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Article *in* Journal of Heat Transfer · February 1999

DOI: 10.1115/1.2825951

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The Influence of Particulates on $CaCO_3$ Scale Formation

N. Andritsos[1] and A. J. Karabelas[1]

Introduction

In many industrial heat exchanger systems, as in cooling water circuits, particulate matter is almost always present in the process streams, even if side-stream filtration takes place. The presence of suspended particles may not only affect the rate of precipitation fouling (due to dissolved inorganic solids), but may also drastically modify the compactness and the rest of the physical properties of the deposit layer. A considerable part of the particulate matter is of colloidal dimensions, which can easily pass through a filter. These colloidal particles may be indigenous (through bulk precipitation and silica polymerization or from removal of deposits) or may enter the process streams with the make-up water. There is experimental evidence in the literature that the presence of particulates tends to increase the fouling resistance. Using river clay as suspended solids, at a concentration of 25 mg/L, Lee and Knudsen (1978) found a significant increase of the fouling resistance. Similarly, Watkinson (1983) reported that particulates contributed significantly to enhance deposition even at low concentrations; the presence of ~250 mg/L particulates (apparently resulting from bulk precipitation in the system) gave deposition rates almost two orders of magnitude greater than the rates calculated using the wall crystallization model of Hasson et al. (1978). Bramson et al. (1995) examined the effect of calcium sulfate particle addition on scaling of a heated metal surface covered by a falling film. Using a relatively high particle concentration (2.5 g/L) they obtained a considerable enhancement of $CaSO_4$ deposition rate. Additionally, they reported that coprecipitation of $CaCO_3$ led to more adherent and tenacious scales as compared to a pure $CaSO_4$ scale layer. Recently, Bansal et al. (1997) studying $CaSO_4$ crystallization fouling in a plate heat exchanger reported that the effect of particles on crystallization depended on their nature; the presence of $CaSO_4$ particles significantly increased the crystallization rate, while noncrystalline alumina particles reduced crystal growth rate. The latter is attributed to higher removal rates associated with the reduction of deposit strength.

Calcium carbonate is one of the dominant scale-forming species in heat exchangers and similar equipment, and its deposition has already been studied in this laboratory (Andritsos et al., 1996, 1997). The work reported here is based on an experimental investigation of the effect of well-defined commercial calcium carbonate particles and silica nanoparticles on the deposition rate and morphology of deposits, formed during the flow of a solution supersaturated with respect to $CaCO_3$. The term *combined* shall be used for such runs. The effect of the above particles on the spontaneous precipitation in a supersaturated calcium carbonate solution is also examined. Isothermal conditions are maintained in all the tests.

Experimental Work

The experimental set-up and the measurement procedure are described in Andritsos et al. (1996). The tap water used in the experiments contains approximately 80 mg/L Ca, 20 mg/L Mg, and 360 mg/L HCO_3^-. A complete analysis of the water is given in the aforementioned paper. A metering piston pump is used to feed the suspension from a stirred tank into the tubular test section. The pump was calibrated volumetrically. The progress of bulk precipitation with or without particles can be monitored through periodic sample withdrawal, either by light absorbance measurements (in a HITACHI 3000 spectrophotometer) or by recording the pH change (in runs with pH < 9.5).

A Ludox® (Dupont) suspension was used as the source of silica particles. The size of these colloidal silica particles was almost uniform with a mean diameter 21 nm, and under the experimental conditions used the particles bear a negative charge. Particle concentration in all the tests was 100 mg/L. The commercial $CaCO_3$ (Solvay 90A) particles were assayed by X-ray analysis (in a Siemens D500 diffractometer) and by chemical analysis (ICP 40, Perkin-Elmer). The XRD pattern exhibited peaks characteristic of both calcite and aragonite. The particles were pure $CaCO_3$ with less than 0.2 percent w/w magnesium. The morphology of the particles was examined by SEM (in a JEOL, JSM-840A unit); they appeared to be agglomerates consisting of small needle-like particles with dimensions approximately $1 \times 0.2\ \mu m^2$. The size distribution of suspended particles in tap and in demineralized water was determined by a 2600 Malvern particle sizer; the mean particle size was in the range 5–10 μm. The zeta-potential of these particles at pH 9.5 was −26 mV (Thonon et al., 1996).

Results and Discussion

(a) Effect of Calcium Carbonate Particles. All experiments were conducted in duplicate at 25°C, with a particle concentration 40(±5) mg/L. The flow velocity was varied between 0.43 and 1.5 m/s. Runs were carried out at two pH values, namely 8.8 and 10. In the absence of particles, there is nearly zero deposition rate at pH 8.8, while at pH 10 a considerable

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Contributed by the Heat Transfer Division for publication in the JOURNAL OF HEAT TRANSFER. Manuscript received by the Heat Transfer Division, Feb. 23, 1998; revision received, Aug. 12, 1998. Keywords: Experimental, Fouling, Heat Transfer, Scaling. Associate Technical Editor: P. Ayyaswamy.

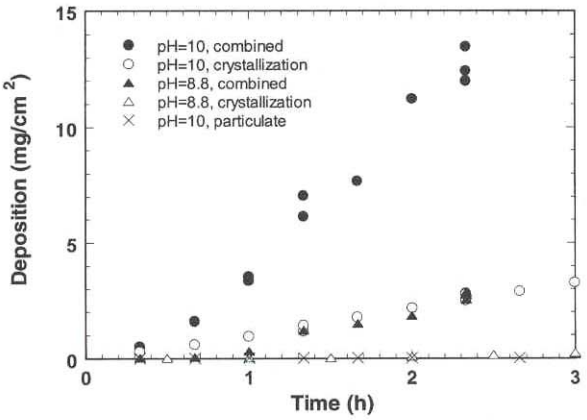

Fig. 1 Effect of particulates on deposit formation with tap water at pH 10 and 8.8 and with demineralized water at pH 10 (particle concentration ~40 mg/L)

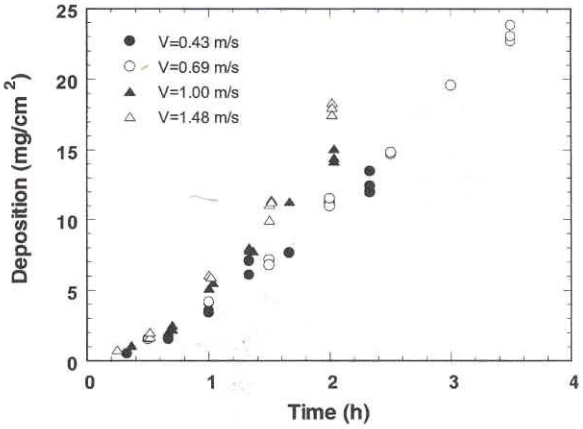

Fig. 3 Effect of flow velocity on the combined deposit formation (particle concentration ~40 mg/L, pH = 10)

mass of deposits is formed (Andritsos et al., 1996) and a marked effect of flow velocity is observed.

Figure 1 shows the temporal evolution of deposit mass per unit area at pH 10 and 8.8 for a flow velocity of 0.43 m/s. The mass of deposits formed under the same conditions depicted with no addition of particles (*crystallization* runs) is also, as well as the mass of deposits obtained with demineralized water at pH 10 with 40 mg/L of particulates (*particulate* runs). A six to eightfold increase of the deposition rate is observed at pH 10, while at the lower pH a substantial deposition rate is obtained in the presence of particles compared with the nearly zero deposition rate in the crystallization run. As expected, only a scanty mass of deposits was obtained in the particulate run; i.e., orders of magnitude smaller than that obtained in the combined runs. Very similar results were obtained in a run with particulates at the pH of tap water (7.4).

In all combined runs, after a short time from start, the scale has a rippled appearance (transverse to the flow direction) with ridges and valleys, as depicted in the pictures (Fig. 2). The thickness of the scale did not vary along the 0.6-m long horizontal test section. For runs at pH 10 rippled deposits first appear at the bottom of the pipe, while a layer of relatively hard deposits forms uniformly around the pipe circumference. With time the rippled deposits cover the entire pipe circumference, but in the lower part there is a greater mass. These rippled deposits can be physically removed with ease, when they are dry, uncovering a uniform layer of hard scale (right on the surface), familiar from runs with no addition of particulates. The mass of these hard deposits compares well with crystallization-only results under the same conditions.

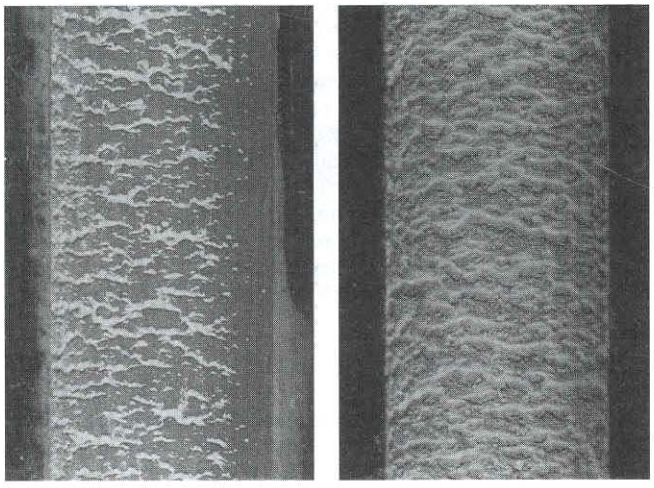

Fig. 2 Pictures of dry deposit obtained after a 1-h run, left, and after a 3.5-h run, right. (Conditions: V = 0.69 m/s, pH = 10 and part. conc. = 40 mg/L.)

Microscopically, the particulate deposits appear to be agglomerates of small needle-like particles, while the deposits from combined tests consist of calcite and aragonite particles and of the added particulates. The presence of these particulates seems to promote the simultaneous formation of calcite and aragonite deposits, while under similar conditions in crystallization runs mostly calcite deposits are observed. SEM examination of deposit ridges shows that they are comprised of aggregates of calcite particles (of the order of 10 μm), while the deposits at the valleys contain aragonite clusters and isolated calcite particles. The XRD pattern of deposits from the combined runs at pH 10 is distinctly different from that of particulates, showing peaks characteristic only to calcite. The XRD analysis and the SEM observations, in connection with results of particulate-only runs, point to the preliminary conclusion that the increased mass deposited in the combined runs is not due to particulate deposition, but rather to an enhanced wall crystallization rate induced by the presence of the particulates.

A similar physical description applies to the deposition results of the runs at pH 8.8. The height and the distance of ridges are smaller than those observed in deposits obtained at pH 10. Most of the deposited mass is in the form of large interpenetrated calcite crystals up to 50 μm in size. Particulates and small aragonite particles can also be observed on the substrate, but their contribution to the total mass of deposits seems negligible. Similar interpenetrated calcite crystals (but of smaller dimensions) are observed in a run at pH 8.6. Figure 1 clearly shows the great increase of the mass of deposits (more than 20 times), promoted by the presence of particulates. It should be also noted that, although tap water at 25°C is a stable supersaturated solution at pH 8.8, the addition of particulates quickly induces bulk precipitation.

The effect of flow velocity (V) on the net deposition rate in the case of particle addition is illustrated in Fig. 3. A 3.5-fold increase of the flow velocity results in a 60 percent increase of the mass of deposits obtained for the same run duration. On the other hand, the deposition rate scales with $V^{0.85}$ in pure crystallization runs (Andritsos et al., 1996), resulting in a threefold increase of the deposited mass for the same velocity increase. Thus, the relative enhancement of the mass of deposits obtained in the presence of particles tends to decrease with increasing flow velocity. This trend may be attributed to a removal rate increasing the velocity. Furthermore, although the velocity increase does not change the macroscopic appearance of the rippled deposits, it is observed that at higher velocities

the deposits are more compact and they can be removed with more difficulty than those formed at lower velocities.

(b) Silica Particles. Only a few runs were carried out (25°C, flow velocity: 0.43 m/s, particle concentration: 100 mg/L), since it was found that the presence of the colloidal silica does not affect the initial deposition rate. Morphologically, however, it seems that addition of particles leads to a reduction of the mean calcite crystal size, crystallized on the metal substrate. Furthermore, calculations for particle deposition suggest that the contribution of particulate silica deposition to the total deposited mass is very small and could not have been detected if it were acting alone under the conditions used in the present experiments. Regarding bulk precipitation experiments, no detectable effect on the induction period is observed with the silica seed addition. This means that the silica particles do not have any nucleation capability, which may be attributed to the noncrystalline nature of the Ludox® particles. Another reason may be the small size of the particles; Walton (1967) and others report that the particles promoting nucleation are of a size greater than 100 nm.

Concluding Remarks

The greatest enhancement of deposition rate due to $CaCO_3$ particle addition was obtained at the smallest velocity (0.43 m/s), with a tendency to diminish at higher flow rates. Although conditions were not exactly the same, enhancement at low velocity (in the presence of particles) was also reported by Watkinson (1983) for $CaCO_3$ deposition, and by Bansal et al. (1997) for $CaSO_4$ scaling.

At present, there is no obvious explanation for the observed synergistic effect of the added crystalline particles on the $CaCO_3$ deposition rate. However, there are strong indications that the extra deposits result from augmented wall crystallization and are not due to an enhanced particulate deposition. This is also in line with the suggestion of Bramson et al. (1995) regarding the mechanism of $CaCO_3$ scaling. On the basis of all the evidence available, one might offer the following tentative explanation for the effect of particles: The surface roughness created by the initial deposition of some particles tends to significantly increase the mass transfer rate enhancing the crystallization rate. Obviously, more data are needed to elucidate this phenomenon. Nevertheless, the results presented here clearly demonstrate what has been found in practice and in the laboratory so far; i.e., filtering out of particles and (in the presence of particles) avoiding low velocity regions are measures for controlling scale deposition.

Acknowledgments

This work has been financially supported by the Commission of European Communities (JOULE Programme) under Contracts JOUE-CT90-0040-C and JOE3-CT97-0053. The help of Mr. V. Hadjiapostolou with the experiments is also acknowledged.

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