THE MECHANISM OF SCALE FORMATION IN THE BOILING OF NONSATURATED AND SATURATED AQUEOUS SOLUTIONS

E. I. Nevstrueva and I. M. Romanovskii

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Various concepts on the mechanism of calcium-sulfate scale formation are considered. An especially formulated experimental investigation is used to demonstrate that the mechanism of scale formation on the boiling of saturated and nonsaturated solutions differs substantially.

Natural salt-containing and brackish water is used in the cooling of various heat-exchange facilities. In this connection it would be interesting to investigate the mechanism of scale formation and the kinetics of the precipitation of the salts from various solutions, thus making it possible to develop methods to prevent or limit the deposition of salts on the heat-transfer [heating] surfaces. An analysis of the quantitative relationships governing the deposition of salts in the boiling of solutions, in addition, makes it possible to draw certain conclusions regarding the processes of mass- and heat-transfer at the heating surfaces.

Various concepts prevail on the mechanism of scale formation in the boiling of solutions, with the boiling of saturated solutions considered in the majority of cases. Many researchers hold that the scale is formed at the triple interface in the form of rings about vapor generation sites as a result of the vaporization of the solution at the base of the bubble [1, 2]. Here it is assumed that the rings about the vapor generation sites, once formed, serve as subsequent crystallization sites, and fill in with the passage of time from the periphery to the center.

Other researchers maintain that the scale circles at the vapor generation sites are formed as a result of the evaporation of the solution microlayer which always exists beneath the bubble and is vaporized in the process of its growth [3]. To demonstrate the validity of their hypothesis, the authors of [3] investigated the deposition of salt from saturated solutions of gypsum containing radioactive sulfur-35. To determine the number of bubbles emanating from a single vapor generation site, high-speed motion-picture photography was employed. The duration of the boiling process at the surface was selected so that the number of bubbles formed at a single vapor generation site would not exceed 7000. The experiments were carried out at very low heat loads, i.e., in the region in which individual isolated bubbles of steam, not interacting with each other, existed at the surface.

During the growth of the vapor bubble on the heat-transfer surface, in the opinion of the authors of [3], the microlayer of the liquid beneath the bubble is evaporated and an extremely thin layer of salt is deposited. As the number of bubbles increases, the thickness of this layer gradually increases. As a result of the fact that the experiments were carried out with saturated solutions, the authors assume that, once having been formed, the scale spots will not again dissolve. Knowing the total amount of salt deposited at a single vapor generation site (determined by the radioactive method), and knowing the number of bubbles, it was possible to evaluate the thickness of the fluid microlayer beneath the bubble, which turned out to be equal to 8000 Å (0.8 μm). It was noted that the diameters of the salt circles coincide approximately with those of the bubbles, while the thickness is virtually constant.

On the basis of such investigations the authors of [3] came to the conclusion that the model of the salt-deposition process proposed earlier [1 and 2] cannot explain the precipitation of a scale layer of uniform thickness. They contend that if the salt deposition resulted from the evaporation of the solution at the triple interface, the scale spot would be in the shape of a crater, with the thickening along the generatrix of the bubbles that were the first to tear away.

Another mechanism is proposed in [4] for the deposition of salts, this based on an analysis of the balance of the forces acting on the ions within the volume of the solution and at the triple interface. An interesting experiment is described in [4] on the boiling of sea water flowing in an annular channel, in concentrators formed of two tubes, one of which (the inner) is heated. It was found as a result of the experiment that in the boiling of the solution the deposition of the salts occurs either at the heated tube (when the width of the slit clearance is greater than the diameter of the bubbles being formed) or on both of the tubes (when the width of the clearance is smaller than the diameter of the resulting bubbles), even though the outside tube is entirely unheated. On the basis of the fact that in the latter case the depositions are entirely identical both at the heated and the unheated surfaces, the author draws the conclusion that an increase in concentration as a result of evaporation is impossible at the vapor-water boundary and, consequently, salt deposition does not come about as a result of evaporation. As a matter of fact, however, the results of the original experiment in no way contradict the possibility of the formation of a solution of elevated concentration at the interface.

To ascertain the possibility of the formation of supersaturated solution at the interface of a layer as a result of the differences in the rates of separation-boundary displacements (during bubble growth) and the diffusion of ions, a special experimental investigation was undertaken. A cylinder filled with an unsaturated solution of calcium sulfate was cooled with ice from below. A flat glass spiral containing a nichrome heater was mounted in the upper portion of the cylinder. Nichrome-constantan thermocouples and sampling devices were positioned at three points along the height of the cylinder to measure the corresponding distributions of temperatures and concentrations.

It was found that, in the absence of boiling, the salt concentration in the upper layer becomes substantially higher than within the depth of the liquid; this as a result of the evaporation of the liquid in the cylinder from the surface. This probably indicates that the rate of ion diffusion for the salts in the solution is substantially lower than the rate of liquid evaporation from the evaporation surface. The special tests carried out in the absence of an open evaporation surface demonstrated that in this case the increase in concentration in the upper layers of the liquid is not found. This makes it possible to assume that the distribution of concentrations (in the absence of any convection currents) is independent of the temperature field.

On the basis of the investigations that have been carried out demonstrating that the rate of evaporation is substantially greater than the rate of ion diffusion in the salt, we can probably maintain that the formation of a supersaturated solution at the interface is possible during the process of vapor-bubble formation and growth. It should be noted, however, that an increase in the concentration of salt at the interface wih the growth of the bubble may result not only from evaporation, but also from the greater inertia of the hydrated calcium and sulfate ions, in comparison with the dipoles of the water. To ascertain which of these factors is decisive in the process of elevating the salt concentration at the interface, a special experiment was set up to bubble air saturated with water vapor through the saturated solution, the air being driven through a porous surface. Simulating the process of boiling on an unheated porous surface, no evaporation at the interface was found, while the elevated inertia of the hydrated ions remained. The absence of salt deposition on the porous surface permits us to maintain that it is the rate of evaporation rather than the rate of ion diffusion for the salts that is decisive in the process of increasing the salt concentration at the interface.

Thus, on the basis of the indirect experimental investigations that have been carried out, we can state that the concentration of the salt ions may be considerably greater at the interface during the process of vapor-bubble growth than within the liquid volume. As a result of the fact that the greatest evaporation intensity is always found at the root of the bubble, the greatest supersaturation of the solution must also take place at the bubble root, i.e., at the heating surface. Moreover, it should be noted that a triple interface is formed at the heating surface during the boiling process, which facilitates the generation of crystals, and furthermore, that solutions of salts exhibiting a negative coefficient of solubility (as, for example, calcium sulfate), which are not saturated within the volume, may turn out to be supersaturated near the wall in the case of elevated temperatures. Thus both the triple interface and the reduced solubility at the wall layer (only in the case of negative solubility coefficients), and the substantial evaporation at the bubble root, enhance the periodic formation of zones of elevated concentrations near the vapor generation sites, which leads to the precipitation of a scale ring.

In the period following the separation of the preceding bubble, prior to the generation of the following bubble at the same vapor generation site, the ring is flushed by an unsaturated solution flowing from the flow core or from the adjacent sections of the wall layer, and the ring may dissolve. Consequently, during the process of the formation, growth, and separation of a large number of vapor bubbles, a dynamic scale grid may constantly be present on the heating surface.

It was demonstrated in [7] on the basis of experimental data that the waiting period (the time from the instant of separation to the instant of generation for the following bubble) is substantially greater than the period of bubble growth (the time from the instant of generation to separation), with this difference increasing as the heat load is enlarged. Therefore, even if the rate of solution is somewhat greater than the rate of salt deposition (crystallization), total dissolution of the ring is possible during the waiting period, in which the center is flushed by the unsaturated solution.

A special experiment was set up to provide an experimental verification of the possibility that a dynamic scale grid exists on the heat-transfer vapor-generating surface by investigating the kinetics of calcium-sulfate deposition from unsaturated solutions. The test was carried out with boiling in a large volume on horizontal surfaces facing upward under atmospheric pressure with jumpwise artificial variations in the concentrations, without reducing the intensity of the boiling process. The experimental results are presented in Fig. 1. The upper curve shows the rise in the temperature of the heat-transfer surface in the time from the instant of the artificial pronounced increase in the calcium-sulfate concentration from a volume of 0.8 to 1.34 g/l. The graph shows that during the first 35 min the temperature of the heat-transfer surface rose by 18° C and stabilized at that level. The lower curve shows the drop in the temperature of the heating surface with time after a pronounced discontinuous drop in the concentration within the volume, this instant coinciding on the graph with the initial point of stabilization for the surface temperature.

An analysis of the curves shown in Fig. 1 shows that the kinetics of the salt-deposition processes at the surface and of the solution of the salt on transition from one level of surface-temperature stabilization to another is identical. This makes it possible to assume that in the concentration region below the one for the beginning of unlimited growth in salt deposition there exists some dynamic equilibrium between the solution and the surface (perhaps a dynamic scale grid) in which the rates of calcium-sulfate deposition are equal to the rates of its solution. Here the scale stay-time at the surface is probably commensurate with the period of the bubble cycle.

The existence of a dynamic grid of rings is most likely one of the factors responsible for a certain in-

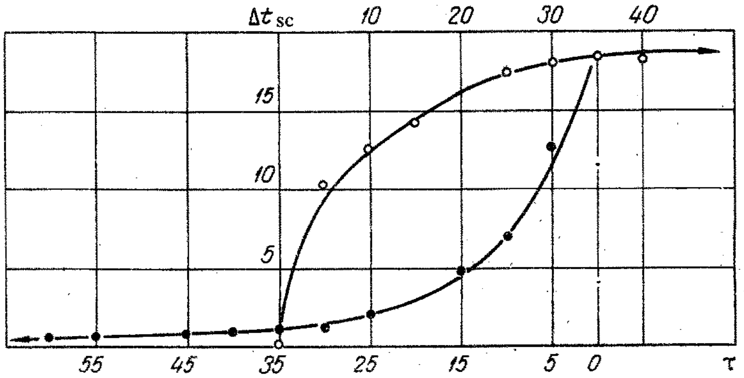

Fig. 1. Kinetics of deposition and dissolution of calcium sulfate on a heating surface at a heat load of 1 MW/m^2 in the region of the dynamic scale grid (Δt_{sc}, °C; τ, min).

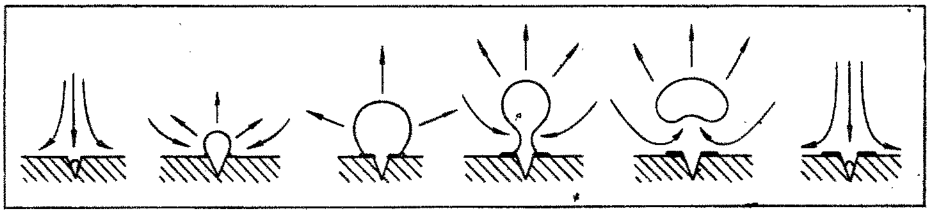

Fig. 2. Operation cycle of vapor generation site.

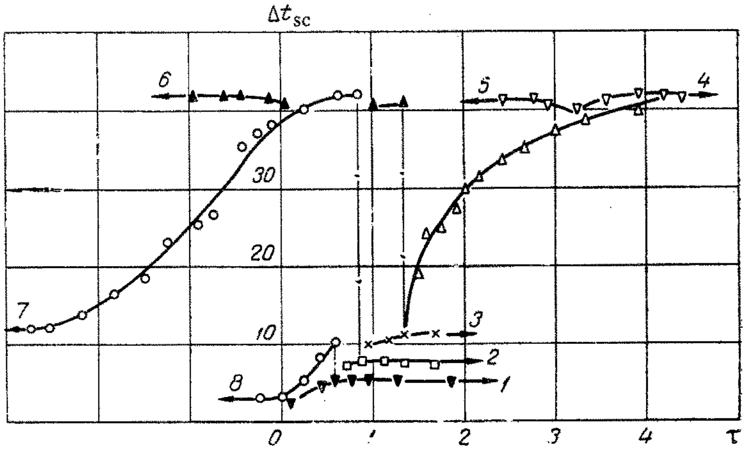

Fig. 3. Kinetics of deposition and dissolution of calcium sulfate on a heating surface at a heat load of 1 MW/m^2 in the region of unlimited scale growth (Δt_{sc}, °C; τ, hr); 1) calcium sulfate concentration 0.97 g/liter; 2) 1.2; 3) 1.3; 4) 1.47; 5) 1.30; 6) 1.18; 7) 1.0; 8) 0.78.

crease in the temperature of the heat-transfer surface during the boiling of unsaturated solutions with concentrations below the one needed for the onset of unlimited growth in salt deposition [5, 6]. It should be noted that in a number of cases some increase in the surface temperature presents no danger whatever for the reliable operation of the heat-exchange equipment, although it leads to a slight drop in the coefficient of heat transfer from the wall to the boiling liquid or in the heat load (depending on the heating method).

On the basis of an analysis of the described experimental and literature data it is possible to assume that the deposition of salts on the heat-transfer surface proceeds in the following manner. Let us examine the operational cycle for several adjacent vapor generation sites (Fig. 2). A vapor bubble is generated at one of the sites at some instant of time. We know that the rate of growth for the generated bubble is very great at the initial instant of time (on the order of 20 m/sec), rapidly dropping to some given level, and then remaining approximately constant throughout the process of bubble growth [7]. During the bubble growth, because of evaporation into a bubble, as well as because of the great inertia of the hydrated calcium and sulfate ions relative to the water dipoles, there is an increase in the salt concentration at the interface. In the boiling of saturated solutions this increase in concentration leads immediately to supersaturation and crystallization begins at the triple interface, since the heating surface exhibits the most favorable conditions for the generation of crystals (particularly with a negative salt-solution coefficient). Since the rate of bubble growth is virtually constant [7], the region of supersaturation for the solution also shifts from the center to the periphery at a constant rate, which must probably lead to the formation of a layer of crystals exhibiting a constant thickness, as was ascertained in [3]. During the waiting period the vapor generation site (as was demonstrated above, this is also the crystal generation site) is flushed by a saturated solution and the spot that has been formed is therefore not dissolved.

In the boiling of unsaturated solutions the formation of a supersaturated solution may not be achieved at the very beginning of bubble growth. The time lag is determined from the rate of bubble growth (the velocity of motion for the triple interface) and the salt content of the solution. The smaller the degree of saturation for the solution, the later supersaturation is achieved and, consequently, the greater the time lag. In this case the scale is formed in the form of a ring about the vapor generation site, and the smaller the degree of saturation for the solution (the saturation resulting from the scale generator), the smaller the width of this ring.

At some specific concentration which is probably comparably small (and which may be referred to as the concentration for the onset of deposition) the time lag is equal to or greater than the period of bubble growth. In this case there is no scale generation.

It may therefore be assumed that over a wide range of concentrations above the concentration for the onset of salt deposition and below the concentration for the onset of unlimited growth in salt deposition on the heating surface there exists a so-called stabilized scale. Indeed, as demonstrated by the experiments carried out earlier in the boiling of unsaturated solutions [5, 6, 8], some limited quantity of salt is deposited on the heating surface and this is subsequently stabilized. This quantity of salt is the greater, the higher the salt content of the solution and the greater the heat load, under identical conditions.

On the basis of the above-described additional and especially designed tests and from an analysis of the resulting experimental data, as well as from the results of other investigations, we can assume that the process of stabilized scale formation proceeds in the following manner.

With a gradual shift in the triple interface during the period of bubble growth on the heat-transfer vapor-generating surface, at the root of the bubble, as a result of evaporation, crystallization of the calcium sulfate takes place. Here, depending on the degree of saturation for the solution, rings or scale circles with various widths are formed. After separation of the bubble during the waiting period the ring or scale circle is flushed by the unsaturated solution flowing to the wall layer from the core flow and from the segments adjacent to the wall layer, thus causing the salt to dissolve. The duration of the growth period and of the waiting period for the bubble at high thermal loads involves thousandths of a fraction of a second. During these brief stay-times for the salt on the heat-transfer surface no significant structural changes in the scale are possible, since the conversion of the hydrated modifications of calcium sulfate to other modifications alone proceeds comparatively slowly. The solubility of the calcium sulfate deposited on the surface cannot therefore change significantly [9].

This process with a shift in time is repeated for all active vapor-generation sites, with a dynamic scale grid formed at the surface. With an increase in the heat load or in the concentration of the salt within the volume, the zones of elevated concentrations at adjacent sites gradually converge. When these zones come into contact, along the entire wall layer a limit of solubility is attained and the dynamic equilibrium between the processes of precipitation and solution shifts in the direction of crystallization, since during the waiting period the vapor generation site is flushed either by a saturated or a supersaturated solution. The rings quickly fill in from the periphery to the center in this case and gradually touch each other. The resulting solid layer of scale continuously thickens, and this is accompanied by a continuous rise in the temperature of the heat-transfer surface. The scale at the wall is constantly at a temperature somewhat higher than the saturation temperature, so that the salt temperature is the higher, the closer the salt is situated to the heating surface. Dehydration of the calcium sulfate is quite possible in this case, as is a reduction in the solubility of the scale.

To check out these statements, we set up a special experiment on the kinetics of the deposition of calcium sulfate from the solution and on the kinetics of the solution of the scale deposited earlier on the surface. The experiment was carried out on the same installation as the experiment whose results are given in Fig. 1, the only difference being that the latter experiment was carried out with artificial changes in the concentration from values below the concentrations for the onset of unlimited growth in salt deposition to concentrations clearly exceeding this quantity. The results of the experiment carried out at a constant heat load equal to 1 MW/m^2, and with a constant volume for the boiling calcium-sulfate solution, are presented in Fig. 3. The concentration in the volume was varied discontinuously by replacing parts of the boiling solution by a boiling solution of a higher concentration (when going to a higher concentration) or with a boiling distillate (when going to a smaller concentration in the volume).

Analysis of the time functions presented in Fig. 3 shows that in the region of concentrations below the concentration for the onset of unlimited growth in salt deposition, i.e., in the region in which dynamic scale exists, the surface temperature is rather quickly (within 15–40 min) stabilized, and here, the greater the concentration in the volume, the higher the level of stabilization (curves 1, 2, 3). As soon as the concentration in the volume exceeds some magnitude referred to as the concentration of unlimited growth in salt deposition, an intense rise in the temperature of the surface begins, with the magnitude of Δt_{sc}—equal to the temperature difference for the wall between the boiling of the solution at the wall and the boiling of the distillate—increasing markedly, which is also a consequence of the rather rapid formation of a solid continuously growing layer of scale (curve 4).

A reduction in the concentration in the volume does not lead to the rapid solution of the scale (curves 5, 6, 7, 8) which now occurs over a period of several tens of hours. Thus, in the given region of concentrations exceeding the concentration for the onset of unlimited growth in salt deposition, the process of salt deposition at the surface predominates over the process of solution. In this region of concentration a stable constantly growing layer of scale is formed at the surface, resulting in the gradual continuous rise in the temperature of the wall for a constant heat load. The prolonged stay-time of the scale at the surface, particularly in the deeper layers, with a sufficiently high temperature level, may probably be accompanied by the dehydration of the solid phase, which also leads to a pronounced drop in solubility. At lower temperatures the dehydration may proceed more slowly or there may be none at all.

The statement that saturation is achieved at the concentration for the onset of unlimited growth in salt deposition at the surface as a result of the evaporation of the wall layer was used to determine the number of times during which the liquid circulated through the boiling layer at the wall.

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High-Temperature Institute
AS USSR, Moscow