CHEMICAL ASPECTS OF BOILER-WATER TREATMENT

A LTHOUGH BOILERS VARY WIDELY in size, complexity and pressure, the chief operating problems from which all may suffer—if care is not exercised in providing the appropriate water treatment—are deposit accumulation, corrosion and foaming or carryover. In spite of their differences, the same sort of physical-chemistry is applicable; but because the ill effects of these problems increase in importance as the operating pressure rises, the water conditions to be maintained in boilers also become more and more exacting with rising pressure. It is convenient to discuss water treatment for low-pressure boilers first in some detail and go into the principles. and then to deal with modifications that are needed for boilers of progressively increasing pressures.

But before water-treatment methods are considered, a brief description will be given of the nature of the three operating problems already mentioned.

DEPOSIT ACCUMULATION

Deposits can form from the water in the first stages of its passage through a boiler, i.e. in the economizer, or even the boiler feed pumps or feed-water heaters. In these places the solids separate from solution because they are less soluble in the hot conditions met there than in the cold. Scaling of feed pumps can proceed to the point where they "draw up" because of the excessive frictional resistance. In economizers, the heat-transfer rate is lowered and the efficiency of heat recovery from the flue gases to the stack falls. Overheating of the metal may occur and there may be difficulty in pumping the water into the boiler. In boilers, scaling is the result of interaction between hardness compounds and other materials which are usually deliberately added to the boiler. The most important change that follows on scaling there is not the reduction in boiler

efficiency—though that is important enough—but the rise in temperature of the boiler metal which is brought about by the layer of scale. The metal temperature is raised by increase in the thickness of the scale and in the heat-transfer rate, while deposits that have a low thermal conductivity are more dangerous than those with a higher conductivity; a steam-filled porous scale is for any given thickness the most dangerous. Because the thickness of deposits generally varies less over the surface of any given boiler than does the heat-transfer coefficient, failures usually occur at the hot spots. The solution then lies in eliminating the hot spots if possible, or improving the water treatment, or both. Sometimes special types of corrosion occur under boiler scales, encouraged by the higher temperature of the metal and the concentration of salts which occurs there. In the extreme, of course, the metal softens and eventually fails by creep. A boiler tube which failed in this way is shown in Figure 1. Hardly less important in the water-tube boilers is the interruption to boiler circulation which follows if adherent scale begins to flake off boiler surfaces and collects in headers at the bottom of a boiler. So-called "starvation" may occur when a tube fails to get cooled by water that should pass through it and a burst may follow: an example is shown in Figure 2.

Figure 1. Boiler-tube failure resulting from scale formation in tube from 200 p.s.i. boiler.

Figure 2. Explosive failure of water-wall tube resulting from starvation.

CORROSION

Corrosion can occur throughout boiler systems and the different means of protection against it in the economizer, if there is one, in the boiler itself, and in those sections of the steam system where condensation can occur, will therefore require to be gone into. The operating problems to which corrosion gives rise include loss of boiler contents, weakening of metal with a risk of explosion, and the harm done by corrosion products. Corrosion of condensate-collecting systems where the otherwise pure water is made acid by dissolved carbon dioxide can be a serious problem for not only are the pipework and other equipment damaged mechanically, but the iron picked up by the water and returned to the feed system can be deposited there and in the boiler in alarming amounts. Caustic cracking, a dangerous type of corrosion that weakens steel, will require special consideration.

CARRYOVER

Foam formation and carryover (the transfer of liquid boiler water with the steam out of the boiler) can cause superheaters to become coated or even choked with solids from evaporated boiler water,

so reducing the heat transfer and sometimes damaging the metal through overheating. The contaminating substances may get as far as turbines and reduce their efficiency by being deposited there; and sometimes foam formation can upset the operation of boiler-water level control systems.

WATER TREATMENT FOR LOW-PRESSURE BOILERS

The water-chemists' methods of overcoming corrosion, scaling and carryover in lower-pressure boilers (i.e. pressure below 200 p.s.i.) will now be considered. It must be said in passing that the near-solution of using absolutely pure water is impracticably costly in all but the extreme cases of very high-pressure boilers and nuclear power station technology, and other procedures which depart from this have proved adequate and are continually being improved upon.

ALKALI ADDITION FOR CORROSION CONTROL

The main consideration which has decided the details of the conventional method of boiler-water treatment is that the corrosion of mild steel in boiler conditions is slowest at a pH value representing distinctly alkaline conditions. The optimum pH is between 10 and 11 as measured at room temperature, and thus the first line of defense against boiler corrosion has been the maintenance of alkaline conditions in the boiler water. This is achieved with sodium carbonate in low-pressure boilers, and with sodium phosphate in boilers working at higher pressures. The reason for the difference in choice here is that the sodium carbonate hydrolyses to caustic soda at ever-increasing rates as boiler pressure increases and this has a number of ill effects. The chief of these is that the large amounts of carbon dioxide released at higher pressures would dissolve in the water formed when the steam eventually condenses and, making it acid, cause it to be corrosive towards mild-steel.

Oxygen is a vigorous stimulant to corrosion in hot water and for boilers at pressures over 200 p.s.i. must be rigorously excluded from the boiler water. At these higher pressures, the small amounts left after physical deaeration can be most damaging and chemical absorbents like sodium sulphite have to be used in the boiler water to remove the last traces. At lower pressures, one can generally depend on most of the oxygen "boiling off" as soon as the feedwater enters the boiler. At present the trend in highly rated low-pressure boilers is also towards using sodium sulphite as a fairly cheap measure of achieveing extra protection. To keep a reserve of sulphite continuously present ensures the absence of oxygen in the boiler water.

CONTROL OF DEPOSIT ACCUMULATION
Conventional Use of Alkalis

The formation of deposits within low-pressure boilers will now be considered. It is well known that the so-called temporary hardness of a water is precipitated when it is boiled. The presence of sodium carbonate in low-pressure boilers already referred to causes practically all the hardness salts in the feedwater to be precipitated there. It has been found that to maintain certain reserves of sodium carbonate in low-pressure boiler waters not only protects them from corrosion but also reduces the amount of scale and deposit which would otherwise accumulate.

One reason for this is that many waters, if fed to boilers without treatment, would give large quantities of calcium sulphate on evaporation and this substance has the property of forming thick hard scales. The presence of an adequate amount of carbonate in boiler water ensures that all the calcium forms calcium carbonate instead, much of it precipitating as a suspension in the boiler water, and only a small fraction generally appearing as scale. Ideally, no deposit problem would exist if all of the hardness compounds that are precipitated in boilers left as a suspension in the blowdown. This ideal state can be approached more closely, i.e. scaling can be reduced, by raising the level of carbonate alkalinity maintained in a boiler water. This is because the solubility of calcium carbonate is then lower and the calcium salt entering in feed is rapidly precipitated as minute crystals; these present a large surface area to the boiler water, denuding it of supersaturation so that growth of calcium carbonate on the boiler metal is reduced. It is because calcium sulphate has a fairly high solubility that it so readily gives thick scales. Conversely, calcium phosphate has a much lower solubility than calcium carbonate so that deposit formation under phosphate treatment is generally less than that with ordinary carbonate conditioning. If there were another calcium salt even less soluble than the phosphate, a still better means of preventing scaling might be forthcoming.

Not all scaling is due to regular growth of the solids from their supersaturated solutions. In some instances a large part is played by the impingement of particles on surfaces and their sticking there rather than bouncing off. Magnesium compounds do not usually play an important role in deposit accumulation; those found appear often to have been entrapped in the calcium deposits as they have formed.

Examination of Deposits for Diagnostic Purposes

Before methods of avoiding scaling are gone into, an insight will be given into methods of scale examination; even a few fragments can provide a great deal of information. Chemical (elemental) analysis is the most common first approach, but it is not a quick method and does not show how the elements are combined though one may often guess. There is a good deal to commend the X-ray powder method (Debye-Scherrer) for a quick identification of the principal constituents if, as is usual, they are crystalline. A typical report for a deposit from a low-

pressure boiler might then read: main constituent calcite (commonest crystalline form of calcium carbonate) with some magnesuim hydroxide and the magnesium silicate serpentine. The presence of some substances reveals lapses in treatment; thus the calcium silicate, xonotlite, is sometimes met, but it will not form if correct carbonate alkalinity is maintained. Possibly the deposit is layered and if, for example, a scraping from the layer next to the metal is shown to be the only part of the deposit containing this substance, it would become plain that the period of incorrect treatment was not in the recent past. A great many compounds have been met in boiler scales; some cannot be made at room temperature and require the high temperatures in boilers for their formation. Sometimes an X-ray pattern shows the presence of a substance which has not been recorded hitherto as was the case when we first observed the basic magnesium phosphate, $Mg_3(PO_4)_2.Mg(OH)_2$. [1] It is now recognized as a common constituent of deposits from high-pressure boilers. It is needle-like and gives soft, very heat-resistant and therefore potentially dangerous deposits. A less troublesome deposit can usually be obtained by adding sodium silicate to the feedwater, a process first proposed by Welsh. [2] Another use of X-ray evidence follows from the fact that the presence of certain substances in deposits is indicative of excessive heating. Thus, serpentine, $3MgO.2SiO_2.2H_2O$, when overheated in boiler conditions is converted into the substance olivine, $2(Mg,Fe)O.SiO_2$, and if this is found in a deposit, overheating may at once be concluded. The mineral analcite (a sodium aluminosilicate), $Na_2O.Al_2O_3.-4SiO_2.2H_2O$, tends to be converted to sodalite, $3(Na_2O.Al_2O_3.2SiO_2).2NaCl$, among other substances when a boiler tube scaled with it becomes excessively hot. Often observations of the kind just described are reinforced by examination under a microscope, when some idea can be formed of how the scale or deposit developed.

Scale Prevention by Softening

Scaling can be reduced by softening the water. There is a wide variety of processes. Some remove only part of the hardness, and some can introduce new problems. Thus base exchange, which undoubtedly has valuable merits (for example, it accommodates variations in water hardness and temperature) nevertheless gives a water which can contain large amounts of bicarbonate. These can cause economizer corrosion and the boiler steam is relatively rich in carbon dioxide. In recent years the merits of the hot lime base-exchange method of treatment have been increasingly appreciated. In this process, the raw water is treated at around $100°C$ with milk of lime which converts the calcium bicarbonate into calcium carbonate, which is settled out. The removal of turbidity is achieved simultaneously. The hot partially softened water is filtered and then

passed through a base exchanger of the sulphonated polystyrene type which reduces the hardness to a level of 0.2 to 0.5 p.p.m. $CaCO_3$. For many boiler systems in the 200 to 800 p.s.i. range this treatment gives a water which is eminently suitable. The lime soda/sodium aluminate process provides a convenient means of dealing with high hardness, high bicarbonate waters, and is particularly effective when they are turbid. Turbid waters require to be filtered before base-exchange; otherwise exchangers tend to become fouled and their performance then deteriorates. There are quite a number of variants on base exchange, such as the so-called "Starvation process" and the "Blend process." The best quality water is of course produced by either distillation or demineralization; both processes are widely used for preparing make-up for power station boilers.

Each softening process is particularly suitable for certain kinds of water and water application and each gives, for any stated water, products of different compositions. The choice of the right softening process, if one is to be used, is seen to be of considerable complexity and importance, for each process brings about its own characteristic changes in the composition.

The prevention of scaling by chelating the hardness entering a boiler is being used increasingly. The word "chelate" requires some explanation. Certain substances called chelating agents can take calcium and magnesium and other ions into their molecular structure so that the solution no longer behaves as if any of these elements were present. The substance Versene (EDTA—ethylene diamine tetracetic acid) is the best example. The process would cost much too much for all but waters of low hardness. It can be cheapened by injecting the material only at intervals while the boiler is on line to give periodic descaling.

Boiler Additives to Prevent Scaling

The most common means by which scaling has been controlled in low-pressure boilers has been by using additives to the boiler feed-water or to the boiler water itself which cause the solid substances formed in the boiler to leave in greater proportions in the blowdown than would be the case in their absence. Tannins, lignins and other substances have been so used for a long time. In recent years a few novel applications of the principle have been discovered and two of them with which we have been associated have now been used extensively in practice. These are the magnesium method of scale control in carbonate-treated boilers, and the use of certain polyacrylates for scale prevention in phosphate-treated boilers.

The first of these came out of a laboratory and field study of sludge accumulation in carbonate-treated boilers. J. A. Gray [3] discovered that sludges from such boilers when settled out were practically impossible to redisperse if they were of

low magnesium content, whereas if they were richer in magnesium the slightest movement of the liquid caused them to flow. This second type was much to be preferred in practice especially for boilers which cease steaming intermittently and so provide conditions for settling. A sludge was found to be mobile if the empirical relationship held that the magnesium hardness of the feedwater exceeded one-fifth of the calcium hardness together with three times the silica content. Work with an experimental boiler in which the effect of the magnesium content of the feedwater on scaling was systematically examined [4] showed that the fulfilment of these conditions coupled with the maintenance of a carbonate alkalinity of 200 to 300 p.p.m. not only gave free-flowing sludges but also a great reduction in scaling. Thus in boiler runs at 150 p.s.i. a scaling rate of about 10 mg/cm^2 day with a hard but magnesium-free feed was reduced to less than 1 per cent by the addition of enough magnesium to give a mobile sludge. While the rate of scaling was rather greater when silica and/or alumina was present as well as magnesium the rate was still rarely above 5 per cent of that for the "blank" run. The conditions were: total hardness of feed, about 500 p.p.m.; dissolved solids content of boiler water 3000 p.p.m. including alkalinity 500 p.p.m.

Full-scale trials, embracing the main types of low-pressure boiler and covering a wide pressure range, bore out the conclusions of the laboratory work. The effectiveness was found to be rather less spectacular with soft than with hard waters. This did not ocassion surprise for the experimental boiler runs had given warning of this. A means of making sludges mobile in carbonate-treated low-pressure boilers and of minimizing scaling had thus been found; it involved alkalinity control of the boiler water and, in most instances, raising the magnesium content of the feedwater by the addition of magnesium salts.

Since that time many hundred of boilers have received this treatment, dispensed generally by briquetted mixtures containing magnesium salts introduced into the feedwater and the application of alkali to the boiler itself.

It is worth referring, in passing, to a discovery made at about the same time. It is well known that there is a tendency for calcium carbonate to form scale on the hot surfaces of economizers passing a hard calcium bicarbonate water; laboratory tests showed that the introduction of magnesium salts into a stream of such a hard water passing through heated tubes substantially reduced this tendency. Frequently a little Calgon is added to feedwater that passes through economizers in order to reduce this scaling; it was also shown that the addition of magnesium salts, useful later on in the boiler, enhances this valuable effect of Calgon.

Special Requirements of Packaged Boilers

The rapid rise to importance of these generally small, highly rated, automatically operated units is

well known. Some operators take the view that unless feedwater is very soft it should be fully softened to eliminate sludge and scale problems. The base-exchange process is then useful, but can lead to boiler water conditions which require correction if it were considered necessary to provide protection against caustic cracking. The magnesium-control process has been successfully employed in some hundreds of boilers of this type, its ease of control being its chief merit together with the fact that it needs only simple equipment. It was mainly with the softer waters (say 50 p.p.m. and below) that it did not always give clean surfaces. An improvement has usually been obtained in these instances by using phosphate as the precipitant of calcium, and employing a polyelectrolyte as an anti-scalant, to which reference will be made later. It is a further feature of packaged boilers that they tend to be afflicted with corrosion when treatments are in use that would be fully successful with earlier types of low-pressure boiler, no doubt because of the greater heat-transfer rates used. It is now frequently recommended that a chemical deoxygenating agent be used to offset corrosion, usually sodium sulphite. Furthermore, with packaged boilers there is much to be said for dosing them with hydrazine during their first week or two when new, to provide a sound film of magnetite. The same principle is applied when, after a boiler has been acid cleaned, hydrazine is included in the boil-out solution—at high concentration. The packaged coiled-tube boilers of the Clayton and Stones Vapour type, in both of which a great deal of evaporation occurs in a single pass of the water through the heated coils, are usually fed with a softened water because conditions of heating are particularly severe. Some promise has been met in trials with unsoftened water dosed with polyelectrolytes of the modified polyacrylate type (see the high pressure section of this paper).

It is particularly important with packaged boilers to apply treatments with methodical care. Means of injecting chemical solutions in amounts accurately related to the feedwater rate are very necessary; and the use of the right equipment pays handsome dividends.

There is another point of practical importance to add here. Many low-pressure boilers including packaged types steam only intermittently. It is then especially important to prevent corrosion during the idle periods, for occasional access of air to the hot wet metal interior is especially harmful. The exclusion of oxygen as far as possible assists; and it is clearly better to leave a boiler full of water containing sulphite than to leave it hot, wet and empty. It often happens that more corrosion goes on in boilers and in superheaters when the boilers are not steaming than when they are. If the boiler can be made dry and kept dry at such times, there is a good reason for doing so. The period in which a boiler is being built and commissioned is also a time

when much damage can be done, especially after hydraulic testing when it lies open to the air and wet.

SCALING AND CORROSION IN ECONOMIZERS

Special conditions for corrosion and scaling obtain in boiler economizers because the water is of too low a pH-value to be fully safe from the corrosion standpoint unless special precautions are taken and the heating of many ordinary raw waters provides conditions for $CaCO_3$ scaling. The use of polyphosphate for the latter purpose has been referred to. Mixtures of polyphosphate with certain tannins (not all are useful) give an even greater degree of protection against scaling. To combat the corrosion tendency a little alkali should be added to feed water, the necessity for it increasing with rising pressure of the boiler. The ideal pH value is 9. Scaling in some economizers can bring about a maldistribution of water between the various flows which are in parallel and in the extreme case a section can become steam-filled and damage to the metal structure may result.

CARRYOVER FROM BOILERS

Carryover of boiler water with the steam can take various forms, ranging between a trace of droplet carryover, which is not uncommon and not very harmful, to the entrainment of gulps of water in the steam through the formation of a stable foam layer. In earlier times, the chief control of foaming was exercised by keeping the dissolved solids content of a boiler water below a level which experience had shown was safe for that kind of boiler, and tables of recommended values have been published [5]. It was a useful approach and is still used, but a greater place is being given to the part played by suspended matter in encouraging foam formation. This part is much more complex and the literature does little more than acknowledge the complexity! The introduction of antifoaming agents some 15 to 20 years ago provided a powerful weapon in this situation; the best of these materials (and dozens have been described in the literature, mostly organic polymers) can control carryover when as little as 0.2 p.p.m. is present in the boiler water, though more is desirable; nowadays some vendors of boiler-water treatment products include antifoams in all their treatments in this field. The earlier levels of concentration of boiler waters are still generally employed but antifoams give, in all but the rarest cases, a much greater degree of safety. Factors other than the composition of the boiler water can encourage carryover and these need consideration whenever carryover difficulties occur. Thus badly fitted baffles in the steam drum, the failure to replace all steam purifying equipment, steam washers and steam cyclones in their correct positions can all contribute, as well as a rapidly rising steam load and high water levels in a boiler. Another cause is the working of a boiler at pressures well below those for which it

was designed, when the steam velocity from the water surface (at any given output) is greater. There is much that could be said here about the measurement and monitoring of steam purity which is more usually important for high-pressure than low-pressure boilers. It must suffice to say that more investigation is still required. Thus the methods of sampling of saturated steam currently practiced, frequently fail to take into account the fact that much of the liquid water is carried along the walls of steam pipes, and that the "solid" phases in superheated steam derived from boiler-water substances must frequently be, in reality, wet with molten phases containing, for example, caustic soda. The monitoring of steam purity by measurement of the conductivity of the steam condensate is also fraught with hazards, for damaging amounts of boiler-water substances can often be missed among the carbon dioxide and ammonia which contribute substantially to conductivity.

CAUSTIC CRACKING AND ITS PREVENTION

Caustic cracking is a form of corrosive attack on steel characterized by the development of cracks along the grain boundaries of the metal; it occurs when caustic soda solution of at least 5 per cent strength come into contact with boiler steel in high tensional stress. The serious loss of mechanical strength can cause catastrophic failure. It was most commonly met as a result of leakages through the seams of riveted boilers, but with the currently welded stress-relieved boilers it is much more rare. Some operators consider that there are so few opportunities in modern boiler plant for boiler waters containing caustic soda to concentrate by evaporation to the critical concentrations in contact with stressed steel that the chance of trouble is negligibly small. Nevertheless failures have occurred through caustic cracking of bolts and flanges of blowdown lines and in other similar situations. Figure 3 shows caustic cracking in a bolt from a recirculating pump of a forced-circulation boiler after inadequate precautions had been taken against it. It is for reasons like these that many operators of welded boilers regard the taking of suitable precautions as essential.

Three water-treatment methods are widely recognized as giving at least some protection. The oldest established is the well-known sulphate method in which the weight ratio of sodium sulphate to caustic soda in the boiler water is kept above 2.5. The reason advanced for its claimed effectiveness is that the amount of sodium sulphate represented by this ratio is such as to block leakage paths by its being precipitated as the caustic solution strength increases. Partly because of the frailness of the scientific basis of the method and partly because of evidence adduced on alleged failures of the procedure to prevent cracking, the method has tended to lose ground in favour of two others. In the first of these,
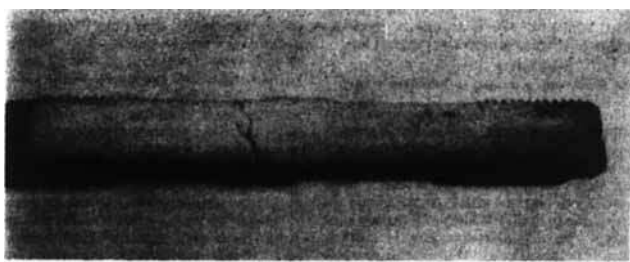
Figure 3. Caustic cracking of flange bolt from circulating pump of boiler.

the nitrate method, the ratio of sodium nitrate to alkalinity (expressed as caustic soda) in the boiler water is kept above 0.4. It is seen at once that less of the "inhibitor" is needed here than in the case of sulphate, but sulphate often gets into boilers incidentally and deliberate additions, if required at all, may not need to be large; sulphate is a common constituent of raw water. The mechanism has not been studied, but is possibly related to the oxidation and thereby removal of hydrogen generated in the attack of steel by strong caustic soda, for caustic cracking has many features in common with the hydrogen embrittlement of steel. The final method is the so-called "co-ordinated phosphate" method devised by Purcell and Whirl [6] in which the boiler water is kept alkaline by the presence of sodium phosphate, but free caustic soda is never permitted to be present. This is achieved by adding acid phosphates, or polyphosphates which, on hydrolysis in the boiler, give acid phosphates. For years the principle of the method appeared sound. For if such a boiler water is evaporated, solids like sodium chloride and trisodium phosphate will separate, but the mother liquor will never be more alkaline, however far the evaporation proceeds, than a saturated trisodium phosphate solution which the inventors pointed out is of lower pH value than the least strong caustic solution capable of giving cracking. Recent Russian work has shown, however, a slight defect in that, when a trisodium phosphate solution is evaporated, the solid formed is not a trisodium phosphate but one having less sodium per unit of P_2O_5. Correspondingly, the solution contains free caustic soda. Marcy and Halstead in America [7] have shown, however, that if the ratio of Na/P is 2.8 in a sodium phosphate solution, the solid separating on evaporation possesses exactly the same ratio and thus even though evaporation proceeds to dryness no free caustic will form. There is much to be said for maintaining a rather lower ratio, e.g. a mixture of about equal parts of the disodium and trisodium salts; this gives a margin of safety to guard against accidental ingress of caustic soda and the pH value is high enough to give negligible corrosion. The coordinated phosphate method is specially suitable where the feedwater is fairly pure.

CORROSION IN STEAM-CONDENSING AND CONDENSATE EQUIPMENT

The final feature of low-pressure boiler operation which deserves attention is the corrosion that occurs where steam is being condensed and in pipelines and equipment carrying condensate often for return to the boiler feed systems. Figures 4 and 5 show respectively perforation at a bend and heavy pitting. The reason for especially corrosive conditions occurring here is that usually such condensate is acid through the solution of carbon dioxide in it —which in turn comes from the raw water and treatment chemicals. Only a little CO_2 will greatly depress the pH-value. Oxygen is also commonly present, and this contributes to the attack. Not only is there mechanical damage to the materials of construction, but also (and this is of increasing importance at higher boiler pressures) the iron and copper in solution and suspension in a return condensate can give rise to heavy deposits in boiler systems. In power station boilers, particularly rapid corrosion can occur at hot spots in boiler tubes coated internally with iron deposits derived in this way.

The attack on the problem is manifold. The quantity of carbon dioxide in feed can sometimes

Figure 4. Pitting and perforation of condensate line.
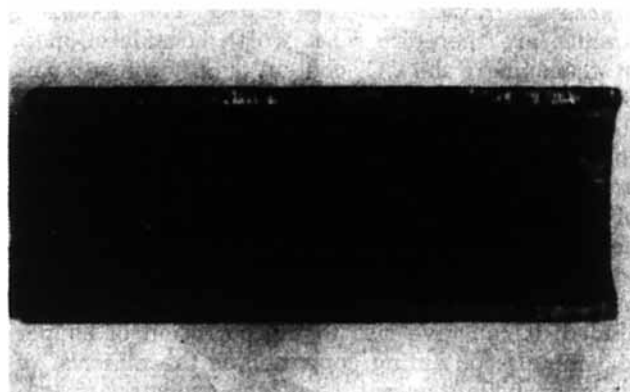

Figure 5. Pitting of condensate line carrying acid condensate.

be reduced, but it is not often possible to reduce it in proportions that make a significant contribution to the solution of the problem except by appropriate measures at the design stage. It is often fruitful to look for means of obviating the access of air and therefore of oxygen and also to ensure that condensate return is kept as hot as possible and splashes no more than necessary, to minimize absorption.

Two successful chemical attacks on the problem have found wide acceptance. In the first a volatile film-forming substance is injected either into the boiler or the steam flow so that it is distributed throughout the steam and condensate system. By far the most important material in use is octadecylamine, which, on solid surfaces, forms a tightly held film of molecules which point their water-repellent long-chain hydrocarbon portion towards the water. 1 to 2 p.p.m. of the amine in the steam suffices to maintain the film in good order and reduces corrosion markedly. A good deal of time might elapse after starting the treatment before the amine appears in the condensate throughout the system because it is tightly absorbed on any untreated surface to which it can gain access. A point of practical importance is that only small doses should be applied at first, for it loosens and detaches iron oxide from rusted areas and, if too much is released too quickly, blockage of lines and steam traps may result. Continuous dosing, rather than in slugs, is more desirable on account of its volatility characteristics. The most convenient form in which to apply the material is as a dispersion in water. There is some doubt on the thermal stability when the vapor is passed through superheaters in advanced steaming conditions.

The other method of combating corrosion in condensate systems is to add to the steam a volatile alkaline substance so that when the steam condenses it is alkaline rather than acid. Three materials have been used for this purpose, viz. ammonia, cyclohexylamine and morpholine. The object is to add such quantities that the pH value of the condensate is between about 8.5 and 9.0. The dose is thus clearly related to the amount of carbon dioxide in the steam—by contrast with the case of octadecylamine where the dose is not so related. The alkalizing amines are therefore most worth consideration in systems where the CO_2 content is only a few p.p.m. Ammonia has the merit of cheapness and being of low molecular weight, less of it is needed than of the other materials to raise the pH value. These merits are somewhat offset by the fact that, because of its high volatility, relatively large amounts are needed in the steam to provide an adequate concentration in the first-formed condensate. Furthermore, in systems where oxygen is not rigidly excluded, it can give rise to the corrosion of copper and metals containing copper. It is the material of choice in boilers operating at high pressures if oxygen is absent, but is not suitable for low-pressure

Figure 6. Apatite formed in experimental boiler in absence of any organic additive.

Figure 7. Apatite formed in experimental boiler with maleic anhydride interpolymer present.

boiler treatment. Both cyclohexylamine and morpholine give rise to less copper corrosion; and both are stable enough for use up to some 1500 p.s.i. The choice between them has been argued in many publications. In the first place the materials are about equally useful for alkalizing a cold water containing CO_2, but cyclohexylamine is slightly the more economical. On the important issue of which is the more capable of raising the pH value of the first-formed water in a condensing system, a physico-chemical study suggests that cyclohexylamine is again the choice. [5]

Figure 8. Apatite formed in experimental boiler with a polyacrylate present.

The toxicity of all the amines is low, but where the steam is to come into contact with food not more than 3 p.p.m. of the filming amine or 10 p.p.m. of the others must be present and if milk or milk products are involved the use is excluded.

WATER TREATMENT FOR BOILERS AT PRESSURES ABOVE 200 P.S.I.

For these boilers, phosphate treatment predominates to the exclusion of carbonate. Because, also, corrosion processes are faster, it is necessary to deaerate feedwater by physical means to bring the oxygen content to below 0.05 p.p.m. at 200 p.s.i. falling to 0.010 p.p.m. or less at 1,000 p.s.i. and a reducing agent is added continuously to remove these last traces. Sodium sulphite is suitable at pressures up to well over 1,000 p.s.i.; hydrazine is an alternative with the merit of not increasing the dissolved solids content of the boiler water. It is at least as important to maintain continuously some excess of sulphite or hydrazine in the water passing through the economizer to protect that item as it is to keep an excess in the boiler itself, and continuous addition to the feedwater is therefore a necessity. Most of the excess of hydrazine decomposes in the boiler into ammonia and in high-pressure boiler practice this is a merit, as already seen, for it helps make the condensate alkaline.

In boilers operating at over 400 p.s.i. an uncommon type of corrosion known as "on load" corrosion with massive magnetite formation gives rise to the conversion of steel into hard magnetite, which tightly fills the pits in the metal, and failure eventually ensues. Copper, oxygen and caustic soda have

all been blamed as the causative agent, but recent work at the C.E.R.L. has implicated chlorides.[8] This work appears to be a significant advance towards solving a difficult problem.

The hardness content of feedwater which can be tolerated at these higher pressures varies from between 10 and 50 p.p.m. (depending on the boiler type) at 250 p.s.i. to under 1 p.p.m. at 1,000 p.s.i. In all cases where hardness enters, however, the build-up of deposits is an inevitable feature of operation. A new treatment has recently been described [9] to help in these cases by considerably reducing the rate of build-up; it consists of a combination of phosphate with a synthetic polyelectrolyte. It was discovered in work with the experimental boiler referred to earlier, in which the effect of polyelectrolytes on this deposit accumulation was being studied. Polyelectrolytes are polymers or condensation products containing repeating acid or basic groups. Of all the materials tested, a group of starch-grafted hydrolyzed polyacrylonitriles gave the most useful effects. The best of them reduced the rate of scaling by 90 per cent. They proved effective over the range 200 to 800 p.s.i. when present at a dose of about 100 p.p.m. in the boiler water. The process is now widely used. A feature of considerable theoretical significance in this work was the great change which these substances brought about in the shapes of the particles of calcium phosphate formed. These are illustrated in Figures 6, 7 and 8. Evidence of this sort leads to the conclusion that the scaling is reduced because of the profound effect which these substances have on the crystallization processes.

WATER TREATMENT FOR VERY HIGH-PRESSURE BOILERS

The subject of water preparation and treatment for boilers operating at around 2,000 p.s.i. and above is too complicated and specialized to be dealt with more than superficially. The main features are that the feedwater must be extremely pure; hardness must be beyond detection by the EDTA titration method. The silica content must not exceed around 0.05 p.p.m. and some say less: the reason is that more than this would give rise to the fouling of turbine blades with silica brought over in solution in the high-pressure steam. The oxygen limit is below 0.01 p.p.m. and the total solids content well below 1 p.p.m. The pH-value of the feed is raised to 9, usually by ammonia addition. Boiler-water conditions are likewise stringent. Not uncommonly a little caustic soda and sodium phosphate are kept in the boiler water (around 10 p.p.m. of each) but there is an increasing tendency for operators to adopt the so-called "zero-solids" treatment in which the only chemicals deliberately added to the feedwater are hydrazine and ammonia.

CONCLUSION

It will have been seen that the water chemist has a variety of means of tackling scaling, corrosion and priming in boilers, whether they operate at low or high pressures. Many are the fruit of complicated and interesting research and investigation, and doubtless other palliatives for trouble will continually appear. It is important that the choice of the optimum method of boiler treatment be made with care and, in any new or modified installation at as early a stage as possible, so that the operational details can be integrated into the plant design and not left as an after-thought. This is a situation where the co-operation of engineer and chemist is essential; that co-operation can contribute much to the trouble-free operation of any boiler plant—upon which so much depends.

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SOUTH VIET NAM

McCOY'S NAVY

Among the stately carriers and dashing destroyers of the U. S. Seventh Fleet, there eixsts an ugly, unlikely division of four ships that is known as "McCoy's Navy." Its officers and men are recognizable from afar by their luxuriant beards and deep suntans, and the approach of their elderly craft can be detected by the clatter of chipping hammers pecking away at rusty decks. The ships themselves have high, unsheered bows and an ungainly 12-knot waddle, while the most advanced piece of electronic gear aboard any of them is a popcorn machine. Yet Inshore Fire Support Division 93, as McCoy's Navy is known officially, is one of the most valuable units in the South China Sea. It serves as the seagoing artillery of the South Vietnamese army.

Filling the Gun Gap. Created during last fall's "gun gap" to add desperately needed firepower to the ground war, McCoy's Navy consists of three World War II—vintage LSMRs (for Landing Ship Medium, Rocket) and the only inshore-fire-support ship in the world, the U.S.S. Carronade (aptly named for an 18th century cannon). Originally designed to pulverize beachheads for invading U. S. Marines, each ship mounts a battery of 5-in. rocket launchers and a single 5-in. naval rifle. Since the Marines had already landed when McCoy's Navy showed up last April, the beach smashers had to learn to become pinpoint artillerists. It was no easy task. The spin-stabilized 5-in. rocket is not nearly so accurate as a naval rifle shell. Moreover, no one knew if the squat, underpowered ships could safely negotiate Viet Nam's tortuous Mekong River Delta—a prime necessity if their rockets' five-mile strike range was to be applied effectively against inland Viet Cong installations. Slowly but steadily, the rocket men overcame the built-in limitations of their ships and in the process wrote a new manual on shore bombardment.

Only the Carronade was equipped with a fire-control computer, and it was soon beyond repair, owing to a lack of spare parts. Lieut. Commander Roy E. McCoy, 38, who runs the division from his Empire desk aboard the Carronade, quickly jury-rigged an alternative system, known as the "bow and arrow" method. Spotters ashore send target coordinates to the ships' Combat Information Centers, where men with aluminum ballistic slide rules (copied from a cardboard original found aboard one of the ships) swiftly tot up the deflection, angle-bearing and elevation of the rocket launchers. Then, just to make sure, one officer stands on the bridge to double-check the course of the rockets. Last week, as McCoy's Navy plastered everything from ammo dumps to Viet Cong villages in support of Saigon's Operation Franklin, accuracy on all targets ranged from 96% to 99%.

"Better You than Them." McCoy's first test came on the third night the Carronade was on the line. A U. S. Army adviser called in from an outpost that was being overrun by Viet Cong, desperately demanded fire support. McCoy explained that his 5-in. gun was out of commission and all he had was rockets. "Never mind," answered the adviser. "Better you than them." The Carronade cut loose, slamming rockets into the attackers, only 200 yds. from the friendly troops. That night confidence was born in the accuracy of naval rocket fire. "We got to the point," says McCoy, "where we became artillery. A love affair developed, and advisers in the outposts told us they couldn't sleep at night unless we were there. It would take six destroyers to replace us."

All told, McCoy's Navy has killed 665 Viet Cong, destroyed 4,367 buildings, sunk 297 gunrunning sampans, and fired 31,251 rockets. Most important, not a single South Vietnamese outpost within range of his rockets has been overrun during the three months his "little armada" has been in action. "The PT was the boat of World War II," he says. "Now we're it."

TIME, 5 Aug., 1966