

## THE FORMATION AND EFFECTS OF SCALE IN STEAM BOILERS

The formation of any appreciable quantities of scale in naval boilers is normally an event of some rarity, thanks to the general insistence upon the exclusive use of distilled water and to the close attention directed by the personnel to the maintenance of the purity of the feed. The mechanism of scale formation is, however, a subject of considerable interest to the naval engineer in connection with sea water evaporators, and it is, therefore, proposed to describe briefly some modern views on this subject and to mention the causes of such deposits.

**Boiler Scale. Mechanism of Formation.**—It is important in considering the possible mechanism of scale-formation to know whether the solubility in water of the various substances concerned, increases or decreases with rise of temperature. Materials which increase in solubility as the temperature is raised are said to have a "positive solubility slope" (this refers of course to the "slope" of the solubility-temperature curve), while the term "negative slope" is used to describe those whose solubility decreases with temperature rise.

The principal substances found in boiler scale are calcium sulphate, calcium carbonate, magnesium hydroxide, calcium and magnesium silicates; common salt (sodium chloride) is seldom, if ever, deposited in boilers. All of these, except sodium chloride, are believed to decrease in solubility as the temperature is raised; this has been shown to be true in the cases of calcium sulphate and magnesium hydroxide, and also as regards calcium carbonate, the solubility of which is, however, largely influenced by the concentration of  $\text{CO}_2$  in the solution. Sodium chloride, on the other hand, has a positive solubility slope.

There are numerous theories regarding the manner in which boiler scale may be deposited, but of these only three will be considered here, viz. :—

- (1) By actual settling out of suspended solids.
- (2) By crystallisation of salts from super-saturated fluid.
- (3) By the formation of bubbles on the heating surfaces.

The first of these is the most primitive conception of the mechanism of scale-forming, and assumes that the particles become accidentally attached to the plates, composing a nucleus upon which thick deposits are gradually built up. This idea is often advanced as an argument in favour of the use of so-called "anti-incrustators" (either solids or colloidal materials), and also is exploited by the exponents of electrical systems for scale prevention. The consider-

able research work carried out regarding boiler water reactions during the past decade has led to a more general acceptance of other theories, although it is of course evident that precipitation of solids and the subsequent formation of scale can and does occur under suitable circumstances such as in intermittently-operated boilers, worked at high densities, and in which the circulation is sluggish.

It was noted, however, by some of the earlier observers that deposition was heaviest on the most highly-heated parts of the boiler, and this observation, coupled with the discovery that calcium sulphate decreased in solubility with an increase in temperature, led to the suggestion that this substance might be deposited on the hotter parts of the boiler before the cooler body of the liquid became supersaturated. Tests in a small experimental boiler showed that while the deposits *on* the heating surfaces consisted mainly of salts with negative solubility slopes, the scale on the cooler parts was entirely composed of substances whose solubility increases with rise of temperature (*i.e.*, with positive solubility slopes). It was also found in other careful tests that of the total amount of calcium sulphate fed into the boiler, 89 per cent. deposited on the heating surfaces, 3 per cent. appeared as sludge, while the remainder passed away in solution in the blow down; the feed water was remarkably free from solid particles, which were at that time supposed to form scale by fortuitous attachment to the heating surfaces, a theory which these observations tended, therefore, to disprove.

The water in actual contact with the heating surfaces will be hotter than the main body of the water, and if therefore the main body of water is saturated with a substance having a negative solubility slope, the water in contact with the heating surface will be supersaturated and will precipitate. If the solubility slope be positive, the water adjacent to the heating surface will be undersaturated, and no salt will be deposited. In the former case the deposition of salt will continue as long as the rate of heat transfer is high enough to maintain these conditions. Growth, will of course cease when the layer of deposit is so thick that the temperature of the water near the heating surface falls to a value corresponding roughly to the saturation point at the prevailing density.

The foregoing provides one explanation of how supersaturated solutions can be formed in proximity to highly-heated surfaces, but it is evident that this can hardly be applicable to water tube boilers fed with water which is nowhere near saturation point, unless, indeed, the temperature gradient at the heating surface vastly exceeds anything that has hitherto been supposed. The theory however, satisfactorily explains many of the facts observed in connection with the scaling of evaporator coils (*see* Paper No. 10, p. 97, and also p. 19 of issue No. 12). The actual process of evaporation in a boiler must of course take place almost entirely at the hottest surfaces, the cooler portions of the tubes, etc., serving merely

to warm the water ; it has, in fact, been determined by actual observation that steam bubbles are formed on the hot metal, from which they are detached when conditions permit. There is no doubt that the mere physical process of evaporation of the water must result in local concentrations of any salts in solution, and supersaturation is likely to be induced by these means, especially if favoured by the solubility slopes of the dissolved salts. A similar state of affairs may well arise even when the solubility slope is positive, since if the rate of evaporation is high enough, local concentration may be sufficiently rapid to override the increased solubility due to rising temperature.

Some illuminating experiments were recently undertaken in America, an experimental evaporative surface in contact with a saturated solution of calcium sulphate being so arranged that it could be kept under observation and photographs taken of the progress of scaling. It was seen that a small ring of crystals was formed beneath each bubble of steam or of dissolved gas during its period of formation and attachment to the surface. Each ring was evidently deposited at the line of juncture between the heated surface, the gaseous bubble and the surrounding fluid, and this observed fact is capable of rational explanation. The resistance to heat flow is greater across the bubble than through the adjoining liquid, thus giving rise to local overheating of the plate and to a consequent increase in evaporation at the junction of the bubble and the plate. The fluid in the liquid film would probably be already supersaturated (since the main body of the liquid was fully saturated) and the effect of the local overheating would be expected to cause deposition of the excess dissolved material. Subsequent growth of such crystalline rings appears to proceed by bubble formation, in a similar manner, till eventually all traces of the ring nuclei are covered up. It appears quite probable that rings of deposit may also be formed from crystals of substances with positive solubility slopes, provided that the rate of bubble evolution exceeds that of resolution of the material.

It should be noted that the above experiments were carried out with initially saturated solutions, and that although similar rings of deposit were formed when dilute solutions were used, the rings re-dissolved within a few seconds of the evolution of the bubble. Evidently then with normally pure feed the rate of bubble formation would have to be very rapid if deposits are to be built up in this manner.

There is experimental evidence to show that the determining factor (other than temperature) as regards rate of scale growth is not the solubility itself but rather the *rate of change* of solubility with that of temperature (*i.e.*, the solubility slope). This is in agreement with the theory of scale formation just advanced, and is of importance as regards the operation of very high pressure boilers. It has been suggested on the one hand that owing to decreased

solubility with rise of temperature there is likely to be a tendency to excessive scale deposition in such boilers. On the other hand however, since the solubility slope of calcium sulphate actually decreases with rise of temperature it is not improbable, from the point of view just mentioned, that scaling may decrease as the boiler pressure is raised.

There is not a great deal of evidence available in this connection, but it is certain that a large number of super-pressure boilers now in use give no trouble on account of scaling. A few such boilers have, however, had tube failures associated with scale deposits but as in some of these cases the adoption of high pressures was accompanied by the use of higher rates of forcing, it appears more than likely that the unduly high heat transmission was at the root of the trouble. It should be noted in this connection that the solubilities of very few salts are known in the temperature ranges now common in boiler work, while the effect of pressure on solubility appears to have been but little explored.

The most troublesome impurities to be expected in marine boilers are salts which are derived from sea water which may have contaminated the feed supply.

The principal constituent of sea water, sodium chloride is comparatively harmless, due to its positive solubility slope.

The harmful constituents of sea water from a corrosion view point are the chloride and sulphate of magnesium. The former decomposes under the influence of heat and the chlorine reacts to form hydrochloric acid and attacks the boiler plates. The sulphate of magnesium is a potential source of chloride of magnesium which it can form by reaction with sodium chloride—it can also form the insoluble salt sulphate of lime by reaction with carbonate of lime, but is otherwise harmless.

Calcium sulphate, which has a negative solubility slope, is the most important scale-forming element.

Lime is deliberately added to feed water for the purpose of maintaining "alkalinity" and this substance in practice forms a large percentage of such solids as are present in the feed. The lime is actually added in the form of calcium hydrate, formed by mixing quick-lime ( $\text{CaO}$ ) with water. The solubility of the hydrate varies very widely indeed with temperature, being 115.5 grams/gallon at 60° F., 52.3 at 212° F., and about 7 grams/gallon at the temperature corresponding to saturated steam at 200 lbs./sq. in. pressure. Thus any additions of lime made after the concentration has reached 7 grams/gallon must come out as solid matter.

Lime is, therefore, usually the principal constituent of such small quantities of scale as are sometimes found in naval water tube boilers—this type of scale is fortunately brittle and easily removed.

Minor impurities may be found in boiler feed water, such as traces of iron and aluminium salts, silicates, mineral and organic acids, grease, carbon dioxide and air; these are usually derived

from lubricating oils and from the products of corrosion in the feed system. These impurities, even if present in considerable quantities, would not in themselves form scale upon the heating surfaces, although many of them are highly undesirable from the point of view of corrosion.

**The Practical Effects of Boiler Scale.**—The formation of scale on the heating surfaces of a boiler interposes a layer of insulation in the path of the heat flow from the hot gases to the water or steam. The more important practical effect of this additional resistance is that it leads to local overheating of the boiler metal on which scale has formed, and the temperature attained may eventually be high enough to cause the metal to “creep” or yield under the existing stresses; distortion and possibly failure will follow.

The insulating effect of porous scales is now believed to be greater than that of the hard slate-like type, although it is frequently held that the contrary should be the case since the pores may allow the water to obtain access to the metal itself. Actually, as the scale must be at a higher temperature than that of the boiler water it is probable that the interstices of the scale contain vapour; a cellular body with air or gas-filled cells forms the ideal type of heat insulator. Experience with sea water evaporators confirms this view, as the reduction in output caused by the crystalline, somewhat porous scales formed when working at densities in excess of 35° is appreciably greater than that due to the hard sulphate scales occurring at lower densities. It should be mentioned that porous scales may also entail trouble as regards corrosion, but cases of this are extremely rare and have never as far as is known been encountered in H.M. Navy.

It is evident of course from consideration of the *modus operandi* of heat transmission that the effects of scale will be somewhat different when heat is received solely by “radiation” to those experienced when “convection” is involved. The temperature of the wall of a boiler tube depends upon the rate at which heat is being transmitted and also upon the resistances opposed to the heat flow by the films of gas, steam or vapour and by the deposits on the inner and outer surfaces. The greater the resistances on the water (or steam) side of the wall, the higher must be the temperature of the tube in order that a given heat transference may occur; or, put in another way, the greater these resistances, the less will be the heat flow between gas and water for given temperatures.

Thus when heat is being transferred by convection, the formation of scale upon the water side of the heating surface causes a rise in the temperature of the metal with a subsequent reduction in the rate of heat transmission.

The quantity of heat radiated to a boiler tube from a furnace is largely independent of the rate with which that heat is removed from the receiving body, until the receiving surface attains a

temperature comparable with that of the radiator. The effect of scale upon the water side of a surface receiving heat by radiation is thus to cause a rapid rise in the temperature of the metal because the reception of heat continues at a sensibly undiminished rate while its transference to the water is obstructed.

Tube failures due to scaling are generally confined to those tubes which actually "see" the furnace, as both scaling and heat transmission occur at high rates in such parts of the boiler. It has been estimated, as a result of experimental work on the conductivities of boiler scales, that deposits of non-porous scales only  $\frac{1}{10}$  in. thick will cause failure of fire row tubes, while very porous scales of less than one-tenth this thickness may produce the same effect.

In view of the above figures, the rarity of tube failures attributable to scale in Naval practice is a high tribute to the success attained on service in excluding salt and oil from the boilers.

It is perhaps desirable to remark that as the rate of forcing is reduced, the rate of heat transmission to the fire row tubes is not reduced to the same extent, so that in the unfortunate event of scale being formed on the tubes only a low forcing rate is permissible if tube failures are to be avoided.

The very small quantity of scale which could possibly be accumulated without overheating of the fire row tubes will have practically no effect on the efficiency of the boiler, as the heat which is prevented from passing into these tubes for the most part will pass into succeeding rows, where the heat transference is improved by the consequent higher gas temperatures.