MECHANISM OF HEATING-SURFACE SCALING DURING FORCED FLOW OF PURE CALCIUM SULFATE SOLUTIONS

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This article presents experimentally determined results of the calcium sulfate crystallization mechanism on heating surfaces. The proposed method can be used for studying the solubility of scale-forming compounds in any salt system.

There have been a number of studies of calcium sulfate crystallization on heating surfaces under varying conditions in the last few years [1-12]. However, the crystallization mechanism of calcium sulfate on heating surfaces has not been thoroughly studied and there is no clear definition of the temperature range of the crystallization process [1-6], the hydrated forms of calcium sulfate crystallizing on the heating surface [1-3, 7-10], and the processes taking place within the scale [3, 9-11].

The aims of this study were to: 1) establish the temperature at which crystallization/solution of calcium sulfate scale occurs on a heating surface under convective heat transfer conditions, 2) determine the type of calcium sulfate hydrate crystallizing on the heating surface, and 3) study the kinetics of precipitation/solution and the processes taking place in sulfate scales.

The studies were carried out with forced flow of pure calcium sulfate solutions in an electrically heated horizontal smooth steel tube, 5.8/6.4 mm diameter × 260 mm long. Chromel—Alumel thermocouples were welded to the outer surface of the tube at five points along the length for wall temperature measurement. Maximum wall temperature was always at the tube outlet under convective heat transfer conditions where scaling always began. All experimental data given in this article were, therefore, taken from the readings of the fifth thermocouple which was located 252 mm from the inlet of the heated section. Water temperature at the inlet and outlet of the test section was measured by Chromel–Alumel thermocouples. An axial pump was used for closed loop circulation. All experiments were carried out under convective heat transfer with the following conditions: 1) 120-250°C heating surface temperature, 2) 0.4 - 0.7 MW/m^2 heat flux, 3) 1780 $kg/m^2 \cdot sec$ mass velocity, 4) 1-50 atm pressure, and 5) 20 - 200°C outlet water temperature. Pressure was selected so that saturation temperature always exceeded heating surface temperature. Chemically pure calcium sulfate dihydrate was always used to prepare the aqueous solutions, since all hydrated types of calcium sulfate are converted to gypsum at temperatures up to 100°C in water [12].

The experiments were carried out systematically (program developed in the laboratory): all parameters except solution temperature at the experimental tube outlet were fixed, and the experiment was carried out in stages.

1. Solution inlet temperature was gradually increased (Fig. 1, curve ABC). Corresponding tube-wall temperature increases were observed. Calcium sulfate has a negative temperature solubility coefficient over the investigated range. The relative concentration (C/C_{sat}) at the tube wall increases at higher temperature and constant concentration. Spontaneous scale deposition (BC) begins at some value of C/C_{sat} considerably greater than unity. This is registered by the rapid tube wall temperature increase at the outlet sector of the experimental tube.

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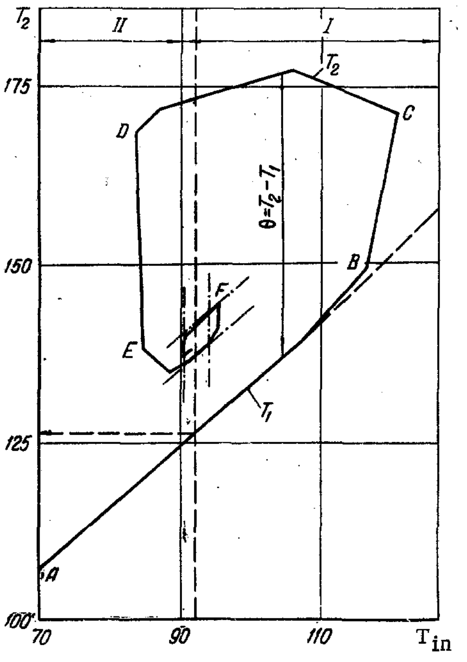

Fig. 1

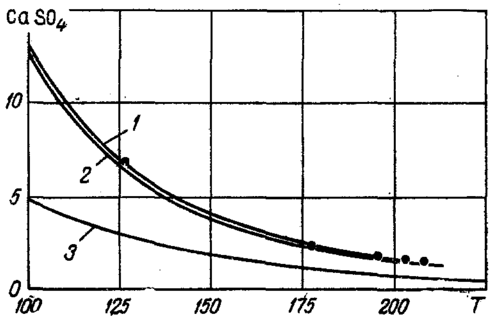

Fig. 2

Fig. 1. Change of steel tube inner surface temperature T_2 during scaling and solution of calcium sulfate as a function of solution inlet temperature. Conditions: 0.4 MW/m^2 heat flux, 1780 $kg/m^2 \cdot sec$ mass flow-rate, and 0.0071 molal solution. T_2 and T_{in} are in °C.

Fig. 2. Calcium sulfate concentration at equilibrium between solution and scaling as a function of heating surface temperature (1). Solubility curves of calcium surface hemihydrate (2) and anhydrite (3) according to [13]. T in °C, $CaSO_4$ in $(g\text{-mole/kg}) \cdot 10^3$.

2. Solution temperature was reduced during the second phases (CD). This reduces the temperature of the scale (heat transfer) surface thereby decreasing relative concentration. The difference between wall temperature T_2 and clean surface temperature T_1 (AB) increases as long as relative concentration is greater than unity. Difference ($T_2 - T_1$) decreases when relative concentration is less than unity, indicating scale being dissolved (DE).

3. Inlet solution temperature is again increased until temperature difference in the scale starts to rise (EF).

This operation is repeated until the spread between inlet solution temperatures for scaling and dissolving calcium sulfate is reduced to 1 - 2°C. Wall temperature on the clean regime curve (AB), corresponding to the midpoint of this interval, is taken as the heating surface temperature for equilibrium between scaling and dissolving.

Results of one experiment are shown in Fig. 1. Equilibrium was reached at 92°C solution inlet temperature and 126°C heating surface temperature (T_1). This curve shows that scale is dissolved at 125°C and scale formation occurs at 127°C. The ordinate through 92°C solution temperature, therefore, divides the range covered by Fig. 1 into two sections. The solution with 0.0071 g-mole/kg H_2O is supersaturated with respect to the hemihydrate in section I at $T_2 > 126$°C. It is not saturated in sector II but is still supersaturated with respect to the anhydrite solubility curve. Since scale is completely or partially dissolved in this area, it can be stated that the hemihydrate, rather than anhydrite, crystallizes in this temperature range.

Similar tests were carried out with 0.0071, 0.0022, 0.0015, 0.0013, and 0.0011 molal solutions. Equilibrium temperatures of the scale heating surface were 126°, 178°, 196°, 203°, and 208°C. Figure 2 compares the experimentally derived solution concentration, at which equilibrium between the scale surface and solution is established (as a function of heating surface temperature), to calcium sulfate crystal hydrate solubility polytherms [13]. This

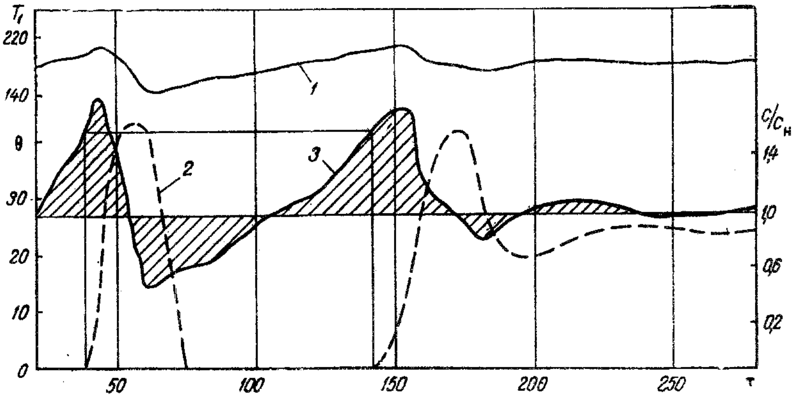

Fig. 3. Time change of heating surface temperature (1), scale temperature drop (2), and relative hemihydrate concentration (3) in an experiment with 0.6 MW/m^2 heat flux and 0.0022 solution molality, T_1 and θ are in °C, and τ is in minutes.

comparison shows that the function derived agrees with the hemihydrate polytherms within the accuracy of chemical analysis (2×10^{-4} g-moles/kg H_2O). It can, therefore, be accepted that calcium sulfate scale deposition, in the investigated range of temperatures with convective heat transfer, is limited by the hemihydrate solubility curve at a key temperature equal to the heating surface temperature.

An experiment conducted for 13 h at 152 - 153°C wall temperature with 0.7 hemihydrate relative saturation and 1.8 anhydrite relative saturation is further proof that anhydrite does not crystallize on the surface. Relative saturation of the solution with respect to anhydrite was almost 2 at the heating surface temperature but no scaling was observed.

Figure 3 shows the time variation of scale heating surface temperature T_1, temperature difference ($T_2 - T_1$) across the scale layer, and relative concentration. This experiment was conducted with 0.6 MW/m^2 heat flux and 0.0022 solution molality. Equilibrium wall temperature was 178°C. Figure 3 shows that spontaneous scale growth on the clean tube surface started at 1.84 relative solution concentration. The scale was completely dissolved when the relative concentration was reduced to less than unity. The solution remained supersaturated with respect to the anhydrite polytherm. The scale remained on the heating surface for about 30 min. This period, evidently, is not long enough for adequate scale dehydration. Spontaneous scaling starts at the same supersaturation (as at the beginning of the experiment on a clean surface) when relative concentration is increased a second time after completely dissolving the hemihydrate surface layer down to the surface of the anhydrite formed in the scale core in other experiments or after all scale was completely dissolved in this experiment. Relative concentration (spontaneous calcium sulfate hemihydrate scaling begins), in the range investigated, are well represented by the equation

$$(C/C_{sat})_{sp} = 1.26 + 0.42\,(0.01T_1 - 1) \pm 0.15. \qquad (1)$$

Hemihydrate is dewatered to anhydrite when scale layers not in contact with the solution stay on the heat transfer surface for a longer period (about 3 h) and higher than 155-160°C scale temperature.

Figure 2 shows that the smallest deviation of concentration from unity (either up or down) resulted in increase (decrease) in the scale layer temperature drops if the hemihydrate layer is not completely dissolved during the experiment. Figure 4 shows the experimentally derived rate $d\theta/qd\tau$ of scale formation at relative concentrations greater than unity and calcium sulfate dissolving rate at relative concentrations less than unity as a function of relative concentrations in experiments with 126° and 178°C equilibrium wall temperatures. Figure 4 shows that the rate of scaling and dissolving of hemihydrate is high even at relatively low deviations of the solution—heating surface system from equilibrium. A substantial change in scale temperature differential is observed in 1-2 h. The functions

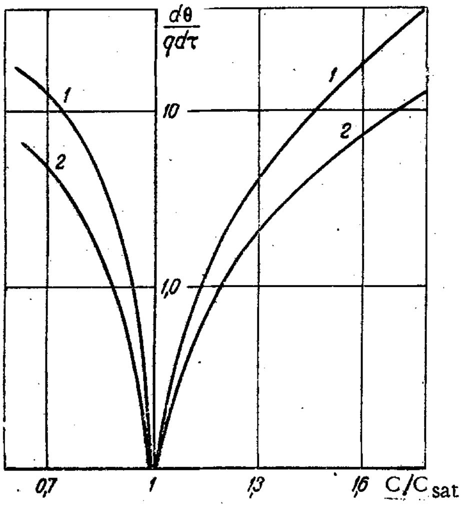

Fig. 4. Experimentally determined dependance of calcium sulfate hemihydrate scaling and solution rate vs relative concentration in tests with (1) 126° (2) 178°C equilibrium temperature. $d\theta/qd\tau$, in $°C \cdot m^2/MW \cdot min$.

for scaling and dissolving are practically symmetrical, indicating that the dissolving and scaling rates are practically equal for the same relative concentration deviation from unity.

Density and thermal conductivity data on calcium sulfate scale obtained earlier [14, 15] were used to determine the Nusselt diffusion number using the experimental data and equation:

$$\mathrm{Nu}_D = \frac{\rho\lambda d}{q\,(C - C_{sat})\,D} \cdot \frac{d\theta}{d\tau}. \tag{2}$$

The diffusion coefficient of calcium sulfate is expressed as

$$D = k_0 T_1/\mu, \tag{3}$$

where $k = 3.923.10^{-15}$ N/°K

Comparing experimentally determined Nu_D with calculated values based on the analogy between heat and mass transfer using the equation

$$\mathrm{Nu}_D = 0.021\mathrm{Re}^{0.8}\mathrm{Pr}_D^{0.43}$$

showed that they agree with an accuracy of ± 30% both for calcium sulfate crystallization on the heating surface and hemihydrate scale solution. The key temperature was assumed to be the heating-surface temperature.

It was noted above that spontaneous (no time lag) scale growth on an extraneous surface (even that of calcium sulfate hydrate) starts when supersaturation is high. Scaling starts after some induction period at lower relative concentrations. Longer periods are required at lower relative concentrations. Longer periods are required at lower supersaturations. The absence of an induction period during contact of solution with the heating hemihydrate surface leads to the assumption that two types of nuclei (crystallization centers and their initial-growth crystals) are formed during the induction period on the heating surface. A sharp temperature gradient exists at the heating surface and maximum supersaturation is observed at the wall. These facts indicate that nuclei are more likely to be formed at the wall rather than in bulk solution volume and the growth rate of centers formed along the surface is greater than that along the tube radius. The scale does not significantly increase tube wall temperature as long as it is monomolecular in thickness and does not form a continuous layer. A continuous monomolecular scale ring is formed at the tube outlet section after the induction period. New crystal layers are laid down on this ring. The length of the ring increases, at the same time, along the surface counter to direction of flow up to the point where relative concentration is unity at tube wall temperature. Increased scale thickness results in higher wall temperature detected by the thermocouples.

The nuclei formed are denser and their growth is faster at higher relative supersaturations, reducing the induction period. Crystallization-center formations and their growth are accompanied by spontaneous formation of new nuclei around them at supersaturations equal to and greater than spontaneous relative concentration. This results in practically instantaneous formation of the monomolecular ring and its subsequent expansion. The induction period is thus reduced to zero.

The induction period at lower than supersaturation concentrations can be of definite practical interest in setting up the water management of some cooling systems whose continuous operating period is measured in minutes and hours. Higher supersaturations can be tolerated with shorter continuous operating periods.

NOTATION

C, molality of calcium solution, g-mole/kg H_2O; C_{sat}, solubility at temperature of heating surface, g-mole/kg H_2O; C/C_{sat}, relative concentration; $(C/C_{sat})_{sp}$, relative concentration at which spontaneous growth of deposits starts; T_{in}, solution temperature at inlet; T_1, temperature of heating surface; T_2, interface temperature of scaling tube wall, °C; $\theta = T_2 - T_1$, temperature drop in scaling layer, °C; q, heat flux, MW/m^2; τ, time, min; ρ, scale density, kg/m^3; λ, thermal conductivity of scale, W/m·deg.

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