The identification of minerals in boiler deposits. Examples of hydrothermal synthesis in boilers.

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MANY examples of the hydrothermal synthesis of minerals are scattered throughout mineralogical literature. The present paper has been written to bring to the attention of mineralogists the fact that such hydrothermal syntheses are occurring continually in industrial boilers, particularly when control of water softening procedure is not completely efficient.

The main reasons why chemists in recent years have become interested in the nature of the deposits in boilers is that heat interchange surfaces of boilers must be kept clean for as long as possible, so that a minimum of spare boiler capacity is needed to cope with the periods when such plant has to be shut down for cleaning, and that a boiler can operate with maximum heat interchange efficiency while it is working; moreover, certain types of boiler scales have such low thermal conductivity that metal tubes to which these adhere may become overheated and finally fail.

In order to appreciate the conditions in which deposition of solid phases is occurring, it is convenient to mention that evaporation in boilers takes place at pressures varying from below 100 lb./sq. in. to 2000 lb./sq. in. in the case of the most modern boilers, i.e. at temperatures below 164° and up to 336° C.

The composition of the water entering boilers is extremely variable; thus many high-pressure boilers, particularly those producing power only, are serviced with distilled water containing only the chemicals necessary to reduce corrosion and to deal with possible leakage from condensers: on the other hand, purified water is often used even in high-pressure boilers where steam is needed not only for power production but also for heating: finally, in low-pressure boilers raw water is still sometimes used, but there is a general tendency even at low pressures to use purified water, as the economic advantage of running with clean boilers is usually decisive.

In this paper we are most interested in the results of using raw or chemically treated water in boilers. It is convenient to classify raw waters into three main types:

(*a*) Those derived from limestone or chalk areas, and consequently containing a high ratio of temporary to permanent hardness (200 parts temporary hardness and say 50 parts permanent hardness/10^6).

(*b*) River and lake waters of the Midland counties, containing both temporary and permanent hardness (say 100 parts temporary and 150 parts permanent hardness/10^6).

(*c*) Soft, moorland waters often peaty and consequently slightly acidic in character (up to 50 parts permanent hardness/10^6).

We will deal first with boiler deposits which are likely to be found when raw waters are used without purification. From type (*a*) it is most likely that calcite will be the major constituent of boiler scale, but type (*b*) will generally deposit both calcite and anhydrite; type (*c*) may deposit scales containing anhydrite and a silica-containing phase. Comparatively little detailed work has been done on the nature of deposits formed by raw water, as the industrial problems nowadays arise from purified water evaporation and the main effort has been concentrated on identifying constituents of scales formed from purified water.

It is unnecessary now to discuss the results obtained by various softening processes, but in general purified water may contain the following ions, Na, Ca, Mg, Al, Fe, CO_3, Cl, PO_4, NO_3, SiO_2, SO_4, OH. In addition, traces of Cu, Zn, Ba, Sr may more rarely be present, the two former generally from corrosion of boiler equipment. The presence of organic matter from the raw water should not be overlooked as this may have an effect on the habit of crystalline deposits. This mixture provides ample opportunity for a wide range of insoluble products to separate as concentration proceeds. It will be appreciated that as purified water is being fed into a boiler system approximately steady state conditions exist; thus there is a reservoir of more concentrated solution in the boiler from which the more insoluble salts are being deposited whilst they are being replenished from the incoming feed water; soluble salts would increase in concentration but for the fact that these are controlled by removing a definite proportion of the solution periodically.

The degree of concentration of soluble salts which can be permitted tends to be lower the higher the pressure at which the boiler is operating and the higher the purity of steam required. To illustrate this point, and to give an idea of the media from which boiler scales separate, the table which follows has been included.

TABLE I. Composition of boiler water in parts per million at various boiler pressures.

Boiler pressure (lb./sq. in.) ...	1350.	880.	800.	800.	625.	180.
Na_2CO_3	34	74	113	86	41	2040
NaOH	83	103	519	156	94	3720
Na_2SO_3	20	25	nil	22	170	*nil*
Na_2SO_4	1220	185	625	523	401	7280
NaCl	158	6	230	103	335	2980
Na_3PO_4	25	135	61	172	61	nil
$NaNO_3$	?	?	?	?	?	present
SiO_2	8	?	?	41 approx.	18–44	present
Total dissolved solids, approx.	1500	528	1548	1105	1102	16,020

No calcium or magnesium ions were detected.

General method of preventing formation of individual phases.

Perhaps the most commonly occurring substance to be formed is calcite, but as this is somewhat less adherent than other minerals to be mentioned later, and as it is more easily removed either by mechanical or by chemical cleaning, it presents no real difficulty in boiler operation. Anhydrite, however, used to be a quite common constituent of deposits, and as it is definitely harmful, and as the process by which its formation may be inhibited is of general application, perhaps it is worth mentioning in rather more detail. Deposition of $CaSO_4$ will occur when the solubility product $[Ca]^{\cdot\cdot}\,[SO_4]''$ is exceeded in the water concentrating in the boiler, and will tend to take place on the heating surfaces of the boiler because the solubility temperature coefficient ds/dt is negative. If now it is possible to arrange that another and less harmful calcium salt is preferentially formed in place of anhydrite, then the latter should no longer be deposited. In practice this is effected in boilers up to 200 lb./sq. in. pressure by keeping a sufficiently high concentration of CO_3 ions in the concentrating boiler water, because if the relation $[CO_3]/[SO_4]$ is held above a certain value, the solubility product $[Ca][CO_3]$ will then be exceeded and calcite will always be precipitated. Above 200 lb./sq. in. pressure it is more usual to use the PO_4 ion to inhibit the deposition of calcite; hydroxyapatite is then preferentially formed. This procedure was initially suggested by Hall.[1] The practical lower limits for the ratios CO_3/SO_4 up to 150° C. and PO_4/SO_4 up to 350° C. were subsequently

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[1] R. E. Hall, Indust. Engin. Chem. (Amer. Chem. Soc.), 1925, vol. 17, p. 283.

fixed by determinations of the solubility of $CaSO_4$ in the presence of calcite or of hydroxyapatite.[1]

Minerals that have been identified.

Though it is thus possible to inhibit the formation of anhydrite, the complexity of the composition of chemically treated feed water ensures that a number of interesting mineral species is likely to be formed in boiler conditions and to be deposited either in the sludge, most of which is removed when the boiler is blown down, or in scale adhering to heating surfaces. Partridge,[2] Powell,[3] and other observers, showed that microscopic and petrological examination was of some value in identifying constituents of boiler scale; normally, however, the crystal sizes in boiler scales are so small and the phases so admixed that optical methods are not always useful. The introduction of the more certain X-ray technique[4] for identification opened the way for a more decisive attack on the problem of the identification of constituents of boiler deposits. As a result of these investigations, a considerable number of minerals has now been identified. The following list compiled from the literature mentioned above, though not exhaustive, gives an indication of the wide range of materials which may be formed in boiler conditions.

Calcium compounds: Portlandite, $Ca(OH)_2$; Calcite, $CaCO_3$; Anhydrite, $CaSO_4$; Hydroxyapatite, $3Ca_3P_2O_8.Ca(OH)_2$; Crestmoreite, $2CaO.2SiO_2.3H_2O$; Hillebrandite, $2CaO.SiO_2.H_2O$; Wollastonite, $CaO.SiO_2$; Xonotlite, $5CaO.5SiO_2.H_2O$.

Magnesium compounds: Brucite, $Mg(OH)_2$; Periclase, MgO; Hydromagnesite, $3MgCO_3.Mg(OH)_2.3H_2O$; Hydrotalcite, $MgCO_3.5Mg(OH)_2.2Al(OH)_3.4H_2O$; Chrysotile, $3MgO.2SiO_2.2H_2O$; Sepiolite, $2MgO.3SiO_2.2H_2O$; Mg hydroxyphosphate, $Mg_3(PO_4)_2.Mg(OH)_2$.

Complex silicates: Acmite, $Na_2O.Fe_2O_3.4SiO_2$; Analcime, $Na_2O.Al_2O_3.4SiO_2.2H_2O$; Cancrinite, $4Na_2O.CaO.4Al_2O_3.2(CO_2,SO_3).9SiO_2.3H_2O$;

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[1] F. G. Straub, Bull. Engin. Experim. Station, Univ. Illinois, 1933, no. 261. L. M. Clark and E. Hunter, Journ. Chem. Soc. London, 1935, p. 385. L. M. Clark and W. F. Gerrard, Journ. Soc. Chem. Indust., 1938, vol. 57, p. 295.

[2] E. M. Partridge, Research Bull. Univ Michigan Engin., 1930, no. 15, p. 513.

[3] S. T. Powell, Combustion, New York, 1935, vol. 5, no. 3, p. 15.

[4] L. M. Clark and C. W. Bunn, Journ. Soc. Chem. Indust., 1900, vol. 59, p. 155 [M.A. 8-116]. C. E. Imhoff and L. A. Burkardt, Indust. Engin. Chem. (Amer. Chem. Soc.), 1943, vol. 35, p. 873. H. C. Miller, Proc. Amer. Soc. Testing Materials, 1943, vol. 43, p. 1269. T. C. Alcock, L. M. Clark, and E. F. Thurston, Journ. Soc. Chem. Indust., 1944, vol. 63, p. 292 [M.A. 9-103]. M. Reinhard, E. Brandenberger, and G. Oesterheld, Helvetica Chim. Acta, 1942, vol. 25, p. 336 [M.A. 9-284].

Sodalite group, $3(Na_2O.Al_2O_3).2SiO_2.2NaCl$, &c.; Pectolite, $Na_2O.4CaO.6SiO_2.H_2O$.

Copper compounds: Atacamite, $CuCl_2.3Cu(OH)_2$; Chalcopyrite, $CuFeS_2$; Copper metal.

Laminated boiler scales.

It has been stated above that the constituents of boiler scales are laid down in intimate mixture. Like most generalizations, this statement has limitations, for occasionally a scale is found which is well laminated, and the laminae may then be composed of more or less pure mineral species; presumably this differentiation has been caused by a change in some factor in boiler control, such as a variation in feed-water composition, in the rate of evaporation of steam, or in pressure. If it were possible to have accurate knowledge of such variations and to correlate these with the effects produced, a considerable step would have been taken towards the elimination of some types of deposit. However, so far it has not been possible to do this. As an illustration of a complex laminated boiler scale, reference may be made to a scale taken from a Lancashire boiler operating at 125 lb./sq. in. pressure. This scale was 5 mm. thick: on the side adhering to the boiler wall, there was a translucent layer 1 mm. thick, which was composed almost entirely of cancrinite. Next came a hard layer, 3 mm. thick, which contained a mixture of cancrinite and one of the sodalite minerals (probably nosean), and finally the outer layer in immediate contact with water in the boiler contained calcite and chrysotile.

Several interesting points may perhaps be suggested about the mineral constituents of boiler scales from the observations made in the Northwich Laboratories:

(*a*) Of the ten boiler scales which we have examined containing chrysotile, three also contained pectolite; it is possible that the two phases can separate together over a fairly wide range of composition of boiler water and of temperature variations.

(*b*) It seems possible that some of the more complicated minerals which have been identified are not primary deposition products; thus such materials as cancrinite or the sodalite minerals may be built up by the continued action of higher temperatures in parts of the scale nearest the metal heat-interchange surfaces on simpler initially formed substances in the presence of the various components present in boiler water. It will be appreciated that when a scale is once adhering to a heated metal surface conductivity of the system is reduced, and if the same rate of heat flow is to take place the temperature of the metal must rise. The formation of secondary products may require the transfer of suitable ingredients from the boiler water through a layer of scale. With some types of scale this seems not impossible as they are somewhat porous, though the diffusion process must be slow. Two examples of the phenomenon may be given. When sodalite and analcime are found in the same scale, the sodalite occurs in a lamina next to the metal, i.e. in the hottest part of the system, the analcime being on the water side of the scale. On the other hand, in the two scales in which we have found cancrinite or sulphatic cancrinite, this mineral has been in contact with the hot metal, whilst nosean with which it has been associated has been in a layer farther away from the hottest zone, though in the example given earlier in this paper there was an intermediate zone in which cancrinite and nosean were admixed.

There is little evidence in the literature about the conditions in which the sodalite minerals or cancrinite can be formed, though Lemberg[1] considered that he had synthesized a member of the group at 200° C., whilst Friedel[2] prepared sodalite by the action of salt and sodium hydroxide on mica at 500° C. It is clear that a good deal of experimental work would be required to confirm the thesis suggested above.

(*c*) From a comparison of the chemical compositions of some boiler scales with the minerals identified therein, it is sometimes difficult to account for the amounts of magnesia shown by the analysis. It is known that calcite may have limiting amounts of magnesium replacing calcium. We have found that in the calcite contained in some scales containing large proportions of magnesia, there is a significant diminution of the cell dimensions of the calcite as revealed by X-ray powder patterns. This diminution would be expected if a proportion of the calcium in calcite had been replaced by magnesium and it is suggested therefore that some of the hitherto unaccounted magnesia in boiler scales occurs in the calcite fraction. It also seems that magnesia can be present as an amorphous phase, for a sample of scale containing periclase was found in the neighbourhood of a burst in a boiler tube which metallurgical examination showed had been locally at a temperature of about 1000° C.; scale taken from adjoining tubes contained 8 % MgO, but there was no evidence from the X-ray powder pattern of the presence of any magnesia-containing mineral. It is suggested that the periclase was formed by the

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[1] J. Lemberg, Zeits. Deutsch. Geol. Gesell., 1887, vol. 39, p. 559.

[2] C. Friedel and G. Friedel, Bull. Soc. Franç. Min., 1890, vol. 13, p. 182.

decomposition of amorphous magnesium hydroxide or carbonate originally present in the scale.

(*d*) A basic magnesium phosphate, $Mg_3(PO_4)_2.Mg(OH)_2$ is occasionally found in boiler scales. This does not appear to have been described as a naturally occurring mineral, but its composition has been fixed by synthesis (Alcock, Clark, and Thurston, loc. cit.)

Solubility of xonotlite in water up to 300° C.

The main objective in identifying mineral species deposited in boilers is to find the conditions which will prevent their formation. The normal way of doing this is to eliminate one or more of the constituents from the feed water, or to induce the preferential formation of some more insoluble compound which does not have the harmful effects of the products whose elimination is being attempted, e.g. as indicated earlier in this paper, calcite or apatite are less obnoxious than anhydrite. When the prevention of anhydrite was found to be possible, attention was turned to the constituents of scales containing high proportions of silica, since such scales are harmful in boiler practice. Little was known about the mode of combination of silica in boiler scales at the time our examination began and the isolation of xonotlite from several samples (Clark and Bunn, loc. cit.) suggested that an approach to the problem of preventing the deposition of silica-containing scales might be made on somewhat the same lines as had been successful for anhydrite elimination. The first step in examining the possibility of eliminating harmful phases is to determine their solubility, and preliminary work to determine the solubility of some of the calcium silicate phases was in hand at the beginning of the war but then had to be stopped. It is apparent that the problem is much more complex than was initially appreciated when the wide variety of silica-containing minerals existing in boiler scales was not known, and it now seems unlikely that it would be fruitful to examine the solubility of each of the many silica-containing minerals; the problem in fact will have to be tackled by more empirical methods. However, in view of the almost complete lack of data on solubility of calcium minerals in water at high temperatures, it may be interesting to record the result of a preliminary investigation on the solubility of xonotlite.

The solubility of xonotlite, $5CaO.5SiO_2.H_2O$, in water was determined as described for apatite (Clark and Gerrard, loc. cit.). A synthetic sample of xonotlite was heated for up to 160 hours with water over a range of temperatures between 150° and 300° C. Samples of the solutions filtered at the experimental temperature were analysed, calcium being determined by titration of the oxalate with permanganate, and silica colorimetrically as the yellow coloured complex silico-molybdate, using a sodium silicate solution as a standard source of silica for comparison. The following results were obtained:

	150°	200°	250°	300°C.
CaO parts/10^6 H_2O	19	18	10	5
SiO_2 ,, ,, ...	51	65	33	22

Each of these results is the arithmetical mean of determinations in which there was considerable spread, probably because it may be difficult to reach equilibrium in the system CaO–SiO_2–H_2O. Over-great importance should not be ascribed therefore to the increased silica content at 200° C. over that at 150° C. The main trend of the results, however, is quite clear. It shows that xonotlite is incongruently soluble and that the ratio of CaO/SiO_2 in solution decreases with increasing temperature, as does the xonotlite solubility. It appears that during the dissolution a second phase (or series of phases) containing a higher ratio of calcium oxide to silica must be formed as temperature increases, though, of course, in extremely small amounts. This result may be useful to mineralogists who are interested in the deposition of minerals of the xonotlite type.