

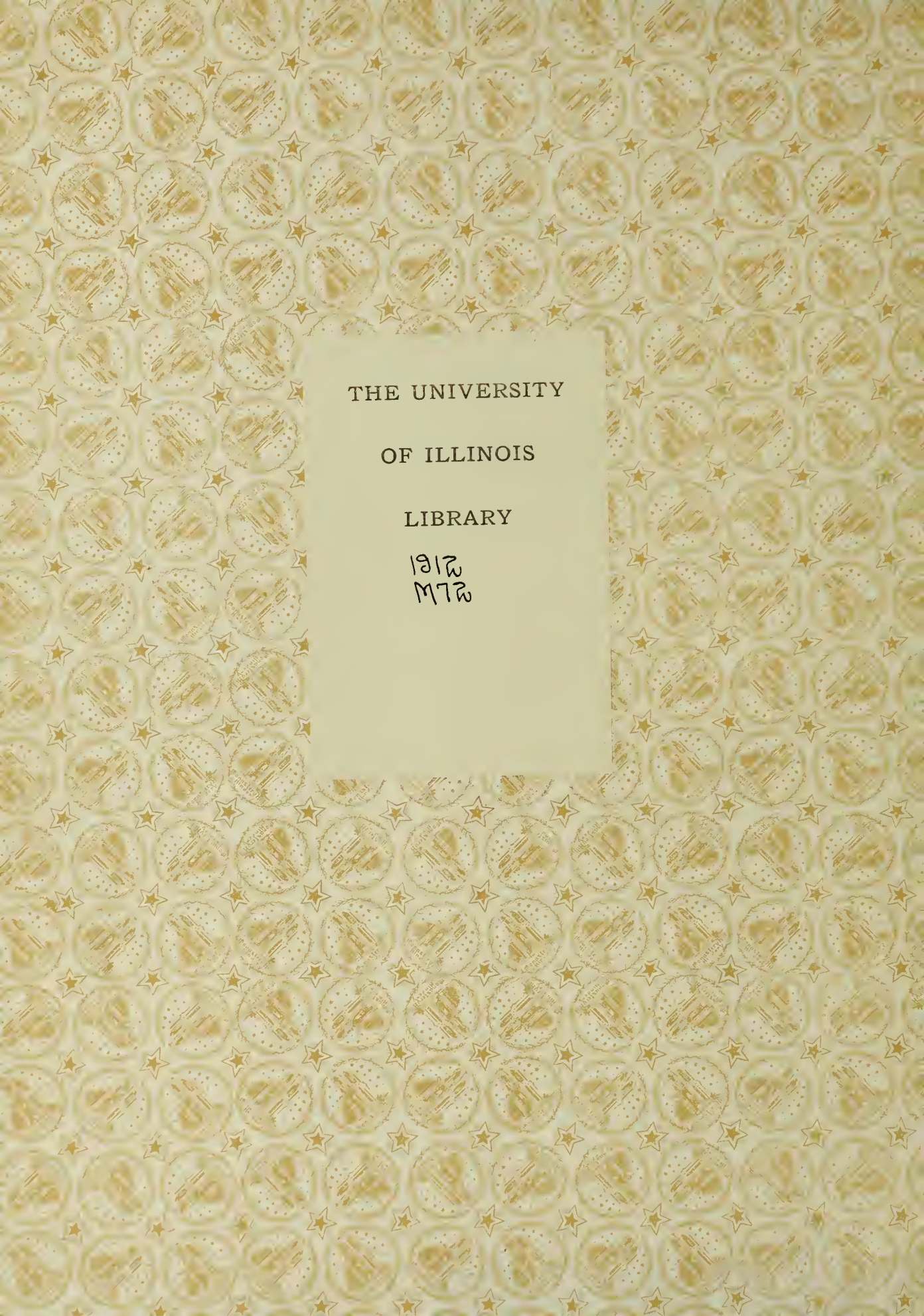
MOHLMAN

**The Relation of the Mineral
Content of Boiler Waters to
that of the Scale Formed**

Chemistry

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THE RELATION OF THE MINERAL CONTENT
OF BOILER WATERS TO THAT OF THE SCALE FORMED

BY

FLOYD WILLIAM MOHLMAN

THE S I S

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Floyd William Mohlman

ENTITLED The Relation of the Mineral Content of Boiler

Waters to that of the Scale Formed.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science.

In Chemistry

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THE RELATION OF THE MINERAL CONTENT OF BOILER
WATERS TO THE SCALE FORMED.

In all modern industries where steam power is used, the problem of a suitable supply of boiler water is a very serious one. Especially is this true in the Middle West and Western States where almost every water is open to some objections when used in boilers. These objections are of three kinds, and are-- Corrosion, Formation of Scale, and Foaming. There are few waters either surface or underground, which do not have one or more of these bad qualities. A corrosive water is probably the most objectionable. But corrosive waters are not so common as scale-forming waters; it may be said that every water except rain water and distilled water may form an incrustant when used in a boiler, the character and amount of the scale formed depending upon the water.

"Steam generation is a continuous process, fresh water being supplied to the boiler as the water evaporated leaves it; this results in a continual concentration in the boiler of the impurities introduced; the suspended matter may be carried in with the feed water, or may be due to substances forced out of solution by heat, pressure and concentration on the impurities in solution and suspension in the feed water." As the pressure determines the temperature, the controlling factors in scale formation are temperature and concentration. "The density of the boiler water increases, due to the concentration of the sodium salt and of the scale-forming salts to the limit of solubility."

The work described in this thesis was started in the hope of finding some definite empirical relation between the mineral content of the feed water, and the chemical composition of the scale formed. On first thought, this would appear feasible, since the precipitation of the incrustants is dependent on two variables, the concentration and temperature. However, it has been found in boiler practice that there are other variables; in order to study the question, it was originally planned to have an experimental boiler constructed, and by evaporation of different waters at different pressures, and collection and analysis of the scale formed, to study the influence of the different variables. However, the experimental boiler could not be constructed at the time the work was started, and a much less satisfactory procedure had to be adopted. Letters were sent to a number of towns in Illinois selected because of the specific character of the waters, asking for samples of scale and the water from which they had been formed. These did not bring many responses, since, owing to the efforts of the energetic salesmen of the various boiler compounds, almost all of the boiler waters were treated with boiler compounds, especially the sulphate waters. Scales were procured from Urbana, Beardstown, Effingham and Freeport, and carefully analyzed. These analyses were then compared with the analysis of the mineral content of the water from which they had been formed.

HISTORICAL AND THEORETICAL.

Ever since the invention of the steam engine, the evil effects of boiler scale have been noticed and studied. In the first half of the nineteenth century, marine engines did not use

surface condensers, and "the evil effects of incrustation made themselves felt with multiplied force, because of the great rapidity with which the crusts formed, due to the large quantity of solids contained in the water. Sea water contains about 2450 grains of dissolved solids per gallon; and it has been shown by J. R. Napier (Proc. Phil. Soc. Glasgow, vol. IV, p. 281) that sulphate of lime begins to deposit before one-half of the water is evaporated."

Rowan, Modern Steam Boiler, p. 611.

Before the use of surface condensers the boiler was blown off as soon as the feed water had reached a certain concentration. This caused a great loss in efficiency.

Not only were the evil effects of scale noticeable in marine boilers, but also in land boilers using natural fresh waters, the formation of scale leading to a considerable loss of heat, and in some cases, to the explosion of the boiler. "By the poor conductibility and non-homogeneity of the incrustations, the metal expands unequally, and leaks appear. If the scale suddenly cracks, the water comes in contact with the hot plates, and immediately an enormous quantity of steam is formed, often exploding the boiler with great force."

L'Eau daus L'Industrie, p. 55.

As to the loss of heat due to the poor conductance of the scale, this has been the subject of extensive investigation. The earlier investigators claimed that a scale 1/16 of an inch thick required an extra expenditure of 15% more fuel; 1/4 inch, 60%; and 1/2 inch thick, 150%.

Dr. J. G. Rogers, in Rowan's Modern Steam Boilers, p. 606.

Later investigation, however, showed that a scale $1/8$ inch thick caused a heat loss of 10.5%; $1/4$ inch of not much more, a loss of 20% being considered very high. It was found that the mechanical structure of the scale is of as much more importance than the thickness in producing the loss, and that the chemical composition has no direct influence on the heat transmitting properties. No accurate conclusions could be derived from the work.

U. of I., Eng. Exp. Sta. April, 1907. Schmidt-Snodgrass.

With the use of higher pressures in the boiler and larger and more complicated boilers, the bad effects of boiler scale became more noticeable. In 1870 - 1880 pressures of 50 lbs. gauge were considered pretty high, while at the present time pressures of 200 lbs. are not unusual. And so about this time boiler compounds of all sorts were used, and the boiler scales themselves and their composition were not studied so much as methods of preventing them. Since then the number of scale-preventatives invented has been perfectly enormous, but there has been little study of the process of formation of a scale.

Since the scale contains the acids and bases combined in a way that is often very different from the way in which they are combined in the water, a study of the minerals in solution in the water before injected, and the changes that take place in the boiler, is the best way to explain the formation of various scales.

The most abundant impurities in feed water are the sulphates and carbonates of calcium and magnesium. Water contain-

ing more than 10 grains per gallon (142.6 pts. per m.) of these substances is usually classed as hard.

"Calcium carbonate is the most common impurity. This is not present as CaCO_3 , as this seldom exists in water in greater quantity than 2 grains per U. S. gallon. CaCO_3 is more soluble in cold water than in hot, and the presence of NaCl dissolved in the water increases its solubility to about 5 grains per gallon. The CaCO_3 is soluble in water saturated with CO_2 , and in this case is

Engineering Magazine, 1897, p. 75.

present as the bicarbonate, $\text{Ca}(\text{HCO}_3)_2$; a saturated solution of CO_2 can dissolve 0.70 grams of CaCO_3 per litre at 0°C and 0.88 grams at 10°C ., the solubility increasing with the temperature."

L'Eau dans l'Industrie, p. 31.

When this is heated, CO_2 is driven off, and the normal carbonate precipitated to the limit of its solubility. This limit of solubility remains almost constant for a particular water under boiler operating conditions. The precipitation is practically complete at 143°C . or 43 lbs. gauge pressure, but starts as soon as the temperature of the water is raised and continues until the limit is reached. The precipitation, therefore, occurs not instantaneously, but gradually, with a diminution of precipitate as the limit of solubility is reached. This is true of all scale-forming salts that are p'p't'd. by heat alone.

J. C. W. Greth. Power, March 2, 1909.

Calcium sulphate is probably next in importance in scale formation. Calcium sulphate exists in nature with different amounts of water of crystallization as the dehydrated salt, anhy-

drite, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and more commonly, hydrated, as gypsum. When gypsum is heated to a point between 110° and 120° , it loses three-quarters of its water rather quickly, and becomes the well-known plaster of Paris. The anhydrous sulphate is nearly insoluble, but the hydrated, with water at 35°C . dissolves in the ratio of 148 grains to the gallon. According to Regnault, water dissolves the greatest quantity of CaSO_4 at 35°C , a liter of water at that temperature dissolving 2.57 g. CaSO_4 , at 0°C . only 2.05 g; from Fresenius, at 12°C , 2.33 gms. CaSO_4 , at 100°C ., 2.17 gms. According to author, 1 liter of a cold saturated NaCl solution

Polytechnisches Journal, 1874, p. 210.

dissolved 8.18 gms. of CaSO_4 , probably through partial formation of Na_2SO_4 and CaCl_2 ; in the evaporation going on in the boiler, however, it precipitates as anhydride. At 120°C . small crystals of $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ are deposited, at higher temperatures, the anhydrous salt.

Mrazek, Polytechn. Jour. 1869, p. 144.

The following table gives the solubility of hydrated CaSO_4 in grains per gallon and gms. per liter:-

T C.	Corresponding pressure, lbs.	Solubility grains per gallon	Gms. per liter.
20°	---	140.6	2.40
35°	---	148.2	2.53
40°	---	142.3	2.43
100°	0	125.9	2.15
140°	37	45.6	.78
162°	79	32.7	.56
180°	131	15.7	.27
200°	484	10.5	.18
250°	575	10.5	.18

Engineering, Dec. 25, 1903.

Evidently not only the high temperature effects the precipitation but also the pressure and the concentrated salt solution, which forms in most boilers after some time. Hoppe-Seyler holds that 125° - 130°C. is sufficient to change gypsum to anhydride in a saturated NaCl solution.

Poggendorf's Annalen 127, p. 161.

Thus it is seen that the form in which gypsum deposits from a solution depends upon the temperature at which the evaporation is carried on. Below 120°C. as soon as the solubility product is reached, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ separates out, and by continuing the evaporation, a deposit of this formula is obtained; above 120°C. to about 140°C., the precipitated sulphate loses one molecule of water, crystals of $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ being deposited; above 140°C. anhydrite is precipitated and as this is so much less soluble than gypsum, at this point, corresponding to about 45 lbs. pressure, there is a sudden drop in the solubility curve.

Sci. Am. Supp. 1892, p. 14020.

Magnesium carbonate has the same general properties as calcium carbonate. It was formerly believed that the normal carbonate of magnesium was insoluble, but later investigation has shown that it is almost as soluble as the bicarbonate. "However it has been the subject of many diverse statements because of its seeming anomalies." A careful digest of studies upon this subject, however, in the light of conditions governing the experiments, indicates that

1. At ordinary temps. the carbonate (MgCO_3), and the bicarbonate $\text{Mg}(\text{HCO}_3)_2$ may both be in solution in considerable quantities.

2. Heating converts the more soluble bicarbonate into the less soluble carbonate.

3. At 90°C . MgCO_3 is soluble beyond the limits of this substance in most natural waters, but at 100°C . it is practically insoluble. This latter condition is brought about by conversion into $\text{Mg}(\text{OH})_2$ and CO_2 , a reaction which does not take place with the similar calcium salt and with magnesium very slowly. The $\text{Mg}(\text{OH})_2$ is very insoluble, rarely over one-half grain per U. S. gallon.

The following table of solubilities due to Engel and Ville, represents the solubility of $\text{Mg}(\text{CO}_3)$ at the given temps:

Temp. C.	Parts MgCO_3 per million.
13.4	28,450
19.5	25,790
29.3	21,945
46.0	15,700
62.0	10,350
70.0	8,100
82.0	4,900
90.0	2,400
100.0	.000

Stabler, Harrison Safety Boiler Works, Pamphlet.

The pressure does not diminish the solubility as the following results show:-

Pressure in atm.	Temp.	Gms. MgCO ₃ dissolved by 1 liter H ₂ O
1.0	19.5°	25.8
2.2	19.5°	33.1
3.2	17.7°	37.3
4.7	19.0°	43.5
5.6	19.2°	46.2
6.2	19.2°	48.5
7.5	19.5°	51.2
9.0	18.7°	56.6

L'Eau dans l'Industrie, p. 32.

Magnesium sulphate is readily soluble in cold water and still more soluble in hot water up to about 122°C., above which temperature its solubility decreases. At about 200°C. it begins to decompose with precipitation of Mg(OH)₂ and formation of H₂SO₄, and at that temperature is corrosive. In the presence of calcium carbonate, it will react with it, forming Magnesium carbonate and calcium sulphate,



In the presence of NaCl it forms MgCl₂ + Na₂SO₄.

J. C. Greth, Power, March 2, 1909.

Silica is present in almost all waters, but usually not in excess of 2 - 3 grains per U. S. gallon; it may be present either as sand or in a colloidal condition. It is not precipitated by heat, but may be carried down mechanically by other precipitates.

Iron oxide and alumina are present in most water, the

iron being dissolved in Nature as the sulphate or by virtue of CO_2 , as the bicarbonate; on heating or aeration the CO_2 is given off, and the iron deposits as Fe_2O_3 . This is present in almost all scales.

Harrison Boiler Pamphlet.

The six salts considered above are the most important in scale formation . They form the so-called "insoluble" mineral in water. The others or the "soluble" are the chlorides, nitrates and sulphates of the alkalis, and the chlorides and nitrates of $\text{Ca} + \text{Mg}$. Of course by double decomposition the latter salts are generally converted into insoluble forms. The salts of the alkalis, however are all more soluble in hot water than in cold, and the only way they can be precipitated is by saturation or by action of some other salt.

Natural waters however, are not such simple solutions as those discussed above. Nearly every water will contain all of the salts described, and it is evident that the solubilities of the salts will be affected to a great extent by that of the other salts in solution with them. When injected into the boiler, the actions are not so simple as when a single solution is subjected to high pressure and temperatures. In the formation of the scale, each salt will probably be affected by the presence of the other salts. There is much about the question that is unreliable and unknown. For instance, at what time is the scale formed, -at the injection of the water, or on concentration? If we know the analysis of the water, is it possible to tell in advance the per cent of the principal constituents of the scale?

This question has been discussed profusely, but there is not much definite, accurate information on the subject. A good many analyses of waters and the scales formed by them have been made, but not many conclusions have been derived from the experimental work.

Fischer says, "Little agreement exists between the chemical composition of the scale and the mineral composition of the water, from which the scale was formed."

Polytechnisches Journal, 1874, p. 208.

M. Cousti states that the chemical composition of the incrustants varies in the different parts of a boiler, due to the unequal temperature of the walls of the boiler, and that the physical properties of the salts are the controlling factors, and not the chemical properties, since the precipitation is caused by physical changes, and not by crystallization of the salts.

Traiti de Epuration des Aunx, 1893, p. 132.

"When several impurities occur in a boiler water, the kind of material precipitated depends mostly upon the temperature or degree of concentration. Thus, should we fill a boiler with water containing mechanically-suspended-matter, this matter will gradually settle to the bottom, forming one layer; next, if the water be heated to 212° , much of the carbonates will be deposited; and, if afterwards the temperature be raised to 300° , the sulphate of lime will be precipitated. By neglecting to blow off a boiler, we may concentrate some one of the solutions of a very soluble salt beyond its point of saturation, when another precipitation takes

place. During all of this time much floating matter will be held in suspension by the circulating currents, and, when we finally draw our fires and the water comes to a state of rest, this will settle, and another layer be formed.

Cary, Engineering Magazine. 1897. p. 232.

The analysis of the water is of undoubted value in determining the substances in solution. There is, however, among chemists, a wide difference of opinion as to the proper method of making combinations from the determinations of the various substances in solution. In reporting the nature of the possible scale formed by a certain water, the reactions between the various salts in solution must be considered. The amount of scale-forming impurities rarely if ever bears a direct relation to the substances in solution after concentration, but it does to the amount of scale or sludge formed. However it is almost impossible to predetermine the nature of scale from the analysis of the water.

The nature and amount of scale formed in a boiler depends largely on the rate at which the boiler operates. For instance, in some boiler plants operating at considerably below their rating, and fed with water containing as high as 30 grains of both carbonates and sulphate scale forming salts, in a given time comparatively little scale is formed, and that quite soft; while in others where the water contains only about 10 grains of these same salts, and the boilers are worked above rating for the same time, a considerable deposit of hard, tenacious scale is formed. The type of boiler has a bearing on the hardness of

the scale. The scale in the water tube boiler is generally harder from the same water than that formed in the return-tubular boiler, or in the old two-flue boiler.

J. C. Greth. Power. March 2, 1909.

Notwithstanding the above facts, the formation of scale is generally a pretty definite process. As the water is fed in it is quickly raised to a temperature of from 320° - 380° F. From the solubilities of the various salts, it is evident that the order of deposition, as the water in the boiler becomes concentrated, would normally be:

1. Calcium carbonate
2. Calcium sulphate
3. Salts of iron and magnesia
- SiO₂ and Al₂O₃, organic matter
5. NaCl

On becoming insoluble, the precipitates remain for some time in suspension, and finally settle on the tubes and plates in the quieter parts of the boiler. The CaCO₃ generally deposits in an amorphous mass, but if the temperature is raised slowly will precipitate in the crystalline form as aragonite. The calcium sulphate then separates as anhydrite, since at the high temperature present the gypsum loses its water of crystallization. Iron and magnesium carbonates then separate as the hydroxides; afterwards magnesium sulphate is hydrolyzed to Mg(OH)₂, this action taking place at about 200°C., with formation of H₂SO₂, and consequent corrosion. SiO₂ and Al₂O₃ are forced out of solu-

tion, as at most they are very slightly soluble. Most of the SiO_2 and Al_2O_3 in the scale comes from suspended sand and clay in the feed-water, and is mechanically carried down by the other incrustants. The alkaline salts, NaCl , KCl , Na_2SO_4 , K_2SO_4 , are rarely present in a scale if the boiler water is changed at frequent intervals.

This is the theoretical, and in many cases, practical process of scale formation. But in analysis of numerous boiler scales, it is found that the method of formation is evidently quite different. "Such general statements that waters containing only the carbonates of lime and magnesia will form a soft scale, and that the calcium sulphate will form a hard scale should be made with caution, for there are hundreds of instances where a hard scale is formed from waters containing only the carbonates of lime and magnesium and also where the scale is quite soft in the presence of considerable calcium sulphate."

J. C. W. Greth. Power, March 2, 1909.

Thus the physical properties of a scale do not always seem to depend on the chemical composition. There are few sulphate scales that are not hard and crystalline, and most carbonate scales are soft and granular, but in some cases these conditions are reversed, and a carbonate water forms a hard crystalline scale, and a sulphate water, a granular amorphous one. What agencies cause these unusual formations?

It used to be believed that the CaSO_4 was the only hard scale-former; Becker however asserted that a scale can be very hard if it contains as much as 20 - 25% of CaCO_3 and no CaSO_4 .

Zeits für Rübenzucker, 1869, p. 834.

Aldeseld believes that the separated CaCO_3 falls to the bottom when the water in the boiler is allowed to become quiet, and then later when it is fired up again or blown off hot, this bakes to a hard crust.

Polyteck. Jour. 1838, p. 322.

M. Bidard of Rowan states that numerous examinations of boiler scales have demonstrated the fact that the presence of organic matter is necessary for the formation of boiler crusts which consist essentially of carbonate of lime. Such crusts he has produced artificially, to verify his theory.

Rowan Boilers, 1876, p. 698.

Fischer states, however, that organic matter does not have any influence on the character of the scale, and that its determination is entirely superfluous.

Polytechnisches Journal, 1874, p. 219.

Sulphate scales are almost always very hard and crystalline, and of a laminated appearance. This is probably due to the CaCO_3 being deposited at once as soon as the water is fed in, while the deposition of CaSO_4 goes on gradually.

Magnesia scales have caused considerable disagreement among the many investigators, as to which salt of magnesium is found in these deposits.

"When the scale-forming material is deposited, it is first in the form of carbonate and sulphate, but gradual heating expels some of the carbon dioxide, and the oxides of calcium and

and magnesium are formed. That portion of the scale next to the iron loses more of its CO_2 , and becomes caustic as long as the fire continues. As soon, however, as the fires are drawn, the oxides of calcium and magnesium become hydrated by absorption of water. Thus the composition of the scale will depend, in a great measure, upon what portion of the boiler the deposit is made.

Scale formed in which the lime all exists as calcium sulphate and in which no magnesium carbonate is present, will be subject to but little variation.

Stillman - Engineering Chemistry. p.96.

Unusual scales are often found. J. Rothstein gives an example of a sulphate scale containing Na_2SO_4 formed from a water purified with NaOH , and another scale containing no Na_2SO_4 from the unpurified water.

Scale, purified water.		Scale, unpurified water.	
CaSO_4	71.4%	CaSO_4	80.13
$\text{Mg}(\text{OH})_2$	11.7	$\text{Fe}_2\text{P}_3 + \text{Al}_2\text{O}_3$	5.85
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$	2.02	$\text{H}_2\text{O} + \text{Org}$	6.72
$\text{H}_2\text{O}, 110^\circ$	1.86	$\text{Mg}(\text{OH})_2$	6.06
Na_2SO_4	$\frac{13.3}{100.28\%}$	SiO_2	$\frac{1.08}{99.82}$

Water after purification,		Water before purification.	
CaO	0.043		0.213
MgO	0.119		0.272
CO_2	0.202		0.167
SO_3	1.407		1.407
Cl	0.039		0.391
Na_2SO_4	1.991		1.53

Thus it is seen that the purified water gives a scale containing Na_2SO_4 , while the unpurified contains none of this salt in the scale. By analysis it was shown that in the purified water the Na_2SO_4 was still far from saturation, and so Na_2CO_3 from the purification must have been the agent causing the separation of the Na_2SO_4 .

J. M. Rothstein. Zeit. Angew. Ch. April 1905. p. 540.

Rothstein also gives analyses of waters and scales formed from them and derives conclusions from these.

Minerals in Water	g/l				
	I	II	III	IV	V
CaO	0.1410	0.1980	0.2130	0.1240	0.1940
MgO	0.1433	0.0864	0.2718	0.1782	0.0912
SO_3	0.2298	0.5193	1.4070	0.6337	0.4562
CO_2	0.2221	0.1496	0.1672	0.2244	0.1230
Cl	0.0745	0.3408	0.0390	0.6580	0.0424
Total hardness	34.10°	31.9°	59.3°	37.3°	32.2°
Temporary hardness	28.25°	19.0°	21.3°	24.6°	15.4°
Permanent hardness	5.82°	12.9°	38.0°	12.7°	16.8°

Scale in per cent.

	I		II		III		IV		V	
	6 At.	10 At.	6 At.	10 At.	10 At.	6 At.	6 At.	6 At.	6 At.	
CaSO_4	15.59	40.65	55.37	80.76	80.13	46.46	47.90			
CaCO_3	43.93	5.02	31.20	0	0	0	0			
MgCO_3	0	0	0	0	0	3.35	0			
Mg(OH)_2	33.06	38.86	4.50	13.95	6.06	30.53	46.98			
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$	1.43	2.97	3.12	0.96	5.83	5.57	1.22			
SiO_2	4.58	6.29	4.20	1.56	1.08	4.14	1.16			
$\text{H}_2\text{O} + \text{Organic matter}$	1.26	4.90	1.51	2.28	6.72	10.28	1.62			
Total	99.85	98.69	99.90	99.51	99.82	100.33	98.88			

Waters I and II at different pressures give scales of different composition; at the lower pressure the per cent of CaSO_4 is lower, that of CaCO_3 higher; at the higher pressure, the per cent of CaSO_4 is increased, that of CaCO_3 lowered. Likewise the per cent of $\text{Mg}(\text{OH})_2$ is lower at low temperatures and higher at high temperatures. We have four compounds in the water, CaO , MgO , CO_2 , and SO_3 ; the greater the pressure, the greater is the affinity of CaO for SO_3 , of MgO for CO_2 . Raw water, at ordinary temperature and pressure, contains four, or at least, three compounds. The CO_2 is entirely or partly united with the CaO , the SO_3 with MgO . Under the influence of heat and pressure, this reaction takes place, $\text{CaCO}_3 + \text{MgSO}_4 = \text{CaSO}_4 + \text{MgCO}_3$, and becomes more active the higher these factors are. It may be said positively, -in calculating the composition of the boiler scale from the results of the water analysis, in boilers with pressures above 6 atm., the CaO should be calculated as CaSO_4 , if enough SO_3 is present in the water.

We see that waters IV and V form no CaCO_3 at 6 atm. while I and II contain significant quantities of this compound. It is not easy to explain this. Waters IV and V contain enough CO_2 to unite with the MgO , and enough SO_3 to satisfy the CaO . The boiler scale forms as $\text{CaSO}_4 + \text{Mg}(\text{OH})_2$.

Let us compare, on the one hand, Waters I and IV, and on the other hand, waters II and V. In spite of like pressures and similarity of the minerals in the waters the scales have a different composition; in scale I there is much CaCO_3 ; in IV, not any; in both the MgO content is about the same. Still more significant is the difference in the scales from waters II and V, al-

though the mineral composition of the waters is almost the same; scale I† contains much CaCO_3 and very little Mg(OH)_2 ; scale V contains no CaCO_3 and much Mg(OH)_2

Rothstein also studied the formation of scale from the following water under different pressures:

	g/l
Total residue, 150°	3.640
CaO	0.450
MgO	0.288
SO ₃	1.461
CO ₂	0.149
Cl	0.167
N ₂ O ₅	0.212
Total hardness	85°
Permanent hardness	19°
Temporary hardness	66°

The water is first heated in the condenser of a vacuum apparatus to 80° - 90°, from here to a boiler with constant temperature of 140°; then to one at 130°, and finally at 94°. Scale was formed in all vessels, and analyzed as follows:

	I	II	III	IV
Thickness of scale	0.1-0.3 mm.	12.0 mm.	2 mm.	1.5 - 2 mm.
Total loss on heating	43.66%	8.87%	5.22%	7.37%
CO ₂	42.71	4.53	0	0
CaO	54.32	38.00	52.1	37.51
MgO	0	5.51	4.8	0
SO ₃	0	46.08	36.21	53.6
SiO ₂	0	1.08	0.75	0
Al ₂ O ₃ +Fe ₂ O ₃	1.2	1.2	1.04	0
H ₂ O+Organic matter	0.95	1.88	3.06	1.36

In the first 97.03% = CaCO_3 ; in II, $\text{CaSO}_4 = 78.33\%$, $\text{CaCO}_3 = 10.25\%$, $\text{Mg}(\text{OH})_2 = 7.59\%$; $\frac{\text{CaO}}{\text{MgO}} =$ about 7. The process of pptn. is not yet ended; in III, $\text{CaSO}_4 = 87.94\%$, and $\text{Mg}(\text{OH})_2 = 6.96\%$; in IV, only CaSO_4 , of the formula $\text{CaSO}_4 + 1/2 \text{H}_2\text{O}$.

The CaCO_3 is the most easily separated salt. This scale was in a thin layer, brown in color, was very hard and in the form of calcite. If Na_2CO_3 was used to prevent scale-formation, the scale was also CaCO_3 ; but here it remains soft, and does not become hard; in the presence of Na_2CO_3 , it takes the form of aragonite.

The CaSO_4 does not all separate at 140° ; we also find it in the other boilers. 140° is not high enough for its sudden precipitation. Below 140° , without doubt, the concentration plays the most important role in its p'p't'n.

The MgCO_3 separates with difficulty and only above 100° , as $\text{Mg}(\text{OH})_2$. In the water from No. IV a large quantity of MgSO_4 was found.

Rothstein, Zert. Angew. Chem. April 1905, p. 541.

EXPERIMENTAL.

The laboratory work consisted in the analysis of scales and the waters from which they were formed. The waters were analyzed in the State Water Survey laboratory. Scales were sampled as accurately as possible, ground very fine in a mortar, and dried at 100° for 1 hour. They were all fused with Na_2CO_3 , since even in the carbonate scales, some of the scale was insoluble in HCl . Trouble was encountered for a while in analyzing the sulphate scales, on account of using too little Na_2CO_3 in the fusion. The usual carbonate rock analysis was used; determining SiO_2 , $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, Ca, Mg in one sample, SO_4 and sometimes Na + K in others. CO_2 was determined by

means of the Parr CO₂ apparatus. H₂O was determined first by loss on ignition minus carbon dioxide, but in almost every case, the H₂O was too high. The Penfield method proved better; the sample was introduced into a bulb at the end of an 8-mm. diameter, hard glass tube, and heated the moisture given off condensed in the glass tube, which was then sealed off just above the sample, and placed open end downwards so that the CO₂ could flow out, and the tube cool. Weighed after two hours, then broke off end, heated and passed air through the tube until thoroughly dry; weighed and corrected for loss of H₂O through the CO₂ give off, and evaporation. This gave pretty accurate results.

This total water given off includes that from the Mg(OH)₂, and water of crystallization and hydration.

There are three general ways of reporting scales and waters,- 1. as ions, 2. as oxides, and 3. combinations of ions or oxides into salts.

Composition of waters.

	Water #1 % com- position, Urbana W. W.	Water II Beardstown, Ill. Riv.	Water III Effingham city s'ply	Water IV Freeport city s'ly
CO ₂	60.31	39.41	33.43	51.13
Ca	16.20	18.08	10.76	19.86
Mg	7.33	7.75	7.85	10.37
SO ₄	.73	16.97	16.41	5.76
SiO ₂	4.61	4.43	15.14	3.78
Fe ₂ O ₃ + Al ₂ O ₃	2.35	.10	6.91	.56
Na + K	7.16	6.27	5.24	3.19
NH ₄ , Cl, NO ₃	1.41	7.00	4.32	5.37

	Water I compos- ition, Urbana W. W.	Water II Beardstown, Ill. Riv.	Water III Effingham city s'p'y	Water IV Freeport city s'p'y
CaCO ₃	43.67	45.46	28.01	49.68
MgCO ₃	27.40	16.50	17.36	30.34
MgSO ₄	-----	15.24	15.54	7.23
FeCO ₃ + Al ₂ O ₃	2.75	.07	8.98	.63
SiO ₂	4.97	4.46	15.75	3.78
Na + K salts	21.21	18.26	14.36	7.66

Water I. Urbana water works.

Water II. Beardstown, Illinois river water.

Water III. Effingham, Little Wabash river.

Water IV. Freeport, purified with lime and soda.

Composition of scales.

	I	II	III	VI	IV	V	VII
CO ₃	53.44	40.90	5.46	6.86	42.79	35.45	32.26
Ca	33.78	24.53	24.89	20.04	31.61	27.55	24.02
Mg	3.06	9.63	5.28	11.60	2.87	5.73	10.81
SO ₄	.78	.32	51.04	34.36	3.86	7.81	1.63
SiO ₂	1.70	8.79	2.05	2.56	6.56	8.13	5.68
Fe ₂ O ₃ +Al ₂ O ₃	3.11	2.89	2.14	6.52	5.45	4.25	8.06
Na + K	-----	.71	-----	-----	.40	.14	-----
(OH) ₂	2.43	10.81	7.65	16.54	5.47	8.73	16.80
H ₂ O	2.28	1.37	2.03	1.58	2.01	2.63	1.50

CaCO ₃	83.62	61.22	9.06	11.38	71.03	58.85	53.55
CaSO ₄	1.11	-----	72.32	48.69	5.48	11.07	2.31
MgCO ₃	4.58	5.92	-----	2.20	3.23	1.64	3.79
Mg(OH) ₂	4.18	18.76	12.63	27.76	6.86	13.71	25.87
MgSO ₄	-----	.40	-----	-----	-----	-----	-----
Fe ₂ O ₃ +Al ₂ O ₃	3.11	2.87	2.14	6.52	5.45	4.25	8.06
H ₂ O	.06	-----	2.03	1.58	2.01	.40	0.19

	I	II	III	VI	IV	V	VII
Na ₂ CO ₃	----	1.48	----	----	.64	.18	----
SiO ₂	1.70	8.79	2.05	2.56	6.56	8.17	5.68

Description of scales.

I. A soft scale which had almost closed up a tube in a feed water heater at the Urbana water works. This scale was soft and crumbly, white, with thick red streaks of Fe₂O₃ through the mass and with no crystalline structure. The pressure in the heater was 100 lbs. or 165° C, but as the water did not remain in contact with the tubes for any length of time it is evident that the CaSO₄ found in the scale even though insignificant in amount, must have been deposited through formation of anhydrite from the gypsum in the water at the high temperature, and not by concentration.

II. This was a soft, friable scale deposited from water I, in a teakettle. It was of uniform appearance, a light gray. Since the temperature of the water here only reached 100° no CaSO₄ was found in the scale. A higher magnesium content is found, however, the Mg(OH)₂ being four times as much as in scale I; the high silica would seem to show that SiO₂ is carried down mechanically rather than being forced out of solution by heat.

III. Scale from a boiler in the C. B. & Q. pumping house on the Illinois River at Beardstown, Illinois. Pressure 110 lbs.; the boiler had not been washed out for about four weeks. This was a very hard dark scale, in thin layers with the laminated appearance of a sulphate scale. It contained the highest per cent of SO₄ of any of the scales studied.

VI. Scale from the boiler in the C. B. & Q. shops at Beardstown using same water as scale III. It was also a hard,

crystalline crust, but not so dark as Scale III, and did not contain as much carbonaceous matter. The pressure was 100 lbs, but this boiler was washed out every two weeks. In this scale the SO_4 is lower than in III (34.36 : 51.04).

The pressure being approximately the same, and the water the same, the length of time before blow-off must have been the cause of this. In No. III, the concentration being allowed to proceed for almost twice as long as in No. VI, the water became stronger in alkalis, which caused the separation of more sulphate, since CaSO_4 can be changed to anhydride and so p'p't'd.at as low a temperature as 130° in a saturated NaCl solution. Also CaCO_3 is more soluble in an alkaline solution than in pure water.

IV & V. Scales from the boiler of a Meat Block Factory at Effingham. This scale as received was seen to be of two different kinds, one a soft, rather amorphous gray crust, about 4 - 5 mm. in thickness, the other a harder, more crystalline, appearing scale, about 1 mm. thick and about the same appearance as Nos. III and VI, although not so decidedly crystalline. No. IV, the soft scale, contained less CaSO_4 (5.5 : 11.0) than No. V, less $\text{Mg}(\text{OH})_2$ (6.86 : 13.71), and more CaCO_3 (71.0 : 58.9). It is seen that scale No. V, even though hard and crystalline, and of about the same appearance as No. VI, contains much more CaCO_3 . The difference in composition of Nos. IV and V, and III and VI can only be explained by difference in boiler conditions, as the waters from which they are formed are about the same. In fact, the Effingham water contains less CaCO_3 and Na salts and more SiO_2 and $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, conditions which would be considered as producing a harder

higher sulphate scale. The boiler conditions in the Effingham scale were-, Pressure, 80 lbs, washed out every 15 days.

Scale VII was from the High School at Freeport, Illinois. It was about 2 mm. thick, rather soft and amorphous, and of a pink tinge due to a trace of manganese which it contained, and the high content of Fe_2O_3 . This is about the usual scale formed from a water of the type of the Freeport city supply.

The diagrams show more clearly the relations between the composition of the scales and waters. In the diagrams the ratio between the ions in the water and scales are shown, the numerical values being shown in the following table.

	I	II	III	VI	IV	V	VII
% Ca in water	$\frac{16.20}{33.78}$	$\frac{16.20}{24.53}$	$\frac{18.08}{24.89}$	$\frac{18.08}{20.04}$	$\frac{10.76}{31.61}$	$\frac{10.76}{27.55}$	$\frac{19.86}{24.02}$
% Ca in scale	1:2.08	1:1.50	1:1.37	1:1.1	1:2.90	1:2.56	1:1.21
% CO_3 in water	$\frac{60.31}{53.44}$	$\frac{60.31}{40.90}$	$\frac{39.41}{5.46}$	$\frac{39.41}{6.86}$	$\frac{33.43}{42.79}$	$\frac{33.43}{35.45}$	$\frac{51.13}{32.26}$
% CO_3 in scale	1:.88	1:.67	1:.14	1:.17	1:1.28	1:1.06	1:.63
% SO_4 in water	$\frac{.73}{.78}$	$\frac{.73}{.32}$	$\frac{16.97}{51.04}$	$\frac{16.97}{34.36}$	$\frac{16.41}{3.86}$	$\frac{16.41}{7.81}$	$\frac{5.76}{1.63}$
% SO_4 in scale	1:1.0	1:.43	1:3.0	1:2.0	1:.23	1:.47	1:.28
% Mg in water	$\frac{7.33}{3.06}$	$\frac{7.33}{9.63}$	$\frac{7.75}{5.28}$	$\frac{7.75}{11.60}$	$\frac{7.85}{2.87}$	$\frac{7.85}{5.73}$	$\frac{10.35}{10.81}$
% Mg in scale	1:.42	1:1.32	1:.68	1:1.5	1:.36	1:.73	1:1.0

CONCLUSIONS.

1. The relative proportion of the Ca in the principal content of the water is greater than that in the scale.
2. CO_3 in scale is generally less than in water.
3. SO_4 in scale is low if CO_3 in scale is high and vice-versa.
4. Mg in scale varies inversely as the Ca in the scale.

In sulphate waters, the composition of scale depends more upon the boiler, and the time of blowing off, than upon the composition of the mineral content of the water. The scale varies greatly even in the same boiler and unless uniform heating and feeding is possible, a uniform scale will not be formed. Hence, in practice, no numerical formulae can be derived or applied which will give the composition of the scale as a whole, even if the temperature and pressure in the boiler, and the mineral content of the water are known.

The chemical composition, although it usually determines the physical character of the scale, may not do so, since many sulphate scales are soft, many carbonate scales hard.

General rules can be derived, however to explain the formation of scales:-

In a sulphate water, the SO_4 content of the scale increases more rapidly than the CO_3 content as concentration continues. The CaSO_4 is deposited in much the same manner as the CaCO_3 , since at the high temperature it is changed to anhydrite, which ppts., and which is almost as insoluble as CaCO_3 at these temperatures. The anhydrite is even more insoluble in an alkaline solution than in water, so it may be stated that the longer the periods between blowing off, and the higher the alkalis, the higher will be the CaSO_4 content of the scale. This does not imply that the scale will become harder, since if concentration is carried far enough, the alkaline salts will crystallize out; however, the boiler is generally blown off before this occurs to any extent.

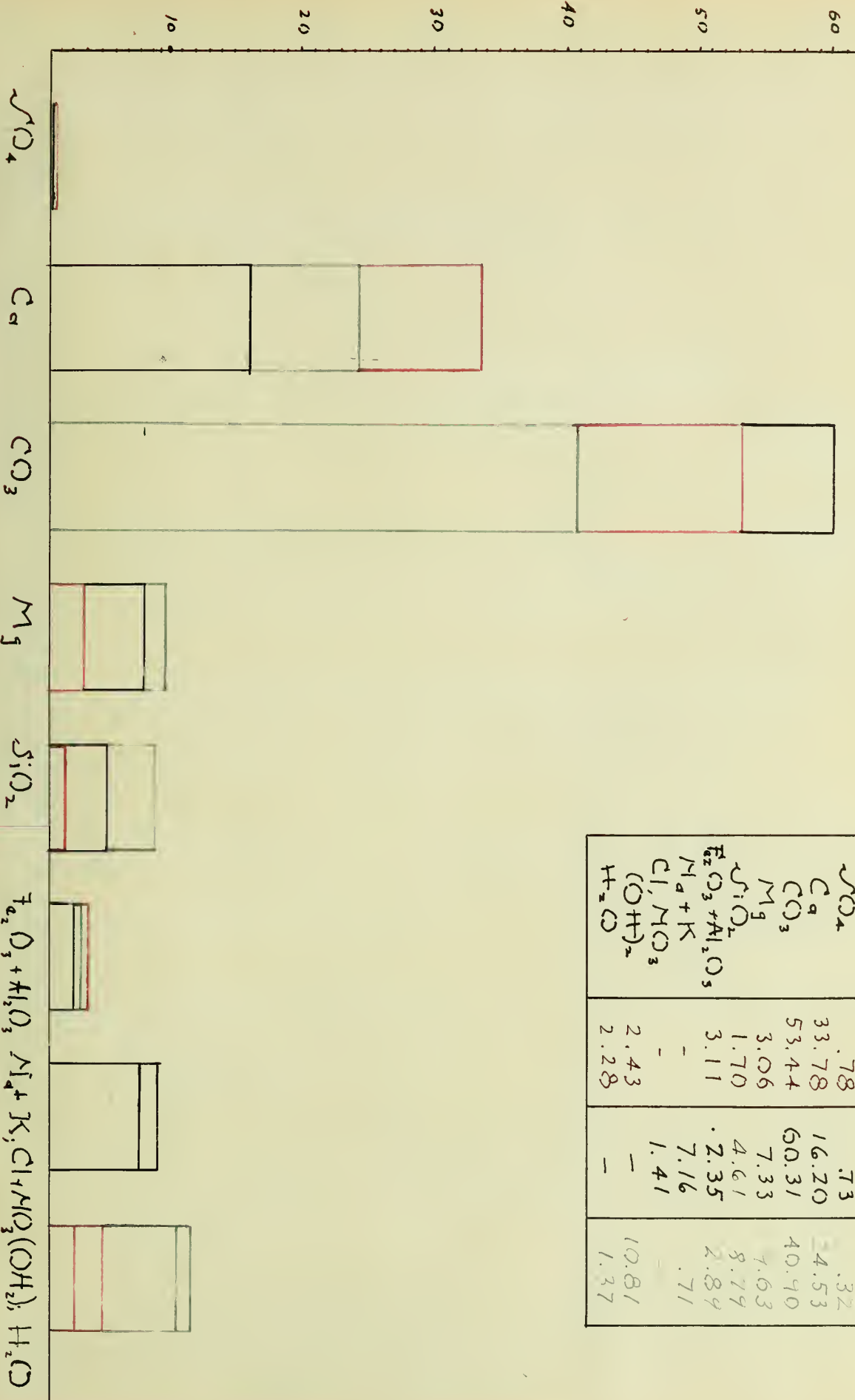
These conclusions should be verified by additional data, but because of the difficulty of obtaining scales from sulphate waters, in which boiler compounds have not been used and because of the lack of information in regard to their sampling, etc., more accurate results could not be derived. An experimental boiler, in which waters of varying sulphate content would be evaporated under similar conditions, is the most feasible way of obtaining exact data.

URBANA

COMPOSITION.

SCALE I WATER I SCALE II

SO_4	.78	.73	.32
Ca	33.78	16.20	24.53
CO_3	53.44	60.31	40.90
Mg	3.06	7.33	7.63
SiO_2	1.70	4.61	8.79
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$	3.11	2.35	2.89
$\text{Na} + \text{K}$	-	7.16	.71
Cl, NO_3	-	1.41	-
$(\text{OH})_2$	2.43	-	10.81
H_2O	2.28	-	1.37

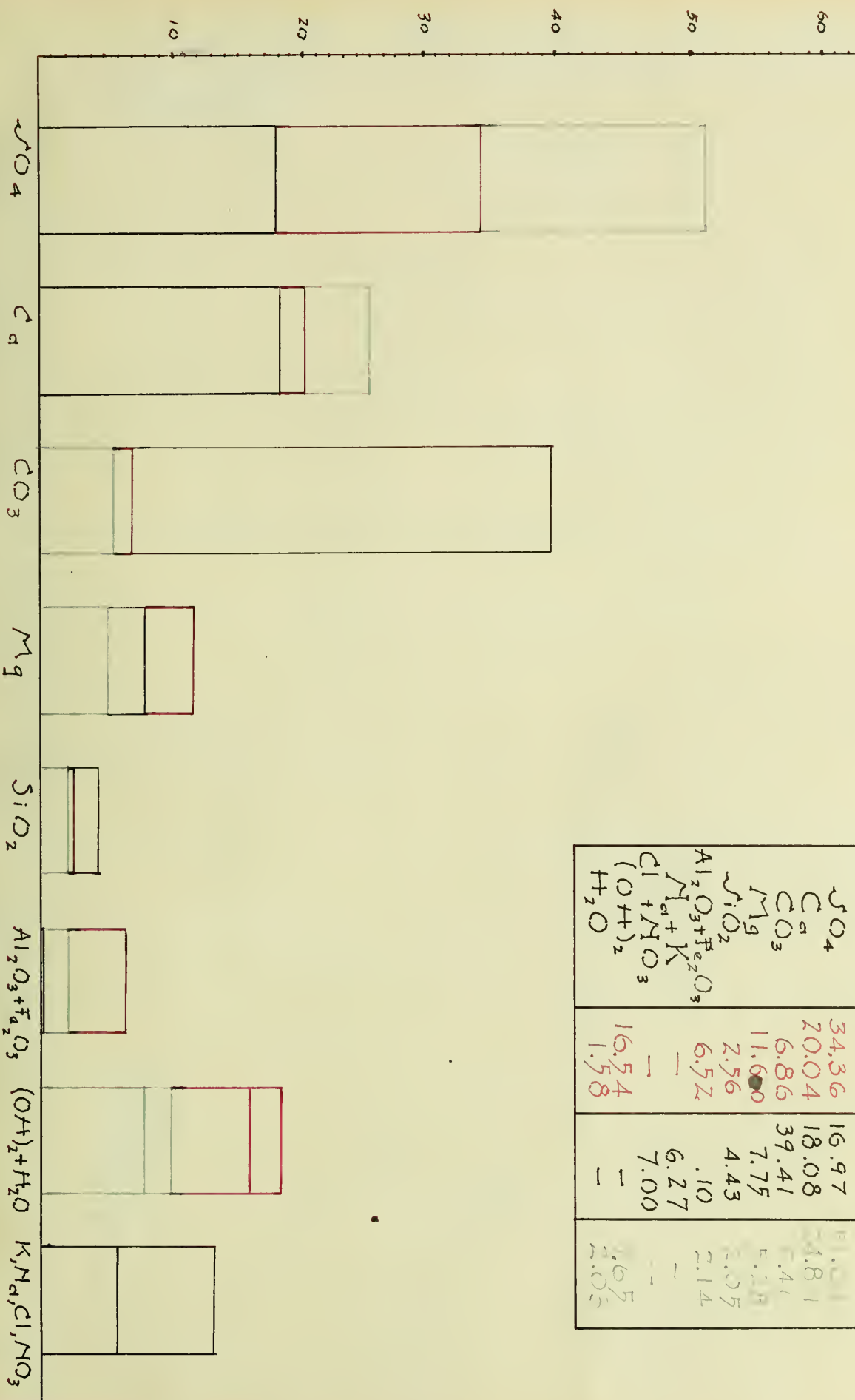


SO_4 Ca CO_3 Mg SiO_2 $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ $\text{Na} + \text{K}, \text{Cl}, \text{NO}_3(\text{OH})_2, \text{H}_2\text{O}$

BEARDSTOWN.

COMPOSITION

SCALE. VI WATER II. SCALE. II



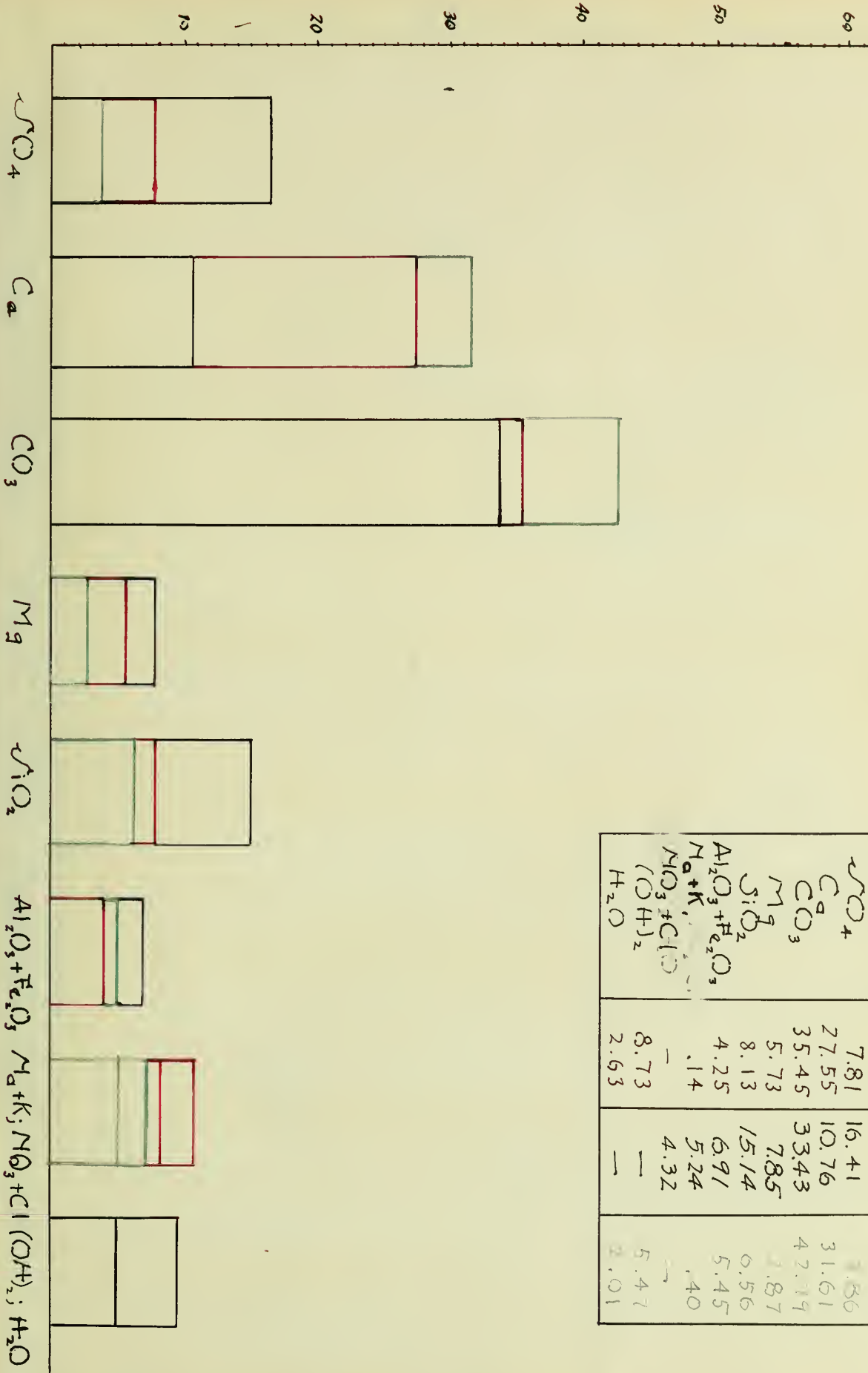
SO ₄	34.36	16.97	16.01
Ca	20.04	18.08	14.81
CO ₃	6.86	39.41	4.41
Mg	11.60	7.75	4.28
SiO ₂	2.56	4.43	2.05
Al ₂ O ₃ +Fe ₂ O ₃	6.52	.10	2.14
Cl+(NO ₃) ₂	—	6.27	—
H ₂ O	1.58	7.00	—
	—	—	2.65
	—	—	2.05

EFFINGHAM

COMPOSITION.

SCALE. V WATER III. IV.

CO_2	7.81	16.41	1.86
Ca	27.55	10.76	31.61
CO_3	35.45	33.43	42.19
Mg	5.73	7.85	2.87
SiO_2	8.13	15.14	6.56
$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	4.25	6.91	5.45
$\text{Na} + \text{K}$.14	5.24	.40
$\text{NO}_3 + \text{Cl}$	—	4.32	—
$(\text{OH})_2$	8.73	—	5.47
H_2O	2.63	—	2.01

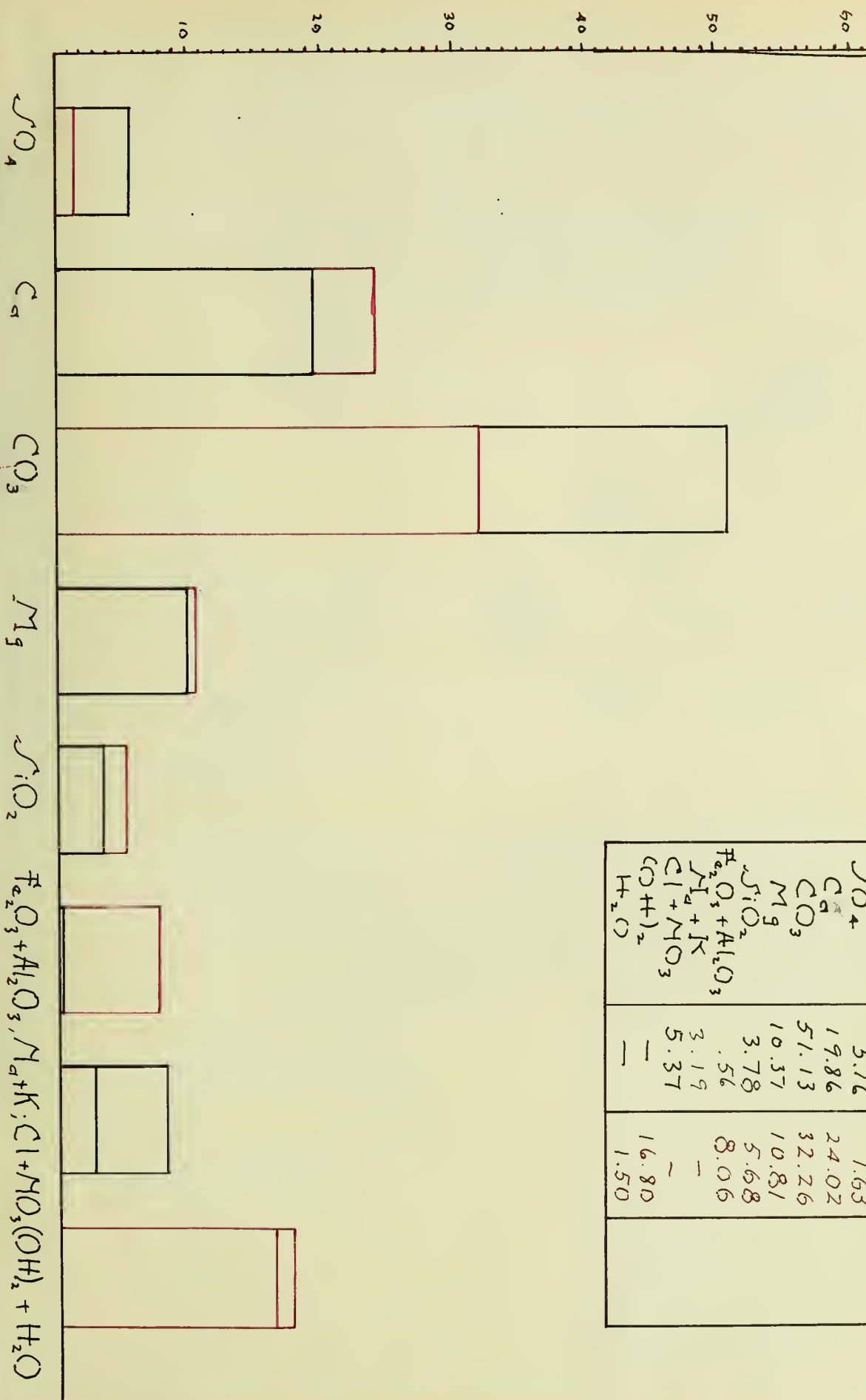


REPORT

COMPOSITION

WATER SCALE

SO ₄	5.76	1.63	
Ca	19.86	24.02	
CO ₃	51.13	32.26	
Mg	10.37	10.81	
SiO ₂	3.78	5.68	
Fe ₂ O ₃ + Al ₂ O ₃	.56	8.06	
Mn + K	3.19	—	
Cl + NO ₃	5.37	—	
(OH) ₂	—	16.80	
H ₂ O	—	1.50	







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