctor Hall terms the formation, "in situ" (33). It appears also, since some mineral salts are not scale forming while others much like them are, that the solubility-temperature relation determines the efficacy of a material as a binder (23) in scale. "In general, any salt which has its solubility decreased by a rise in temperature will precipitate against a heated surface, and because of such place of precipitation cause an adherent scale..." (34). Materials, the solubilities of which increase with increase in temperature are not scale forming and appear in scale only as they are entrapped, absorbed, or adsorbed by the scale mass.

The traditional cause of scale is hardness in water.

In fact, hardness is defined (35) as "a measure of the compounds of calcium and magnesium in a water, which impart to the water the characteristic properties of forming incrustations in boilers, wasting soap, etc." Hardness has been described (35) as of two kinds, so called temporary hardness and so called permanent hardness. The terms, now entirely devoid of proper meaning, are suitably defined thus: Temporary hardness (35) "a term formerly but inaccurately used to designate the hardness remaining in water after boiling at atmospheric pressure, but now used to refer to 'non-carbonate hardness,' or that hardness due to the sulphates and chlorides of calcium and magnesium." Permanent hardness (35) is "a term formerly used to designate the hardness removed from water by boiling at atmospheric pressure, but now used to designate 'carbonate hardness' or that hardness due to calcium and magnesium carbonates and bicarbonates." Blame for scale formation has traditionally been centered on carbonates and sulphates of calcium and magnesium. According to the new logical view which takes the temperature-solubility relation of materials into account, carbonates alone are not regarded as scale forming, a fact borne out by recent boiler operating practice. Sulphates of calcium and magnesium are still classed as tending to promote scale growth. Other materials, such as silicates, not classed as hardness in

water are also now found to be scale forming agents (36).
Hardness is then properly viewed as not a precise measure
of the scale forming tendency.

The several bad results of the incrustation of boil-
ers have not always been considered in their proper im-
portance. That scale deposit, once formed, requires
eventual removal from a boiler, usually by mechanical
means, is self evident. The cost attendant upon scale re-
moval, an obvious bad result of scale, can be calculated
in any given situation on the basis of an average price to
be paid for every pound of incrustant removed. The effect
of the thermal insulating value of scale in promoting heat
loss is often cited (37) and now usually overdrawn. In
any plant, at all modern, operating under conditions of
the present time, scale deposits that are ever tolerated
cannot greatly lower the efficiency. This is a fact part-
ly because even an appreciable decrease in pure boiler ef-
ficiency does not result in a corresponding decrease in
overall boiler plant efficiency and partly for the reason
that, with the rates of driving of boilers, high-pressures,
and high superheats now in effect, boiler metal tempera-
ture limitations must be considered (38). If a boiler
plate is, when clean, heated to near the maximum tempera-
ture at which its loss of strength is not excessive the
application to it of a scale film of a thickness not ex-

ceeding a few hundredths of an inch may produce little
heat loss but an intolerable rise in the temperature of
the plate (39).

FOAMING AND PRIMING;
EXCESSIVE CARRYOVER OF MOISTURE IN STEAM

Foaming and priming are related boiler ills that are
properly considered together but logically differentiated
at least by definition. Foaming (35) is "the formation of
froth or bubbles upon the surface of the water in a boiler
which interferes with the free escape of the steam."
Priming (35) is "the entrainment of water in steam leaving
a boiler." Whatever the distinction between the much con-
fused conditions of foaming and priming, the net unde-
sirable result of those conditions is excessive carryover
of boiler water or the production of wet steam.

In a given boiler or steam generating vessel, where
adequate disengaging surface and steam volume are pro-
vided, factors chiefly responsible for moisture carryover
are

    (1) The position of the water level maintained

        in the vessel

    (2) The rate of steaming

    (3) The nature and amount of the solid matter in

        the concentrated water solution in the vessel.

The two factors first named are subject to direct control
and their influences can usually be evaluated in any

actual case of boiler operation. The third factor is usually not subject to direct control, and determination of its effect is a matter of the greatest complexity in every case. It is this third factor having to do with all solid matter, dissolved, suspended, or in any state, in boiler water that is here to be considered.

Through years of boiler operation it has been recognized that the moisture content of steam tends, in general, to increase with increase in suspended dissolved, or total solids in the water. It has often been pointed out (40), and it is a matter subject to simple laboratory demonstration, that there can often exist a rough complementary relation between the two classes of solids in boiling water. It is observed that minimum foaming tendency is had when dissolved solids are low if suspended solids are high. Conversely, suspended solids should be low, in amount, if dissolved solids are high. Influence of the nature of dissolved matter has been the subject of some dispute. Some practical experimenters (41) have given evidence of proving the hydroxyl-ion concentration the principal cause of wet steam. It has recently been very appropriately pointed out by Foulk (42) that much danger of error lies in broad generalizations concerning the effects of impurities in boiler water on foaming and priming. The specific causes of these troubles are as yet seen to increase with

every advance of the horizon of knowledge in their field.
Formation of foam on boiler water is not necessarily
closely related to moisture carryover. In the relation
that does exist the design, shape, and size of the boiler
probably wields a large influence.

The beginning of a fruitful understanding of foaming
and priming is seen in a physico-chemical theory of foam
formation due to Foulk (35, 43, 44). That theory attrib-
utes the possibility of bubble film development to posi-
tive or negative surface adsorption of material in water.
In the counteracting or canceling tendency exercised by
solutes on liquid surface conditions, some of which mater-
ials are positively adsorbed and some of which are nega-
tively adsorbed, may be the clue to the fullest solution
of the wet steam problem. It is the present writer's ob-
servation that in the choice of working fluids for ex-
ternal-combustion power plants of the future the use of a
substance devoid in its liquid state of the polar proper-
ties of water could amount to virtual elimination of the
boiler ill of liquid carryover in the heat-conveying vapor.

Extending as they do beyond the steam generating
vessel to engines, turbines, and to entire steam systems,
the bad effects of foaming and priming can be costly (35)
in the extreme. They can account for mechanical breakage
of prime movers, for turbine blade errosion, for steam line

incrustation, for the stoppage of turbine steam passages
sufficient to grossly reduce full throttle power outputs,
and for extravagant blow down from boilers.

<div align="center">CORROSION;
RUSTING OR PITTING OF METAL SURFACE</div>

Corrosion (35) is "the eating away of the surface of
metal by chemical or electrochemical action, either re-
gularly and slowly as by rusting in air, or irregularly
and rapidly as by pitting and grooving in the interior of
boilers." Corrosion products tend to be stable compounds;
chiefly hydroxides of the metals at ordinary temperatures,
oxides only at high temperatures. In the sense of the de-
finition given the simple oxidation occuring at the high-
est temperatures is largely omitted from consideration
and discussion of it will likewise be omitted here.
Furthermore, only corrosion under water or in the presence
of an abundance of moisture will be considered. Illustra-
tions of corrosion reactions may, for the present purpose,
be conveniently limited to the corrosion of iron, both be-
cause that metal predominates in boiler plants, and be-
cause most of what can be said regarding the corrosion of
iron applies with evident modification to other common
metals (45).

While the effects of corrosion are matters of common
observation, and practices usually adequate for corrosion
control are fairly well established, the mechanism or pro-

bable direct cause of corrosion is explained only in terms
of several theories. The theory that appears to explain
the most observed facts and that lends itself best to in-
terpretation into situations in the boiler plant is the
electrochemical theory (45, 46, 47) or what is sometimes
referred to in its original conception as Whitney's elec-
trolytic hypothesis. The reactions in terms of which the
theory pictures the occurrence of corrosion involve the
passing into solution of iron through the plating out of
solution of ions of hydrogen, thus (45),

$$Fe \text{ (metal)} + 2H^+ \text{(ionic)} + 2\ OH^- \text{(ionic)}$$

$$= Fe^{++} \text{(ionic)} + 2\ OH^- \text{(ionic)} + 2H \text{ (atomic)}$$
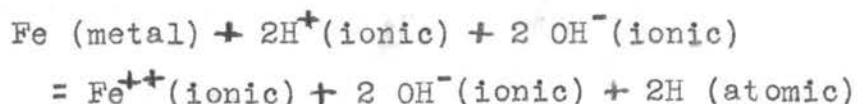
Since both H^+ and OH^- ions occur in aqueous solution it is
to be noted that, in effect, the iron is passed into solu-
tion as iron hydroxide. Secondary or supporting reactions
are obviously necessary if the direct solution of iron is
to long continue in any case. For the action to proceed
to its ultimate end without a diminuation of its rate
toward zero two conditions are obviously to be satisfied,
first, the components entering into the reaction must be
supplied in abundance or excess, and second, the products
of the reaction must be removed in part or in total as
formed. Lack of satisfaction of the two requirements
stated permits the reaction to speedily reach practical
termination in any case. Supply of the components of cor-

rosion, so long as there is iron to corrode, is measured by the abundance of hydrogen ions, i.e., by the hydrogen ion concentration or pH value of the solution in contact with the iron. Removal of the reaction products can proceed in one or more ways. The rather low solubility of ferrous hydroxide in water can result in summary blocking of corrosion if iron is not removed from solution by some means almost as it is passed into solution from the corroding surface. Here oxygen, commonly of atmospheric origin, plays its usual part in a manner not set forth in the equation. It has the power to convert the ferrous hydroxide in solution into relatively very insoluble ferric hydroxide. Ferric hydroxide being forced from solution ceases to exert a restraining influence on corrosion. Removal of hydrogen from the corroded surface (hydrogen depolarization) takes place, either directly through the combination of the atomic hydrogen into molecular hydrogen able to escape as gaseous bubbles, or indirectly as the result of combination of the atomic hydrogen with any oxygen present to form water. Chemical equations describing hydrogen removal are as follows:

$$2 \text{ H (atomic)} = H_2 \text{ (molecular)}$$

$$2 \text{ H (atomic)} + \tfrac{1}{2}O_2 \text{ (molecular)} = H_2O$$
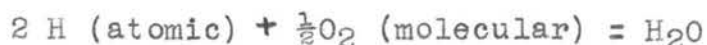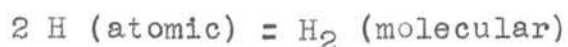
The formation of molecular hydrogen gas, although it takes place freely in the action of strong acid on iron, is op-

posed by the work of withdrawing the infinitely small par-
ticles of hydrogen from the surfaces on which they are
liberated and of forming them into bubbles large enough
to rise into the solution in contact with those surfaces.
This work effect is said to be due to hydrogen overvoltage.
It depends, among perhaps many influences, upon the nature
and condition of the surface on which the hydrogen is de-
posited, on temperature, pressure, and amount of agita-
tion. Only under the driving force of a high hydrogen ion
concentration does liberation of gaseous hydrogen provide
the depolarization usually observed in corrosion.

The second equation last foregoing, showing the re-
moval of atomic hydrogen by oxygen, describes a probable
common step in corrosion in neutral or even in alkaline
solutions. Oxygen, being soluble in water and ever pre-
sent in natural waters, finds ready activity in corrosion
situations. It is probably dissolved oxygen that more
than all else facilitates removal of corrosion products,
thus shifting a chemical equilibrium in the direction of
continuing corrosion. Dissolved oxygen largely accounts
for hydrogen depolarization in the majority of boiler
plant situations, at least where extremely high surface
velocities are not encountered. Oxygen of like origin
facilitates corrosion by aiding iron to escape from solu-
tion as corrosion puts it into solution.

It has been indicated heretofore that boiler plant corrosion problems are largely those of the neutral or alkaline ranges. The effect of alkalinity in those ranges, or the action of pH value greater than 7, should therefore receive particular attention. Hydrogen ion concentration, pH, measuring as it does the concentration of hydrogen ions available for the initial major corrosion reaction should measure the tendency for corrosion to occur. It shouldnot be overlooked, however, that when two or more reactions occur in series to complete some process the reaction speed of the process is essentially a function of the slowest reaction in the series. There is evidence that the first or major corrosion reaction, the exchange of hydrogen for iron, can occur with comparatively great rapidity, depending on the support of the secondary reaction or reactions. Except in decidedly alkaline solutions, then, the depolarizing reactions, which appear to be subject to the dissolved oxygen supply, generally control corrosion speed. Hydrogen ion concentration appears to have little effect. In solutions of an alkalinity corresponding to pH 10 or higher, corrosion rate decreases (45) much in proportion to increase in alkalinity. Whether this control of the process is due, as pure theory indicates, to increase in the driving voltage of the corrosion cell or largely to the effect of high pH

on the solubility of ferrous hydroxide does not detract
from the use that should be made of pH value in combat-
ing corrosion. The writer has had opportunity to ex-
amine water left in a boiler during more than fifteen
years, during which time the boiler was out of service.
Considerable corrosion product was evident in the form
of the characteristic precipitate of red ferric rust.
The pH value of the water was found to be 9.6, the fre-
quently quoted pH of a saturated solution of ferric hy-
droxide. The pH value was, then, or could have been, an
influence to hinder further corrosion. It is significant
that pH value determined the cessation of corrosion in a
spite of the difficulty with which oxygen gained entrance
to the system.

It may be that in much power plant work undue stress
is being laid on the removal of dissolved oxygen from
water to minimize corrosion. Promotion of the sale of
deaerating equipment, coupled with a lack of understand-
ing among engineers of the role played by hydrogen ion
concentration, results in the attitude commonly observed.
Not all oxygen is removed by ordinary treatments. Any
control exercised by hydrogen ion concentration is control
logically exercised. Let boiler metal corrosion be re-
garded as the product of an energy cycle in which the
usual intensity factor may be pH value and a chief quan-

tity factor oxygen dissolved in water. Then, by analogy
with the problems of heat cycles (the Carnot, for illus-
tration) in which the factors of energy measure are tem-
perature and entropy, logical promotion of corrosion
cycle inefficiency is through manipulation of pH value.
Increase of pH value, above an initial figure of 9 or 10,
can be made to render corrosion forces less effective.
A limit to the efficacy of pH control is reached when at
extremely high hydroxyl ion concentration any protective
films on the metal are dissolved. The pH values cited
apply specifically to iron or its derivatives. They may
be different for brass, aluminum, and other metals.

In specific situations of corrosion in comparatively
pure water, factors other than dissolved oxygen and hydro-
gen ion concentration may control. Free or aggressive
carbon dioxide (45) appear to promote boiler metal cor-
rosion. Speller states that the action is chiefly in-
direct through acid reaction or through removal from the
metal of protective carbonate film. Acid-generating salts
sometimes cause serious boiler metal corrosion. Magnesium
chloride is particularly objectionable because it is re-
generated in its corrosion reaction, thus being concen-
trated in boilers. Speller (45) shows the reaction to
proceed as follows:

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

$$Fe \text{ (metal)} + 2HCl = FeCl_2 + H_2$$

$$FeCl_2 + Mg(OH)_2 = Fe(OH)_2 + MgCl_2$$
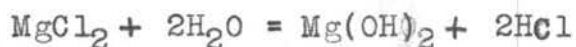
Magnesium chloride is present in high concentration in sea water (48). Plants supplied with feedwater derived from sea water or in which sea water is used in cooling steam condensers are likely to be troubled by such corrosion. The usual remedy involves forcing the reaction described by the last equation back toward the left through the addition of caustic, perhaps sodium hydroxide, to boilers. Such treatment should never be undertaken without adequate embrittlement protection.

Solid films formed by various means on corroding metal retard corrosion (45) in many cases. Carbonate scales undoubtedly afford some protection to boiler metals. Boiler operators are reluctant to place direct dependence on wholly beneficial films but prefer to regard appearance of the films as evidence of conditions not basically undesirable. Mildly adherent films of iron hydroxide tend to form at corroding surfaces subject to pH values elevated reasonably above the equilibrium point. Silicates, as natural soluble silicates or sodium silicate artificially supplied to water, can be made to form coatings on boiler metal largely impermeable to oxygen. Those scales can easily provoke more trouble than they remedy. The alkaline

action of sodium silicate may often be more effective than
its film producing power. More effective and less hazard-
ous alkalies could be used to bring about the necessary
high hydroxide concentration. Passivifying agents, analo-
gous to the chromates widely used in ice plants, are in-
effective at boiler temperatures (45). Protective paint
coatings applied to boiler interiors have been reported
beneficial in a few cases where they were carefully applied
and maintained.

EMBRITTLEMENT;

CAUSTIC EMBRITTLEMENT; METAL CRACKING

Embrittlement, now perhaps a misnomer, is the name
applied to boiler metal failure involving a type of
intercrystalline cracking. The type of failure defined
(49) is abnormal to mild steel and is different from true
corrosion or true stress failure. Definite identification
of the embrittlement failure, means for its prevention and
probable explanation of its cause, have been the subject
of original investigation by S. W. Parr and of much recent
study by F. G. Straub and associates at the University of
Illinois, Urbana, Illinois. For a background of informa-
tion on this subject the reader is referred to University
of Illinois Engineering Experiment Station Bulletins,
Numbers 216, 177, 155, and 94.

Recognition of the boiler ill of embrittlement dates

from the latter part of the nineteenth century although more than twenty-five years had elapsed in the twentieth century before there was certainty that metal embrittlement presented a distinct type of boiler failure. Recognition of the embrittlement hazard even now may be said to be peculiarly limited to a few geographic areas in which actual boiler failures have imposed an expense of property and life. The American Society of Mechanical Engineers in its "Suggested Rules for the Care of Power Boilers" under date of 1926 (28) cites intercrystalline (embrittlement) failure of boiler metal as occurring in "(a) boilers in certain localities fed with well water containing sodium bicarbonate, but not an appreciable quantity of sodium sulphate (similar cracking has not been reported in the same localities in boilers fed with surface water free from sodium carbonate or containing sodium sulphate equal to or exceeding the sodium bicarbonate); (b) boilers fed with water in part composed of condensate from leaky caustic evaporators; (c) boilers fed with sea water distillate to which compounds were added resulting in high concentrations of sodium alkalinity."

Embrittlement failures occur most readily in stressed metal. The cracks peculiar to embrittlement develop below the water line and especially on dry sides of joints in normally stressed boilers. There is rough similarity of

the failure to the hydrogen embrittlement (50) occurring due to hydrogen occlusion in metal subjected to excessive acid pickling. Within the last few years blame for embrittlement has been rather definitely placed on sodium alkalinity (51) and the agent of the action has been largely identified as sodium hydroxide. Although stress probably is a factor and localized and concentrated stresses should be minimized through good design and proper construction, boilers must always be stress-bearing. Assurance of safety and freedom from material damage can be had, therefore, only through the maintenance of boiler-water conditions under which embrittlement may be expected not to occur.

Methods for the prevention of embrittlement were developed almost concurrently with definition of the distress. Discovery that high alkalinity and low sulphate concentrations in boiler water favored embrittlement pointed to the need for minimum causticity and to the use of sulphates for the avoidance of trouble. Sulphate in any of its suitable forms, sodium sulphate, magnesium sulphate, sulphuric acid, is officially recognized by the American Society of Mechanical Engineers and has shown its worth in all practical applications (52). A research program is now being formulated (53) for the ultimate validation of the A.S.M.E. sulphate specification. The Boiler

Code of the Society prescribes (28) that there be maintained in boilers minimum ratios between soda alkalinity and sulphate as follows:

Working pressure of boiler, lb. gage	Relation of sodium carbonate alkalinity		Sodium to sulphate	
0 to 150	1		to	1
150 to 250	1		to	2
250 and over...............	1		to	3

Numerous materials other than sulphates appear as embrittlement inhibitors (51) if laboratory findings are to be relied upon. Some of those materials await all practical justification of their use, others even now used in a few practical situations are difficult to maintain in effective form in boiler water or for some similar reason are not likely soon to be accorded general dependence. Inhibitors referred to include normal carbonates, phosphates, tannates, chromates, nitrates, and acetates. Some, properly maintained in boiler water, are apparently many times as effective as sulphate. The probable action of inhibitors has sometimes been regarded as a mechanical plugging or stopping up of intercrystalline spaces by the inhibitors, the most of which are sparingly soluble. Some authorities (51) now take the view that crystallization of the inhibitor on the metal surface brings about an electro-chemical situation unfavorable to embrittlement.

The origin of alkalinity in boiler water may well be
considered since sodium hydroxide receives such a large
share of the blame for embrittlement and since boiler
waters are always alkaline. The sources of alkalinity are
both man-made and natural. Among the man-made causes there
is the direct possibility of overtreatment of feedwater
with sodium carbonate. Sodium carbonate is found in some
natural waters, it is used as a reagent in some treatments
and in many boiler compounds, and it is a reaction product
of yet other boiler-water treatments. Under boiler condi-
tions sodium carbonate, and other carbonates and the bi-
carbonates, breaks down to yield the hydroxide as illus-
trated by the equation:

$$Na_2CO_3 + H_2O = 2\ HaOH + CO_2$$

The action is forced toward the production of caustic by
the removal of carbon dioxide gas, CO_2, with steam passed
from the boiler. Equilibrium in the action, dependent on
time, temperature, pressure, concentrations, etc., may be
established in actual boiler operation with the production
of sixty or eighty per cent of the maximum caustic (54),
or what corresponds to the conversion of all but forty to
twenty per cent of the normal carbonate. In addition to
the natural process just described to account for it in
boiler water, caustic soda has long been an important con-
stituent of boiler compounds (21) and may thus find entry

direct to boilers. It is reported to the writer (55) that sodium carbonate is still the major constituent of the boiler compound used in the U.S. Navy.

The gravity of the embrittlement hazard, even since its intensive study, is portrayed by the statement by Straub (51) that "during the interval between January, 1925 and January, 1930, twenty-five new instances of embrittlement involving some sixty boilers were brought to the attention of the investigators. At least one million dollars was involved in replacing or repairing these boilers. Property damage resulting from one explosion resulted in a loss of almost one quarter of a million dollars, as well as the loss of one life."

EXCESSIVE BLOW DOWN

Excessive blow down is seldom included in a list of boiler ills. It is probably the most prevalent of boiler troubles. It exists as a trouble alone, it grows out of other troubles and out of measures taken to remedy them, and it is often not seriously regarded when boiler-water conditioning programs are undertaken.

As a byproduct in the generation of relatively pure water vapor from impure water there develops in the boiler used in the process a concentration of impurity. To some extent undesirable elimination of the concentrate occurs by way of the steam nozzle, the additional necessary elim-

ination is through the medium of blowing off or blowing down the boiler. The process of blowing down a boiler, through letting out boiler water, really involves the dilution of remaining boiler concentrate with comparatively pure feedwater. Except as blow down serves the purpose of purging a boiler of its byproduct of suspended and dissolved impurity it serves no real useful purpose and entails a loss. The loss includes, at least, a loss of heat in the boiler water discarded and a loss of the water blown down.

Regulation of blow down to the minimum amount consistent with satisfactory boiler operation is, since blow down practice grows largely out of habit and tradition, basic to alleviation of the difficulty. The amount and frequency of the blowdown should be determined by scientific investigation of every case rather than by the whim and habit of the boiler operator. Heat exchangers can be used to transfer a large part of the useful heat in blow down water to feedwater or to, in some other way, return it to the boiler circuit. In a small percentage of installations, where high solid matter concentrations have to be dealt with, such devices are economically justifiable. The boiler water is lost in any event. Relieved as it is of its scale-forming salts and containing any chemicals maintained in the boiler for feedwater softening or for

metal protection, the blow down water, if purified, should be of greater value than raw water of the same temperature. Suspended impurities can be reduced to some extent by suitable filters placed in circuit with the boiler or by chemical coagulants applied to make blow down more efficacious. Loss of water must be tolerated in proportion to the dissolved impurity to be eliminated.

APPENDIX   D

WATER TREATMENTS USED IN BOILER PLANTS,

THEIR ADVANTAGES, THEIR LIMITATIONS

WATER TREATMENTS USED IN BOILER PLANTS,

THEIR ADVANTAGES, THEIR LIMITATIONS

A doctrine in boiler operation might be to provide
feedwater quite pure, but that always being impossible,
purify such as is available to the extent practicable, and
convert impurities not removed to unobjectionable or to
least harmful forms. Treatments are obviously required by
the latter two stipulations. A resume' of the principal
water treatments used in boiler plants is in order as is
some consideration of the distinctive advantages and the
limitations of each treatment.

EVAPORATION, THE PRODUCTION OF DISTILLED WATER

Evaporators, as here denoted, are essentially especial-
ly constructed low-pressure boilers designed to produce
pure water (vapor) from impure water. It is at once ap-
parent that the use of evaporators to prepare feedwater is
a multiplication of boilers upon boilers. Even with the
best evaporator design there is no trouble peculiar to
boilers that does not appear in the evaporator. With evap-
orator-boiler combinations all difficulties of a boiler
operating alone exist to some degree in the evaporator or
are in reduced seriousness divided between the evaporator
and the boiler.

The apparent advantage of evaporators is that they
can produce a small make-up for a boiler system, of purity

comparable to condensate from the system, without permit-
ting the principal solid matter deposits to occur on
boiler surfaces subjected to great heat transfer rates,
to elevated temperatures, or to high pressures. Such scale
deposits as do occur in evaporators can, furthermore, be
quickly removed when the heating surface takes the form of
self-scaling tubes. The series operation of an evaporator
with a boiler is usually necessary when high soluble salt
concentrations, such as in sea water, are encountered in
raw water. Militating against the provision of evapora-
tors is the item of increased complication and expense as
well as a number of practical shortcomings. With some
natural waters evaporator scale deposits grow so quickly
that evaporator cleaning is a large expense. A short clean-
ing cycle entails rapid destruction of evaporator tubes
due to often repeated "cracking down" of scale. Pretreat-
ment, mechanical or chemical, of evaporator feed may be
necessary to lengthen the cleaning cycle and to cause the
evaporator scale to be of such a nature that it can be
easily "cracked down." With even moderate impurity con-
centration in an evaporator the solid matter carryover is
likely to be appreciable and may scale pipe lines and cause
water difficulties in boilers to which the condensed vapor
is fed. Moisture in evaporator vapor is more than is
usually thought to be the case. The writer has found from

actual tests of evaporators at steaming rates recommended
by the manufactures that several per cent of moisture was
not uncommon (See Fig. 3). Even a true measure of that
moisture does not give a proper measure of the impurity
carryover because solid matter in the vapor is seldom what
it would be if it were all contained in entrained moisture
and that were at the concentration of water in the evap-
orator. Evaporation of boiler feedwater involves yet other
difficulties often overlooked. The vapor product, though
freed of dissolved gases in the evaporator, requires degas-
ification before it is used, otherwise it must be carefully
kept from the air, because freshly distilled water readily
takes up a new charge of gas with a preferential tendency
to absorb oxygen (21), the more objectionable of the two
principal atmospheric gases. It is often pointed out that
by the recovery of heat from evaporator vapor the overall
thermal efficiency of an evaporator installation can be
made to approach one hundred per cent. It is not so often
noticed that in many heat-power systems the degrading or
lowering of temperature level of thermal energy required to
create the driving force in an evaporator of excellent net
heat efficiency is enough to appreciably lower the ef-
ficiency of the system through making energy less readily
available for the doing of work. Note the data of Fig. 4.
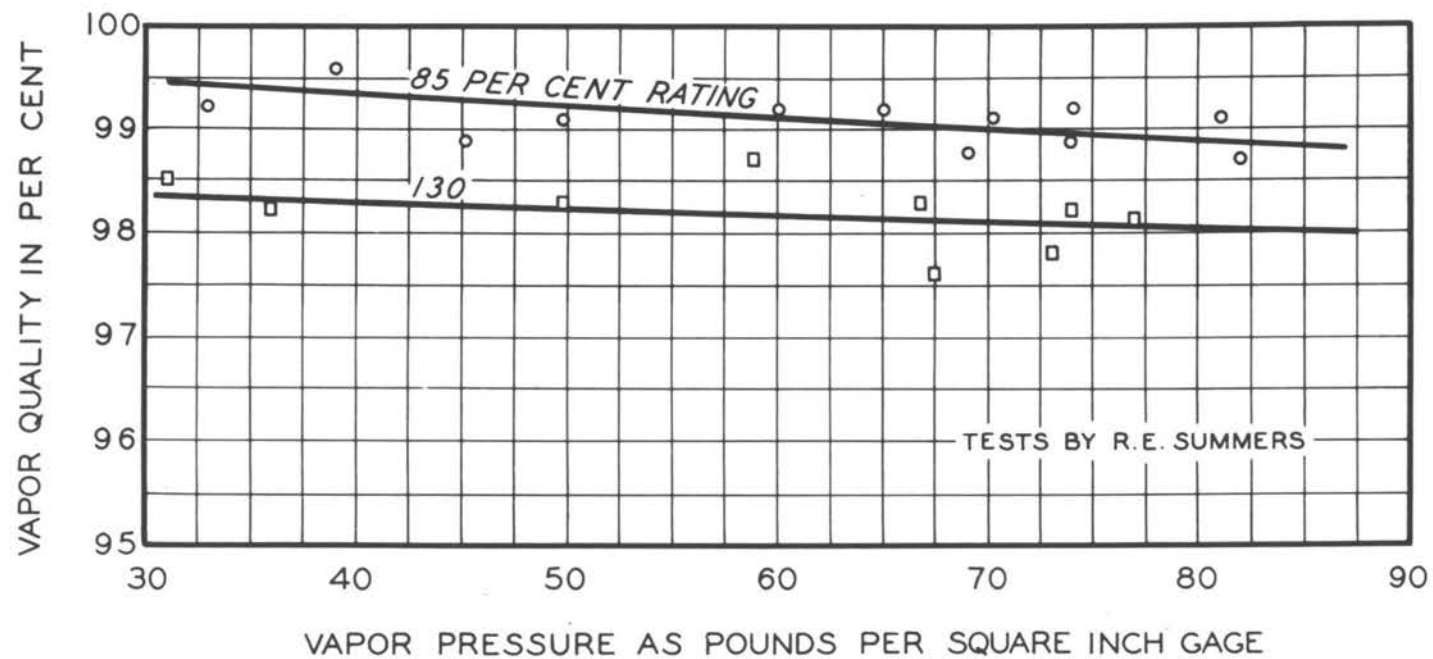Evaporation, then for reasons cited herewith, does not
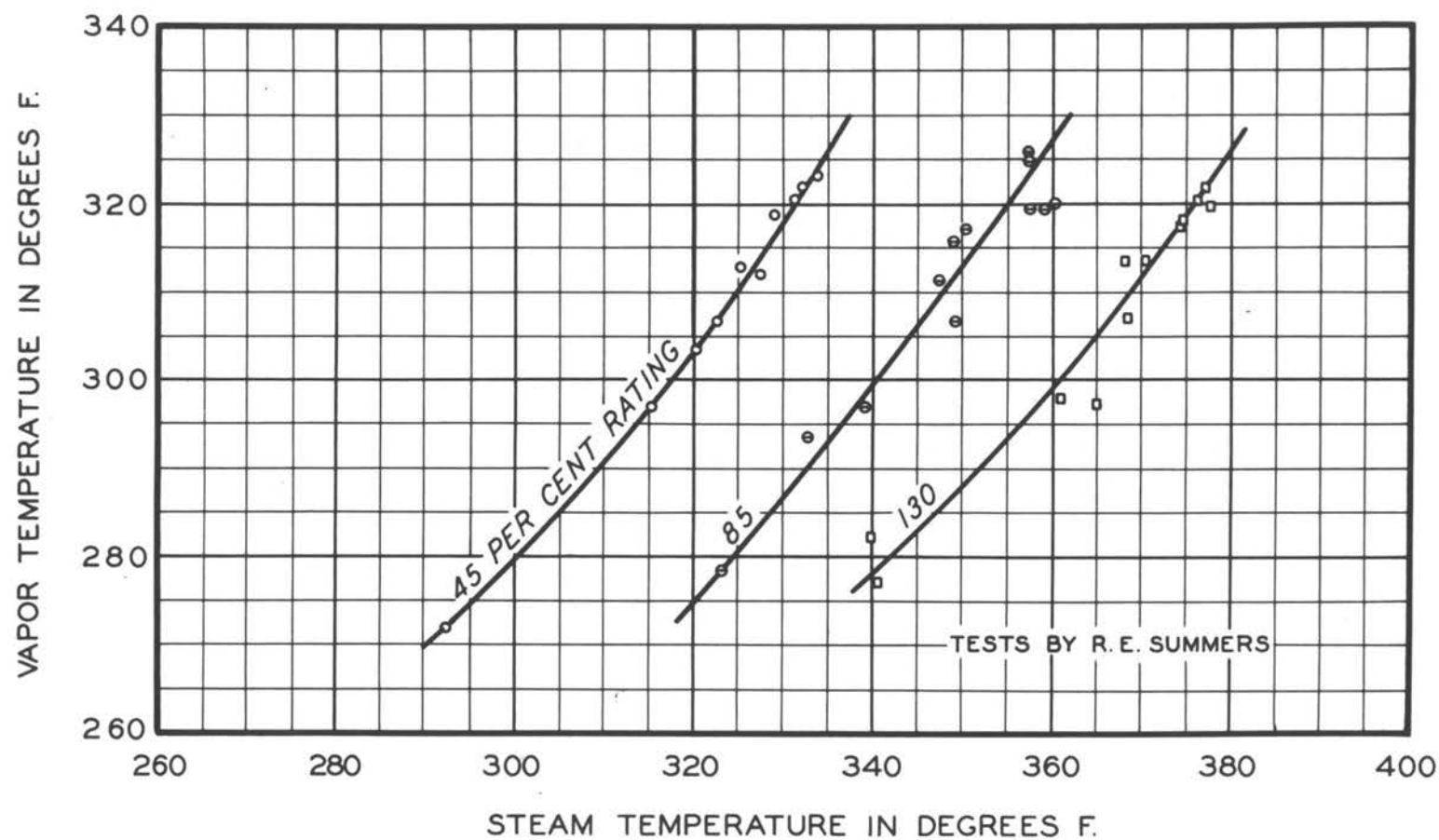
FIG. 3. EVAPORATOR VAPOR QUALITY.

FIG. 4.   TEMPERATURE RELATIONS IN A FEEDWATER EVAPORATOR.

always serve as a complete substitute for water softening.
It is an adjunct to other water treatments in many situations.

HEATING; DEGASIFICATION; DEACTIVATION

Heating of water in a vented container prior to introducing it into a boiler can force from it a considerable
percentage of its dissolved gases. The action described is
true because, in water, at the boiling point of pure water
for any set pressure, the vapor pressure of dissolved gas
must become zero. It should not be overlooked nevertheless
that time is a requisite to chemical and physical change.
A surprisingly long heating period is necessary to effective degasification (56) in actual practice. The effect
of thermal degasification may often be obtained by vacuum
degasification when heating is not possible or not feasible.

Temporary hardness, so called, consisting for the
most part of carbonates bound in solution by carbon dioxide,
is reduced by boiling water in which it occurs. The ultimate limit of precipitation possible is determined by
the solubility of the corresponding carbonate at the boiling temperature. A notion of the time of boiling necessary
for complete carbon dioxide removal is conveyed by data
published by Sofnol, Ltd., of London, England (57). Discharge of the corrosive gas oxygen from solution is also

possible through heating. Removal of oxygen by chemical

absorption or chemical degasification has been tried.

Deactivators containing ferrous hydroxide are reported

in use in Europe. A direct addition of ferrous hydroxide

to feedwater has been made in plants in this country (52,

58). Several other reducing agents have been tried in ex-

perimental boiler installations. Some such reducing

agents are pyrogallic acid, an extract prepared by boiling

chips of red oak, ferrous sulphate, sodium sulphite, and

sulphur dioxide as sulphurous acid. Those reducing agents

are effective only when their reaction rates with respect

to oxygen are higher than the reaction rate of oxygen on

boiler metal (46).

<div align="center">

FILTRATION,
THE REMOVAL OF SUSPENDED SOLIDS FROM WATER

</div>

Filtration as applied in boiler plants is chiefly

confined to the use of pressure type filters to clarify

raw water or to remove precipitates from treated water.

While filters have been operated in direct circuit with

boilers to remove suspended solids directly from boiler

water such use is by no means general. The larger applica-

tion of filtration to reducing the concentration of sus-

pended solids in boiler water is found in the pretreatment

of boiler feedwater.

Filters generally have a useful function to perform

in the preparation of turbid water for boiler use. While

mineral matter in suspension is not ordinarily the cause
of strongly adherent scale it can contribute to the forma-
tion of scales, or to sludges due to other agencies. It
is a large factor in foaming and priming as intimated here-
tofore. Suspended organic matter can cause objectionable
boiler metal coatings, foaming and priming with their at-
tendant ills, and even corrosion. Filtration is able to
cope with materials that chemical action will not affect.
It is the logical process to follow chemical treatments
that remove dissolved matter by precipitation. It is nec-
essary preliminary to the treatment of even slightly turbid
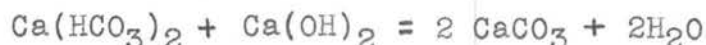water by zeolite.

Application of coagulants such as alum or sodium
aluminate to the rapid and thorough separation of suspend-
ed particles from a solution is so closely associated with
filtration practice as to require mention at this point.
Coagulants properly applied to sludges passing to a filter
increase the efficiency of separation and promote rapid
and effective filter cleaning as subsequently necessary.
The life of a filter bed can be lengthened by the action
of a floc from a coagulant in preventing excessive penetra-
tion of sludge into the bed.

All the treatments considered foregoing are designed
for the removal of one class of water impurity. The
treatments next to be considered, sometimes known as

softening processes, are intended primarily to change the
nature of impurities dissolved in water. Removal of mater-
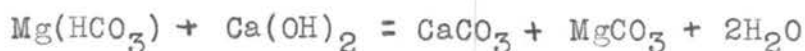ial can be regarded as somewhat incidental to the chemical
changes involved.

WATER SOFTENING BY THE LIME-SODA PROCESS

Perhaps the oldest and the most common process for
the treatment of hard water is the lime-soda process.
When that process is used lime, either slaked or unslaked,
is added to the water to act on the temporary hardness as
represented by the following chemical equations written for
slaked lime:

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

(The calcium carbonate forms a precipitate)

and

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

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

(The magnesium hydroxide and the calcium carbonate
form precipitates)

It is significant that temporary hardness is thus removed
bodily with the exception of a little calcium carbonate
and magnesium hydroxide, both of which are slightly sol-
uble. Nothing is substituted for the undesirable mater-
ials save excess lime. The maximum removal of calcium is
governed in part by the solubility of calcium carbonate
which amounts to a few grains to the gallon of water. The

presence of any soluble carbonate, such as excess sodium carbonate from the other part of the process, reduces the solubility of calcium carbonate (59) through common ion action. In the same manner, excess lime promotes reduction of residual magnesium hardness.

For the permanent hardness the process substitutes a soluble sodium salt, thus:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

(The calcium carbonate forms a precipitate; the sodium sulphate stays in solution and is not scale forming.)

Removal of permanent hardness due to magnesium requires supplementary treatment with a hydroxide such as sodium hydroxide or calcium hydroxide:

$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4$$

and

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

(The magnesium carbonate and sodium sulphate are soluble; the calcium carbonate and magnesium hydroxide form precipitates.)

Among the distinctive advantages of the lime-soda process the following merit attention here:

(1) It is not proprietary. The process is available to all who desire it, and the chemical reactions involved are generally known.

(2) The reagents required are commercial products

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used for other purposes. They are cheap and are generally available.

(3) The process theoretically effects bodily removal of temporary hardness down to the solubility of calcium carbonate or magnesium hydroxide.

Shortcomings of the process are:

(1) It is slow to act, especially in cold water.

(2) It does not, even ideally, give complete softening.

(3) Overtreatment is a tendency. It becomes a necessity if speed and completeness of softening are important.

(4) The precipitation of calcium carbonate is incomplete and the precipitates are difficult to remove. Settling and filtration of the water are required subsequent to the chemical addition.

(5) The process largely substitutes sodium salts for permanent hardness.

Modifications of the lime-soda process are designed to remove or to minimize shortcomings cited for the basic process. Heating of the water before treatment, thus providing so called hot lime-soda treatment, can assist in the removal of temporary hardness through carbon dioxide expulsion. Furthermore, the chemical actions are speeded at high temperatures and the settling of the precipitates is rendered more thorough and more rapid. Solubility of calcium carbonate is, however, somewhat greater in warm than in cold water. Addition of a coagulant such as sodium aluminate, as in the lime-soda-sodium aluminate process, promotes the completion of chemical action and speeds the

treatment through assisting in the removal of the pre-
cipitated reaction products. Substitution of especially
prepared barium salts for sodium carbonate gives rise to
the lime-barium process. The barium salts formed by re-
action with the permanent hardness are largely insoluble
so that the process produces water particularly free from
dissolved solids resulting from treatment. Since barium
sulphate is practically insoluble, the use of a barium
reagent, carbonate or hydroxide, results in a consequent
minimum of soluble solids. The use of barium has some
disadvantages, however. The necessary chemical prepara-
tions are largely proprietary, and expensive, and barium
salts left in the treated water are poisonous (45), ren-
dering the water, or steam from it, unsafe for many in-
dustrial operations. Combination of lime treatment with
zeolite treatment is considered subsequently.

WATER SOFTENING BY BASE EXCHANGE, THE ZEOLITE PROCESS

A process for water hardness removal known to chem-
istry for nearly a century (21) but even now not general-
ly understood and but recently applied in boiler plants
is the zeolite or base exchange process. There is found
in nature, and now manufactured, a class of sand-like
sodium aluminum silicates, or zeolites. It is the sodium
contained in zeolite which is responsible for the value
of the mineral in water softening. If water containing

hardness, such as calcium sulphate, is passed through a filter in which are incorporated granules of zeolite, the zeolite will exchange its sodium content for the hardness-forming element in the water (60). In the process the water will receive non-scale-forming sodium salts and the zeolite will eventually be exhausted. If zeolite is des-ignated as Na_2Ze, sodium zeolite, its water softening ac-tion can be illustrated by the equations:

$$Ca(HCO_3)_2 + Na_2Ze = CaZe + 2NaHCO_3$$

$$CaSO_4 + Na_2Ze = CaZe + Na_2SO_4$$
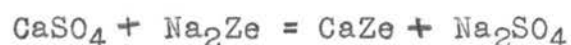
(The calcium zeolite remains in the filter bed; the sodium salts are delivered to the effluent soft water.)

The action of zeolites on magnesium hardness is similar to that shown for calcium.

One striking thing about zeolites is the manner in which they can be regenerated or returned to their active condition once they have been exhausted. Sodium is in-troduced into exhausted zeolite by passing a brine of sodium chloride, ordinary table salt, through the zeolite filter bed, replacing the calcium and magnesium as shown by the equations:

$$CaZe + 2NaCl = Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl = Na_2Ze + MgCl_2$$

(The soluble calcium and magnesium chlorides are re-

moved in the weak brine.)

It is particularly significant that the zeolite treatment leaves a high concentration of sodium salts in water. Those materials may be objectionable due to their accumulation as soluble solids and due to the high alkalinities that they produce. Inasmuch as most natural waters are comparatively high in temporary hardness, it is apparent that zeolite usually produces a greater dissolved solid concentration than is produced by lime-soda treatment. When foaming and priming and dangerously high alkalinities result from zeolite action on high-carbonate water, pretreatment of the water with lime may be necessary.

For the zeolite process alone the following named advantages usually apply:

(1) It theoretically gives complete softening of water with a preferential action on sulphates.

(2) With it there is no difficulty of reagent proportioning and no possibility of overtreatment.

(3) The chemical required, once the zeolite bed is installed, is exceedingly cheap and is available everywhere. The loss of zeolite is only the small loss of mineral due to attrition.

Practical disadvantages of the process may include:

(1) It is, in effect, largely proprietary. Initial purchases are limited to a few companies. An air of mystery tends to enshroud practical understanding of the process. Salesmen of equipment and supplies have in the past overlooked conditions vital to purchasers when pressing sales.

(2) It does not give complete softening of water.

(3) It leaves a large dissolved sodium salt by-product in treated water. That is a potential source of boiler metal embrittlement and may contribute to foaming and priming. Pretreatment with lime or after-treatment by evaporation is often necessary.

(4) The process can not be employed in hot water as heat damages the zeolite.

(5) Preliminary filtration of turbid water is neces-sary to prevent accumulation of solids on the zeolite.

USE OF BOILER COMPOUNDS; INTERNAL BOILER WATER TREATMENTS IN GENERAL

In this paper the water treatments first considered are those designed to eliminate certain matter from water; those next in order chiefly render objectionable impuri-ties less objectionable through changing them chemically, removing little or nothing from the water; treatments now to be considered involve actual addition of substance, with no removal of matter short of introduction of the water into a boiler. The statement has been made (61), and was much subscribed to, that a boiler is a device for the manufacture of steam and is not a place for chemical reaction. The intimation, provoked by the wrong wrought by vendors of every nature of boiler compound, is that treatment of water by chemical action within a boiler is much to be avoided. The truth is that a boiler is a place where chemical action does occur whether the operator so desires or not. All the ills of boilers are influenced by chemical laws and action. Impurities in feedwater change

form under boiler conditions as exemplified by the breakdown of carbonates to hydroxides. Treatments go to completion, take on new terminations, or otherwise grossly influence boiler water chemistry. The products of external treatment satisfactory in feedwater may be intolerable in some boiler situations. Conditions arise within the boiler that admit of direct regulation only through change in the chemical condition of water in the boiler. With only a few exceptions, as in the control of feed line corrosion, water problems of boiler plants and steam power plants are ultimately problems in the chemistry of boiler water.

Recognition of the necessity of what is traditionally and loosely referred to as "internal" water treatment does not excuse or even suggest the use of the innumerable boiler compounds on the market. The term boiler compound might in this case be reserved for application to those products of unknown composition used in boilers with unknown true purpose by persons ignorant, as well, of the total effect or lack of effect of such use. All other internal treatment is chemistry simple and definite or complex and theoretical.

Analyses of typical boiler compounds (21) bring to light some surprising facts about what materials are put into boilers and about the prices paid for common substances when those are supplied as active materials in

compounds. A fertile field for experiment and invention by those persons interested in boiler compounds has always been that of silicate chemistry. Just the right air of uncertainty evidently surrounds the appearance of silicates in colloidal state and in indefinite molecular form. All the "colloidal" boiler compounds lose favor when considered in the light of findings of Dr. Hall and the Hagan Corporation.

Certain essential internal treatment, such as that necessary to maintain a pH value high enough to assist in holding corrosion in check and that of the addition of SO_4 ion to boiler water for embrittlement control, has been referred to heretofore. Some additional processes used with definite success should be mentioned.

THE SODIUM ALUMINATE TREATMENT

Sodium aluminate, $Na_2Al_2O_4$, is used as a reagent for internal treatment in some boiler installations. The exact nature of its reaction products is open to dispute. It presumably forms a floc and thereby aids in the coagulation and sedimentation of suspended matter from feedwater or from precipitation of solids within the boiler. As previously noted such reduction of suspended solids is in some cases a specific for excessive carryovers. Commercial sodium aluminate for boiler use is a mixture of sodium aliminate with sodium hydroxide. It increases the

alkalinity of water and has some softening action.   It is
reported to have some power to precipitate soluble silica
in proper combination with calcium or magnesium (62, 63).

THE PHOSPHATE TREATMENTS

The use of sodium salts of phosphoric acid, or of the
acid itself, has become rather common in the last few
years.   Those materials are not newly applied, however,
as they have long been constituents of some of the better
boiler compounds.   The phosphates react with salts of cal-
cium and magnesium to form calcium and magnesium phosphate
as precipitates and by-product sodium salts in solution.
Water is evolved by the acid salts and carbon dioxide may
result from action on temporary hardness.   Typical boiler
reactions for trisodium, disodium, and monosodium phos-
phate, and for phosphoric acid are:

$$3CaCO_3 + 2 Na_3PO_4 = Ca_3(PO_4)_2 + 3Na_2CO_3$$
$$3CaSO_4 + 2Na_3PO_4 = Ca_3(PO_4)_2 + 3 Na_2SO_4$$

$$3CaCO_3 + 2Na_2HPO_4 + 2NaOH = Ca_3(PO_4)_2 = 3Na_2CO_3 + 2H_2O$$
$$3CaSO_4 + 2NaHPO_4 + 2NaOH = Ca_3(PO_4)_2 + 3Na_3SO_4 + 2H_2O$$

$$3CaCO_3 + 2NaH_2PO_4 + 4NaOH = Ca_3(PO_4)_2 + 3Na_2CO_3 + 4H_2O$$
$$3CaSO_4 + 2NaH_2PO_4 + 4NaOH = Ca_3(PO_4)_2 + 3Na_2SO_4 + 4H_2O$$

$$3CaCO_3 + 2H_3PO_4 + 6NaOH = Ca_3(PO_4)_2 + 3Na_2CO_3 + 6 H_2O$$
$$3CaCO_4 + 2H_3PO_4 + 6NaOH = Ca_3(PO_4)_2 + 3Na_2SO_4 + 6 H_2O$$
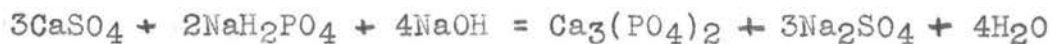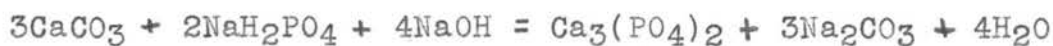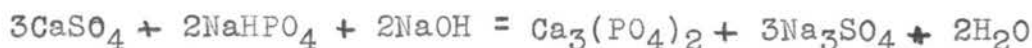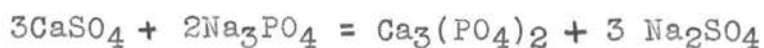
Chlorides are acted on the same as sulphates. Hydroxide is
assumed to take part in the reactions since it is usually
present in boilers as the result of breakdown of carbonate
or bicarbonate and the evolution of carbon dioxide gas.
Precipitation of the hardness-forming calcium as trical-
cium phosphate, $Ca_3(PO_4)_2$, rather than as $CaH(PO_4)$ or as
$Ca(H_2PO_4)_2$ is contingent on a pH value in the boiler solu-
tion of 10 to 12 or higher. The tricalcium phosphate ac-
counts for a maximum of calcium with a minimum of phos-
phate. It is, furthermore, less likely to form adherent
scale than the acid phosphates. What has been set forth
for calcium applies likewise to magnesium and its salts.

Certain unique advantages are found in the applica-
tion of phosphates to boiler waters. Through a choice of
the particular form in which the (PO_4) radical is supplied
it is usually possible to control boiler water alkalinity.
As shown by the equations, phosphoric acid and monosodium
and disodium phosphates have alkali neutralizing power
that decreases in the order of the naming. Trisodium
phosphate merely substitutes alkali carbonate for tempor-
ary hardness. Compared to lime, soda, and some other
water treating chemicals the phosphates are expensive.
They do act to a good degree of completion with the rem-
nant of hardness from some methods of treatment, such as
the lime-soda method. They find ready use in waters of

low hardness. The embrittlement protective value of phosphate indicated by laboratory tests makes phosphate in solution in boiler water doubly valuable.

THE HALL SYSTEM

Culminating a period of researches concerned with the prevention of scale in boilers, Dr. R. E. Hall, for some time physical chemist with the U.S. Bureau of Mines, disclosed a system of boiler water conditioning on which has been granted United States patents numbers 1613656 and 1613701, dated January 11, 1927, and other patents from countries throughout the world. Hall's system involves application of the laws of physical chemistry to the treatment of boiler water (64, 65) in such a manner that the formation of hard, adherent scale is said to be unlikely or impossible.

Basing his process of scale control on the apparent findings that (a) scale is largely precipitated from solution where and as it is found in a boiler and that (b) inorganic materials can be classified as scale forming or non-scale forming according to their temperature-solubility characteristics, Hall's system involves the application of solubility product data, or chemical equilibrium control. Assuming, for illustration, that the sulphates, especially calcium sulphate found naturally in many waters, precipitate as a scale forming material in boilers;

and that the carbonates alone are not responsible for hard
scale, forming but sludge, it is evident that as regards
solubility products, S. P., certain facts can be derived
as follows:

S. P. $CaSO_4 = (Ca^{++}) x (SO_4^{--})$, and

S. P. $CaCO_3 = (Ca^{++}) x (CO_3^{--})$
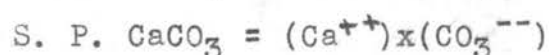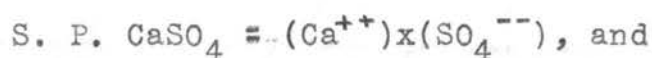
from which, by division and cancelation,

$$\frac{S. \ P. \ CaCO_3}{S. \ P. \ CaSO_4} = \frac{(CO_3^{--})}{(SO_4^{--})} = \text{a constant, K}$$

Then,

$$(CO_3^{--}) = K \ x \ (SO_4^{--})$$

defines a minimum value of carbonate concentration at
which sulphate will not precipitate. Obviously, any
cheap and otherwise satisfactory carbonate, such as sodium
carbonate, can be used to bring about sulphate control.

Development of the Hall system brought out the need
for substitution of a stable radical for the carbonate
radical used in the foregoing expression. As pointed out
elsewhere in this paper, carbonate in part breaks down in
a boiler resulting in the formation of hydroxide. Con-
ditioning of boiler water with carbonate for scale preven-
tion involves, on the one hand, therefore, maintenance of
a minimum effective CO_3-SO_4 ratio and, on the other, a
sulphate-alkalinity ratio sufficiently high to satisfy
the now accepted practice in embrittlement control. Dif-

ficulty with the breakdown of carbonate led Hall to sub-
stitute the stable phosphate radical for carbonate. The
phosphate is supplied in any phosphate salt, as trisodium
phosphate, or as acid phosphate salts, a metaphosphate,
or phosphoric acid, depending on the alkalinity reduction
desired. The desirable relation from the standpoint of
no sulphate deposition, given by Hall, is that the phos-
phate exceed the value,

$$(PO_4^{---}) = K \times (SO_4^{--})^{3/2} \times D^{1/2}$$

wherein D refers to the degree of ionization of the sul-
phate. Recent work (66) indicates that carbonate might
be effectively used in some low pressure boilers in which
its administration in less than dangerous concentrations
has been thought insufficient for scale prevention.

In justice to the Hall method it should be said that
it consists of a system of control rather than the use of
a special chemical. As with the work of all truly modern
organizations engaged in treating water for boiler use,
emphasis is not so much on the exact material used, as it
is on the fundamental principles applied and on the control
exercised.

APPENDIX E

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