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Scale formation in tubular heat exchangers—research priorities ☆

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Abstract

The common case of $CaCO_3$ scale formation in pipe flow is considered in this paper. Results of experimental studies, mainly by the author and his collaborators, are reviewed from the standpoint of the main mechanisms involved, in order to identify key issues that require additional research. The discussion is focused on the initial deposition rate as well as on the morphology of growing crystalline deposits as a function of various process parameters. A critical supersaturation ratio ($S_c \sim 7$ for $CaCO_3$) represents a significant transition from one type of scale formation process to another, including the dominant mechanism, the growth rate, and the morphology of scale. As regards generic topics that need clarification, it is suggested that high priority should be placed on (a) the attachment phenomena of nuclei/crystals on the substrate and (b) the effect of particulate/colloidal matter on scale characteristics. Significant gaps also exist in our understanding of the effects of fluid physical and chemical properties, and of fluid mechanics, on elementary processes (e.g., crystal growth and morphology) and on scale characteristics. Clarifying these aspects of scale formation would facilitate the development of fouling mitigation methods. Modelling efforts addressing elementary processes as well as system (global) evolution are considered essential for developing improved predictive tools, and reliable techniques for estimating physical parameter values difficult to obtain by other means. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: Calcium carbonate; Scale characteristics; Tube flow; Incipient scale growth; Induction period

1. Introduction

Understanding, and being able to predict, the characteristics of scale formation is required for reliable design and smooth operation of heat exchange equipment. However, despite a great deal of work over the past 30 years, the state of the art in this area is unsatisfactory. Indeed, it is impossible at present to predict (with a satisfactory degree of reliability) the temporal variation of fouling resistance R_f which is the relevant parameter for engineering calculations.

For a fixed set of conditions, the temporal evolution of R_f (Fig. 1) reflects the variation of scale characteristics. Two features of this variation deserve our attention:

- *Induction period* t_i, observed under some conditions, and associated with nearly zero (or even negative) values of R_f [1,2].
- *Behavior at long time*, i.e., constant, varying, or asymptotic (R_f^*) fouling resistance observed in many published data sets [3,4].

The practical implications of predicting and/or controlling these characteristics are obvious: extending the induction period t_i, as long as possible, is desirable because it is associated with high heat transfer coefficients and with reduced equipment cleaning costs. Furthermore, the possibility that a system tends to an asymptotic value (R_f^*) is helpful in designing the heat exchanger as it affords a (safe) upper limit of fouling resistance. Unfortunately, reliable predictions of the occurrence and of the magnitude of both t_i and R_f^* are impossible to make at present, despite considerable research efforts over the past 20–30 years [5].

Various types of fouling have been identified in the literature [6,7], depending mainly on the composition of the heat exchanging fluids. This paper is focused on scaling, caused by sparingly soluble salts in water. In particular, the common case of $CaCO_3$ scale formation in pipe flow will be dealt with. Work carried out in this Laboratory will be briefly reviewed in an attempt to outline the main mechanisms

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Nomenclature

K_{sp}	calcium carbonate solubility product . .	$mol\cdot m^3$
k_e	rate constant of polynuclear crystal growth kinetics	$mol\cdot s\cdot m^{-2}$
K_e	dimensionless parameter in polynuclear (exponential) growth kinetics	
R_f	thermal fouling resistance	$m^2\cdot kW^{-1}$
R_f^*	asymptotic value of thermal fouling resistance	$m^2\cdot kW^{-1}$
S	supersaturation ratio, defined in Eq. (1)	
S_{rC}	critical supersaturation ratio, signifying change of precipitation/deposition mechanism	
t_i	induction period for measurable fouling resistance	s
u	average axial fluid velocity	$m\cdot s^{-1}$

Greek symbols

γ_{sl}, γ_{cs}, γ_{cl}	components of interfacial tension between phases at equilibrium, defined in Fig. 12	$J\cdot m^{-2}$
ΔG_{crit}	critical excess Gibbs free energy for homogeneous nucleation	J
$\Delta G \Delta_{crit}$	critical excess Gibbs free energy for heterogeneous nucleation	J
θ	contact angle (Fig. 12)	rad

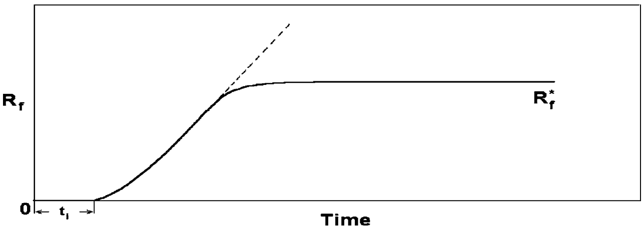


Fig. 1. Possible variation of thermal fouling resistance with time; induction period t_i.

involved and to identify some key issues that seem to require special attention in future research activities.

Even for the restricted case of a single depositing species (i.e., $CaCO_3$) there is a multitude of factors, responsible for scale formation in industrial processes, that may be classified as follows:

- *Fluid composition* including dispersed solid matter (colloidal, other);
- *Substrate surface properties*; i.e., material properties, surface conditions (including roughness);
- *Flow field* (fluid bulk and solid/liquid interface conditions);
- *Thermal field* (heat flux, substrate surface temperature, bulk fluid temperature).

The interaction of the main variables involved in these categories complicates matters immensely, and necessitates extra care in efforts to isolate and systematically study various mechanisms. Here we only touch on the above first and third categories of factors. The substrate material examined is stainless steel. Isothermal conditions are studied over the temperature range ~15 °C to ~45 °C, mainly to examine the effect of temperature of flowing water (supersaturated in $CaCO_3$) on scale characteristics.

In the following, after an overview of elementary processes responsible for scale formation, selected experimental data are reviewed as regards the effect of main parameters. The morphology of growing crystalline deposits is also discussed. In the next section, attention is paid to surface nucleation and to incipient growth of deposited/surface crystals. Modelling efforts are also summarized, concerning initial deposition rates, detachment of growing scale elements, and overall (temporal/spatial) system evolution.

2. Elementary processes

As is well-known, departure from equilibrium (i.e., supersaturation) leads to crystallization from solution. In this presentation, the supersaturation ratio S is defined as

$$S = \left[\frac{(\mathrm{Ca}^{2+})(\mathrm{CO}_3^{2-})}{K_{sp}}\right]^{1/2} \tag{1}$$

where the quantities in parentheses denote activities and K_{sp} is the solubility product of *calcite*, the dominating polymorphic $CaCO_3$ phase encountered in the scale. For wall crystallization or bulk precipitation to occur, a supersaturation ratio significantly greater than unity is usually required. With regard to crystalline scale formation, the following processes contribute directly or indirectly [8,9].

(1) *Nucleation* onto the substrate and (at relatively higher S) in the fluid bulk. Ostwald ripening may be considered as part of this process.
(2) *Diffusion* of solvated ions, molecules or small particles to the surface.
(3) *Surface Phenomena* is a general term to designate various elementary steps such as adsorption of solvated ions or molecules on an existing crystal surface, the ensuing surface reaction, and the incorporation of ions or molecules into the crystal surface. Any of these steps may control crystal growth, or surface "reaction", which may be described by a phenomenological reaction rate coefficient.
(4) *Attachment* of clusters, nuclei, or colloidal particles onto the substrate might be classified as a category, separate

from surface phenomena responsible for individual crystal growth.

(5) *Detachment* of crystalline matter/particles from the surface by flow imposed forces.

(6) *Agglomeration* (or breakage) of developing, in the bulk, nuclei or particles.
Aging phenomena of deposited/surface crystals, through phase transformation (possibly aided by heat transfer), that may harden or weaken the scale.

The intensity of the aforementioned factors (e.g., degree of supersaturation, flow velocity, heat flux) would tend to enhance some of the above processes over others. Under any circumstances, however, it appears that several of these processes (often taking place simultaneously) are responsible for scale formation and scale characteristics. The difficulty of determining the true contribution of each process in a given physical system, is at the heart of dealing with the fouling/scaling problem and is responsible for the poor state of our predictive capabilities.

3. Overview of experimental data

The data reviewed here are reported in detail elsewhere [10,11]. It is pointed out that these data have been taken, under constant feeding conditions, in "*once-through*" flow of the fluid (through the test-sections), and not by recirculation of a finite fluid volume. In this mode of operation, only "fresh" fluid of controlled supersaturation and of the same age comes in contact with the test sections, thus avoiding the possible recirculation of pre-formed colloidal particles that may influence scale formation and complicate data interpretation. Data taken under isothermal conditions (in the range ∼15° to ∼45 °C) are summarized. Semi-annular coupons are inserted [10] in the test sections, so that their inner surface exposed to flow is perfectly cylindrical. The material used for the coupons is stainless steel 316 L and 304 and the finished surface roughness, R_a, is less than 0.5 µm. Data on the initial deposition rate, measured over a period of several hours, are presented.

3.1. Effect of supersaturation

At small supersaturations (i.e., below what appears to be a *critical value* $S_c \sim 7$) the deposition rate is quite small and tends to increase with supersaturation, as shown in Fig. 2. A sharp rise of the initial deposition rate is observed at $S_c \sim 7$. At greater supersaturations the deposition rate remains roughly constant for fixed fluid properties and flow conditions. It is interesting to close examine some typical

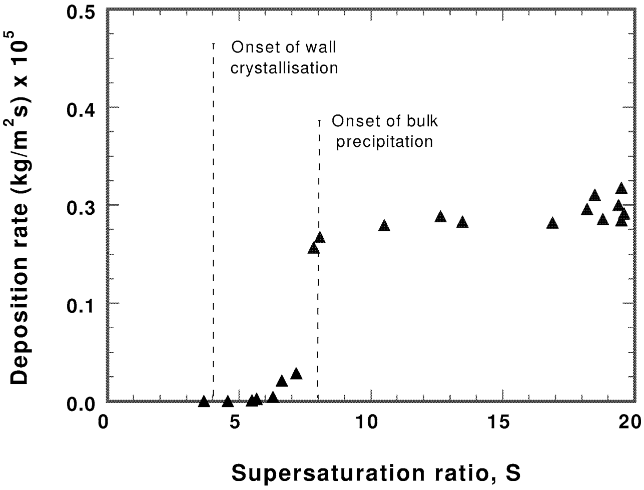


Fig. 2. Deposition rate versus supersaturation ratio at a constant velocity ($u = 0.43\ \mathrm{m{\cdot}s^{-1}}$) and temperature (23 °C).

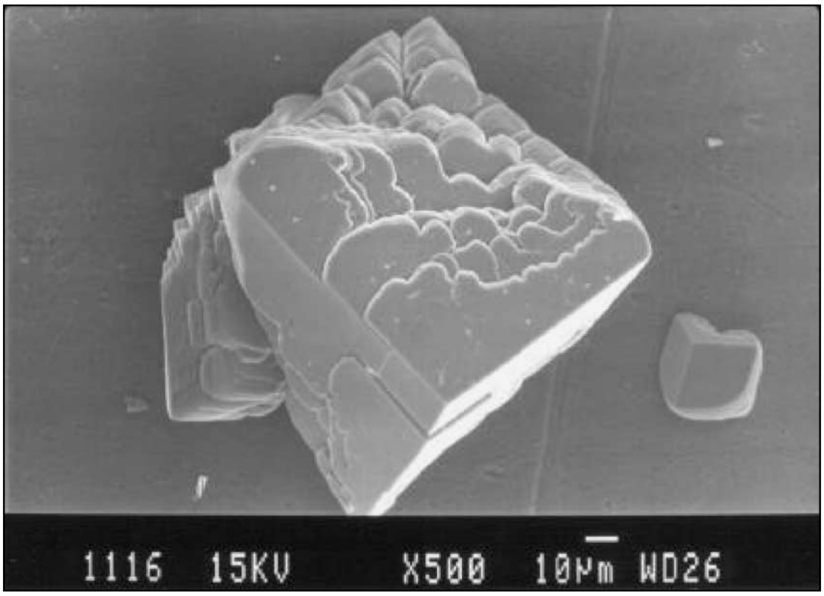


Fig. 3. Large calcite crystals formed at low supersaturation ratios. $u = 1\ \mathrm{m{\cdot}s^{-1}}$, $T = 30\,^\circ\mathrm{C}$, pH = 8.75, $S = 6.9$ and time = 6 h.

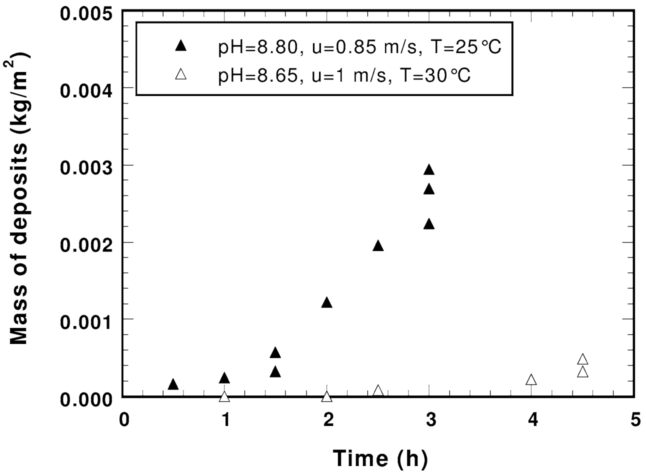


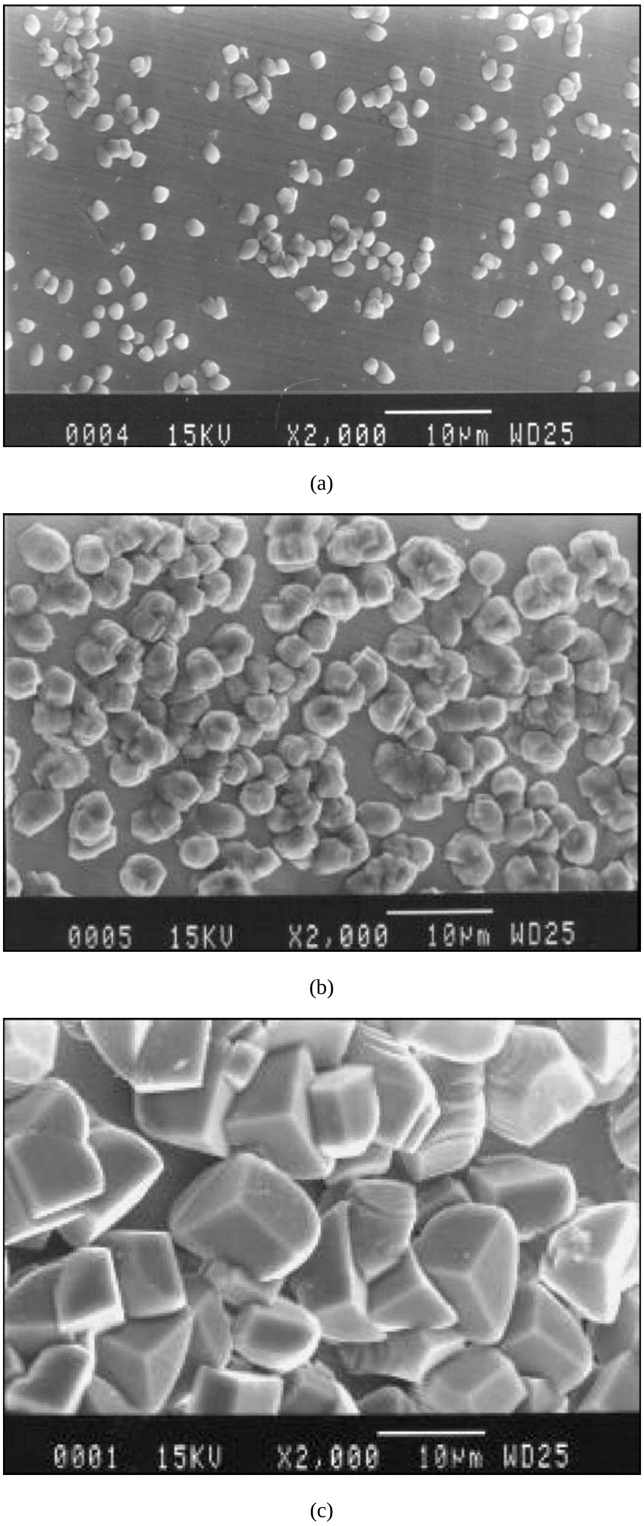
Fig. 4. Rate of deposit formation at relatively low pH and supersaturation, indicating induction period.

cases of initial crystal growth on the substrate, below and above the critical supersaturation, to get an appreciation of incipient scale formation. Fig. 3 includes a SEM picture, corresponding to conditions below but near the critical value S_c, showing that isolated calcite crystals grow on an otherwise bare substrate. The rate of deposit formation corresponding to Fig. 3 is shown in Fig. 4. The case depicted in Figs. 3 and 4 is typical of the *"induction period"* of scale formation. Deposition is initiated with *heterogeneous nucleation on the substrate* and subsequent growth of *isolated crystals*. Ostwald ripening, i.e., dissolution of nuclei in favor of the larger crystals, may occur in this case. *Surface nucleation* under conditions of low supersaturation (usually encountered in practice) and subsequent crystal growth, is a process requiring clarification as will be discussed in a subsequent section.

In Fig. 5, a sequence of SEM pictures clearly shows the first stages of scale formation for supersaturation $S = 15.5$, i.e., above the critical value. It is evident in Fig. 5(a) and (b) that the nuclei rapidly grow to cover the substrate. Quite well formed calcite crystals tend to merge as they grow. Fig. 5(c) depicts the surface "roughness" of the scale in the early stages of formation. One also observes that the crystals grow out of a broad base on the substrate. Fig. 6 includes data on the rate of initial deposit growth under the same conditions as those of Fig. 5. A linear variation, with no induction period is observed.

3.2. Effect of flow velocity

This effect is quite clear for supersaturations above the critical one, as is indicated in Fig. 6, where typical sets of data, of deposition rate as a function of mean velocity, for $S \approx 15.5$, are plotted. These data display a dependence on velocity to a power approx. 0.85, which is typical of convective mass transfer controlled processes. Similar results (with smaller exponent values) are obtained, under isothermal conditions, in other studies [8,12].



(a)

(b)

(c)

Fig. 5. SEM micrographs depicting the growth of calcite deposits at relatively high supersaturation ratios: (a) 2 min after the start of the run, (b) 10 min, and (c) 60 min ($T = 17\,^\circ\mathrm{C}$, $u = 1\ \mathrm{m{\cdot}s^{-1}}$, $\mathrm{pH} = 10.5$, $S = 15.5$).

It is worth stressing here the apparently significant effect of flow velocity on the morphology (and the compactness) of the growing crystalline scale. The SEM picture corresponding to rather low velocity (Fig. 7) reveals that, at $S \approx 15$ and temperature 25 °C, crystal formations protrude outward into the flow. Evidently, such scale layers are not very compact. On the contrary, Fig. 8 shows quite compact scale formation for nearly the same supersaturation but at a higher velocity ($U = 2$ m·s^{-1}). Another notable feature at high velocities is the much smoother top surface of the growing scale layer (Fig. 8), as also reported by Hasson [8]. Apparently, the rather high mass fluxes, prevailing under these conditions, tend to influence the morphology of growing calcite crystals resulting in the peculiar rounded cups at the surface.

3.3. *Effect of temperature*

Aside from its effect on supersaturation, temperature directly influences the $CaCO_3$ polymorph phase development [13]. In the tests reviewed here it was found that below 30 °C, calcite is essentially the only polymorph present, mainly in prismatic form (Fig. 5), exhibiting typical rhombohedral faces on the top (not at high velocities). Above ~35 °C, aragonite appears to be stable, exhibiting characteristic dendritic formations (Fig. 9) emerging out of (and adhering onto) the metallic substrate. However, as pointed out by Andritsos et al. [11], with time (even under these higher temperatures) small calcite crystals tend to cover the substrate forming a coherent “base layer”, on top of which the dendritic pattern of aragonite develops. The latter, characterized by poor coherence and tenacity and by low density, may be (at least partially) removed by increased flow velocities, especially after growth at long times. The practical implications of such a removal need not be emphasized.

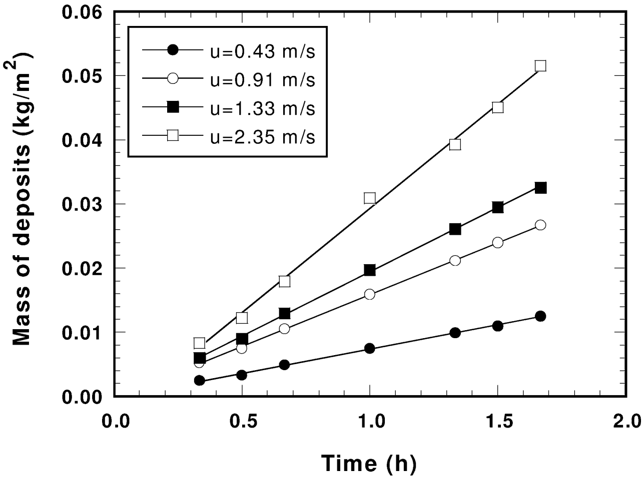


Fig. 6. Rate of deposit formation at a constant pH and temperature for various liquid velocities (pH = 10.5, $T \sim 18$ °C).

3.4. *Effect of particles on* $CaCO_3$ *scale formation*

In several papers reviewed elsewhere (e.g., [5,14]), there is evidence that dispersed fine particles tend to increase the thermal fouling resistance. There are also studies (e.g., [15]) suggesting that the addition of particles (seeding) may be used as a method to prevent significant wall crystallization.

Data were taken [14] in the same experimental setup employed for fouling studies, to examine the effect of small amounts (~40 and ~100 mg·lit^{-1}) of added particles on $CaCO_3$ scale formation at 25 °C. Commercial calcium carbonate particles (of mean size 5–10 µm) and colloidal silica nanoparticles (mean diameter 21 nm) were employed for tests in the velocity range 0.43 to 1.5 m·s^{-1}. No significant effect on the initial deposition rate was found with the silica particles. Only a reduction of the mean calcite

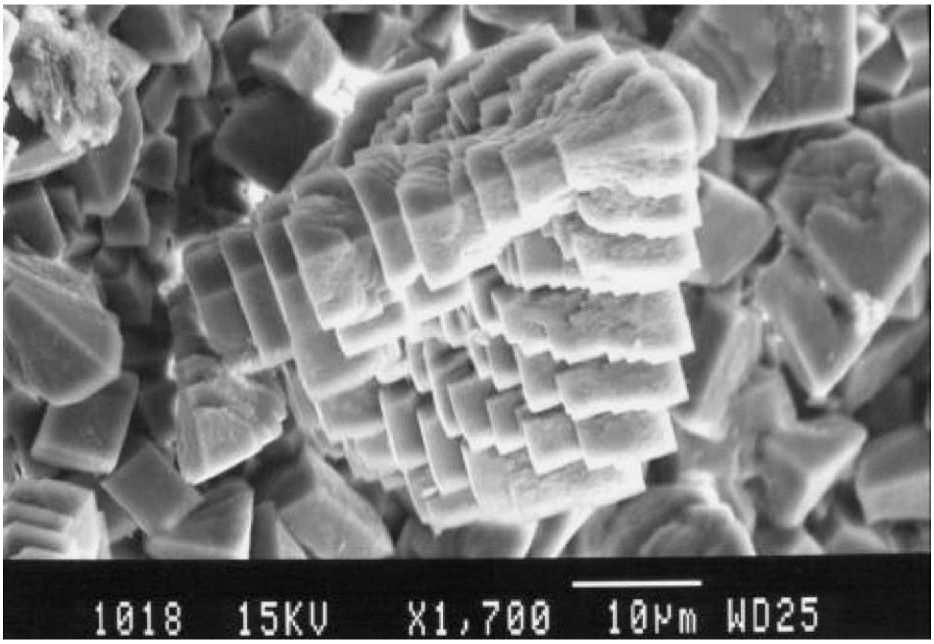


Fig. 7. Top view of calcite growth at low flow velocity ($u = 0.43$ m·s^{-1}); $T = 25$ °C, pH = 11, $S = 15$.

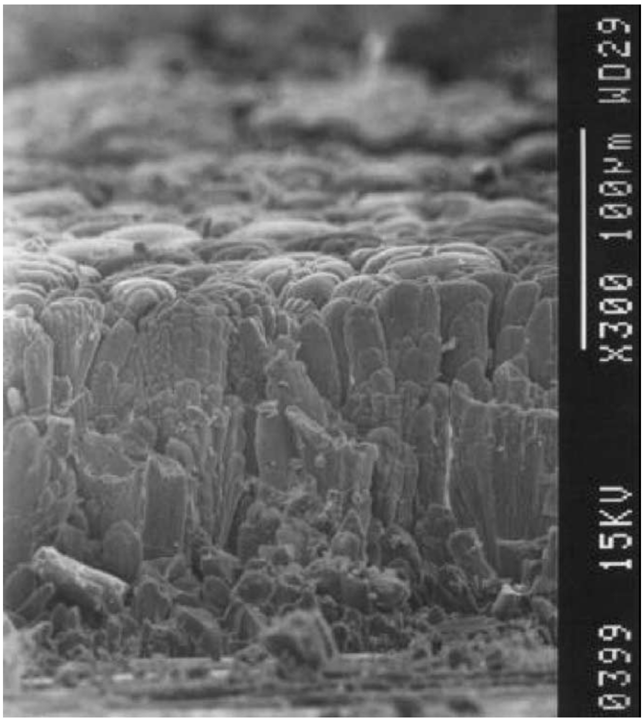


Fig. 8. Side view of calcite deposits 5 hours after start of the run; $T = 18\,^\circ\mathrm{C}$, $u = 2$ m·s^{-1}, pH = 10.5, $S = 15.5$.

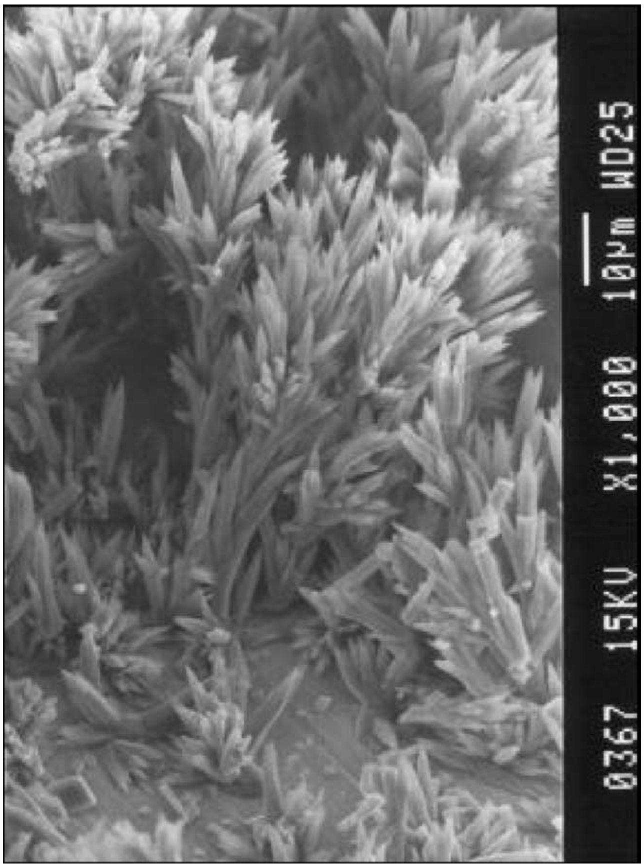


Fig. 9. Morphology of deposits formed at 45 °C after 60 min. Conditions: $u = 0.41$ m·s^{-1}, pH = 9.5, $S = 12$.

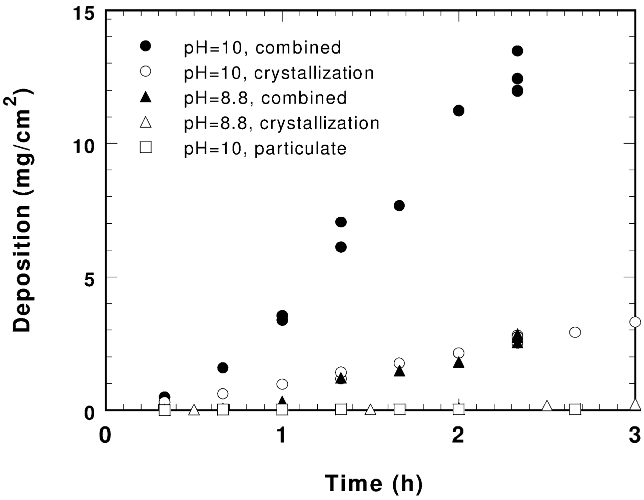


Fig. 10. Effect of particulates on deposit formation with tap water at pH 10 and 8.8 and with demineralized water at pH 10 (particle concentration ∼ 40 mg·L^{-1}).

crystal size, growing on the substrate, may have been caused by those particles.

Very significant enhancement of deposition rate was measured with added $CaCO_3$ particles, at the smallest velocity tested (0.43 m·s^{-1}), as shown in Fig. 10, with a tendency to diminish at higher flow rates. At low velocities, similar results (with enhanced deposition rate) were obtained by Watkinson [16] and Watkinson and Martinez [4]. Bansal et al. [17] experimenting with the $CaSO_4$ system also obtained significant enhancement. However, Hasson and Karmon [12] under conditions different than those of our tests, report that at high velocities, particles seem to hinder the growth rate and to have a pronounced effect on the deposit structure, with a general tendency to increase its porosity. To account for these effects, Hasson [5] argues that particles residing only *temporarily* on the substrate (eventually detached by flow-imposed forces) may offer their surface for crystal growth, thus augmenting deposit porosity and acting to reduce the *net* deposit growth rate.

At present there is no clear explanation for the strong synergistic effect, exhibited by Fig. 10, due to a rather small amount of added particles. The morphology of the deposits suggests that the enhancement is due to augmented wall crystallization (possibly aided by deposited $CaCO_3$ particles) but not due to increased mass deposited from the bulk. This issue of particle (positive or negative) influence on scale formation certainly deserves more attention, and requires additional R&D work, as it may be one of the effects leading to asymptotic fouling resistance under certain conditions.

4. Modelling $CaCO_3$ scale growth

Hasson et al. [18] have proposed an ionic diffusion model to predict the rate of $CaCO_3$ deposition for a set of conditions, including pH, Ca concentration, total alkalinity, fluid velocity, and temperatures (wall and bulk). The formation of deposits is considered to be a combination of the *mass transfer* from the bulk to the interface (of the chemical species involved in the calcium and carbonate equilibria) and of the ensuing *surface reaction*. Although satisfactory order of magnitude estimates are obtained with this model, there is a need for improvement at relatively low pH values (<10) which are of practical interest.

Andritsos et al. [19] have presented an improved model leading to better predictions of $CaCO_3$ scaling rate in the entire pH range. Scale growth is assumed to be controlled by both the mass transfer of active ions to the solid/liquid interface, and the surface (crystallization) reaction. To represent the latter, it was found that the "polynuclear growth" model [20] has advantages over the "parabolic" one, yielding better predictions of the experimentally observed sharp increase of deposition rate near the critical supersaturation $S_c \approx 7$. Fig. 11 shows a comparison of experimental data on initial deposition rate with model predictions. The data of Fig. 2 have been replotted here. It will be noted that the polynuclear model parameter values, for k_e and K_e, shown in Fig. 11 are close to those of other substances reported by Nielsen and Toft [21].

The rather sharp change of controlling mechanism indicated by the preceding experimental data, i.e., from surface reaction controlling at small supersaturations to convective transport controlling above S_c, seems to be confirmed by the model predictions. There is certainly a need for more work to better understand the processes taking place near the critical supersaturation. However, further model improvement may be obtained if one employs the *actual* surface area available (to ionic species) for crystallization below S_c, where surface reaction controls. More specifically, as already discussed and clearly shown in Fig. 3, only a small portion of the tube surface (covered by growing crystals) is essentially available for deposit growth during the induction period. By substituting the *apparent* deposition rate (plotted in Fig. 11), which is based on the *total* inner tube surface area, with a "real" one, using the total surface of growing (isolated) crystals, better agreement is expected between data and predictions. Similarly, a more realistic estimate of the "rough" scale surface may be required, when the substrate tends to be totally covered at supersaturations right above the critical value and the surface area available for the crystallization reaction is greater than the tube inner surface.

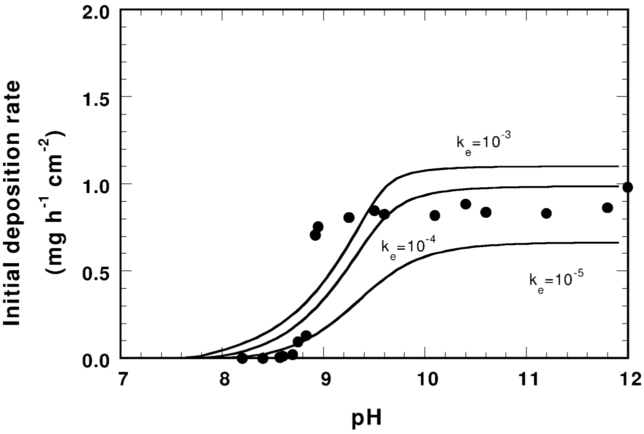


Fig. 11. Measured and predicted [19] deposition rates for a combined convective transport/*polynuclear* growth mechanism. k_e in mol·s·m^{-2} and $K_e = 10$; $u = 0.43$ m·s^{-1}.

5. Interfacial forces—incipient scale growth

The interplay of *surface nucleation* and of *particle/ substrate adhesion forces* [22] on one hand, and of the fluid mechanical *forces acting to detach particles* on the other, is responsible for the extent of the induction period and for the incipient scale formation. Understanding these phenommena and controlling the respective forces may provide the means to mitigate scale growth or to facilitate scale disbonding/removal.

Scale formation starts with "surface nucleation" which is a typical *heterogeneous nucleation* process, poorly understood. According to the classical theory (e.g., [23]) it is described in terms of the excess Gibbs free energy as follows

$$\Delta G'_{\text{crit}} = \phi \Delta G_{\text{crit}} \tag{2}$$

where ΔG_{crit} is the free energy change associated with the formation of critical nuclei in homogeneous nucleation which is normally greater than the critical excess free energy $\Delta G'_{\text{crit}}$ associated with heterogeneous nucleation. The factor ϕ tends to increase from zero to unity with increasing contact angle θ between the crystalline deposit and the solid substrate (Fig. 12). By considering the interfacial tensions between phases at equilibrium one obtains

$$\cos\theta = \frac{\gamma_{\text{sl}} - \gamma_{\text{cs}}}{\gamma_{\text{cl}}} \tag{3}$$

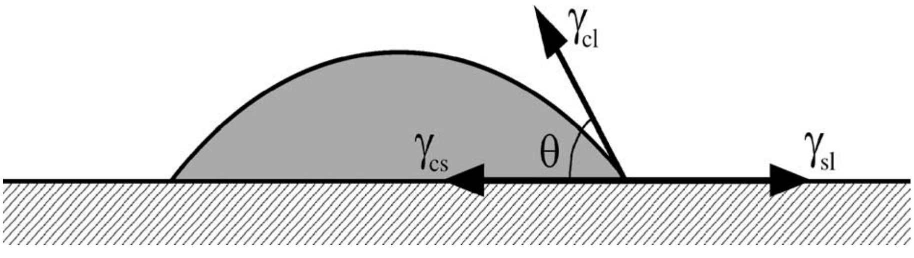


Fig. 12. Interfacial tensions between phases and contact angle θ.

As usual, θ is considered a measure of the affinity of the deposit phase with the substrate. Large contact angles indicate small affinity. Furthermore, small θ angles are associated with reduced critical supersaturation for surface (heterogeneous) nucleation.

Using classical nucleation theory and the Young equation (3), Foerster and Bohnet [1] argue that one may influence the deposition rate (at incipient scale formation) by modifying the surface free energy γ_{sv} of the substrate, because the interfacial free energy γ_{sl} is directly affected by γ_{sv}. Thus, to mitigate fouling and prolong the induction period, they propose to employ low energy surfaces which would effectively reduce nucleation rate and crystal/substrate adhesive strength. By experimenting with a flowing calcium sulphate solution and with several metallic and low energy materials, Foerster and Bohnet [1] present data showing significant prolongation of the induction (essentially "no scaling") period. Moreover, they conclude that DLC (Diamond-Like Carbon) coatings of surfaces offer an interesting option, superior to other materials they have tested.

Müller–Steinhagen and associates (e.g., [24]) have pursued a similar approach, experimenting with ion-implanted metal surfaces and with various types of sputtered surfaces (with AC, DLC, DLC-F); they suggest that the treated surfaces have energies much lower than the untreated ones. In several publications from that Laboratory, summarized by Müller–Steinhagen and Zhao [24], data are presented, with the $CaSO_4$ system and with treated surfaces, showing significant reduction of fouling.

Another approach for treating the effect of surface forces, on the initial stages of fouling, has been followed by Visser [25] who took avantage of relevant work by van Oss [26] on the interfacial forces and in particular on the so-called "Lewis acid/base interaction" of neighboring species. The latter is *attractive* in aqueous media and tends to combine with the Lifshitz–van der Waals forces to overcome the common electrostatic repulsion at usual pH values. In terms of Gibbs free energies, the total energy of interaction between a colloidal particle and a metal surface can be written as follows

$$\Delta G^{\mathrm{Tot}} = \Delta G^{\mathrm{LW}} + \Delta G^{\mathrm{EL}} + \Delta G^{\mathrm{AB}} + \Delta G^{\mathrm{Br}} \tag{4}$$

Here the four terms correspond to Lifshitz–van der Waals component (LW), electrostatic double layer component (EL), Lewis acid/base component (AB) and Brownian motion (Br) contribution, respectively. Obviously, scaling is considered to take place only if the interaction of these components leads to a negative total free energy change ΔG^{Tot}. Visser [25] summarises the techniques (proposed by van Oss) to make relevant measurements and to predict the individual contributions in Eq. (4) and outlines difficulties thereof. It is concluded that for the system calcium phosphate-stainless steel (which bears some similarities to the $CaCO_3$ system studied here) the main driving force for attachment resides in the Lewis acid/base component of the overall interaction energy. Furthermore, it is recommended that an effective way to reduce that component would be to alter the characteristics of the heat-transfer surface. For the particular system studied by Visser, it is suggested to modify the surface by making it more *hydrophilic*. Such an approach is currently pursued in the context of a collaborative EC-funded R&D project, under the acronym MODSTEEL. It must be pointed out, however, that several aspects of the above modified DLVO theory are still unproven and that judgement on its applicability to real situations should be withheld until sufficient new and reliable data, with "modified" surfaces, become available. It will be further noted that the above efforts to modify surfaces are focused on stainless steel surfaces which are fairly smooth and corrosion resistant. The case of mild steel, widely used in industry, appears to be quite different; Keysar et al [27] have shown that the surface roughness of mild steel has a strong effect on the adhesion and morphology of calcite scale, leading to more compact and tenacious deposits.

6. Particle detachment

6.1. Detachment from flat surfaces

The adhesion forces, between nuclei/crystals and substrate, evidently play a key role in scale formation. Particle detachment occurs when such forces are overcome by hydrodynamic forces. If extensive detachment occurs in the early stages of scale growth, the induction period would be prolonged. Quantitative predictions of detachment rates are impossible to make at present, mainly due to the effect of some parameters that cannot be easily quantified; e.g., surface inhomogeneity, microroughness etc.

Experiments carried out under well controlled conditions with monodisperse (micron size) spherical particles [28] were aimed at clarifying some issues of detachment from a fundamental point of view. It was pointed out in that paper that, for particles in the colloidal size range, *tangential* forces dominate, and not lift forces often invoked in the literature. Some experimental results of relevance to this review may be summarized here:

- Smaller particles require higher shear stress for effective removal, as expected.
- A continuous *distribution* of stresses, and not a single-valued critical stress, is required to detach a population of monodisperse particles
- pH exerts a significant influence on the adhesive strength. Predictions based on DLVO theory are in qualitative agreement as regards observed pH effects.
- The mean hydrodynamic wall shear stress required for detachment, which is representative of adhesion forces, is found to be proportional to particle diameter to the -1.8 power. This finding suggests that particle *rolling* is the most likely removal mechanism.

6.2. *Modeling of removal processes*

A modeling effort was undertaken [29] in order to suggest a rational mechanism that may account for the removal aspects of the fouling process and may offer a framework for predicting the temporal evolution of scaling rate. The main premises involved may be summarized as follows

(a) Roughness elements or "out-growths" such as agglomerated crystals, crystal dendrites and branches, are more likely to be detached by the action of flow shear forces.
(b) Removal occurs when the hydrodynamically imposed stress on these roughness elements exceeds an intrinsic adhesive or breakage strength determined by various physicochemical factors (previously outlined).
(c) A dynamic situation is envisioned whereby roughness elements grow due to deposition and suffer breakage when they reach a limiting size. Thus, the kinetics of removal is linked to the growth process and to the polydispersity of strength of the deposit.

In order to obtain a complete description, several simplifying assumptions were introduced regarding the roughness elements (shape, growth rate, number density) and their breakage strength distribution. Despite these simplifications, encouraging results were obtained such as asymptotic fouling behavior and flow effects in qualitative accord with experimental data. In particular, the often observed reduction of asymptotic fouling resistance R_f^* with increased flow velocity is predicted by the model. Fig. 13 shows a comparison of model performance against the data on $CaCO_3$ scaling by Hasson [30]. Here the fouling resistance was adjusted for the lowest velocity and calculated for the other cases. A mean value for the deposition rate was estimated from the data and used to find the time scale.

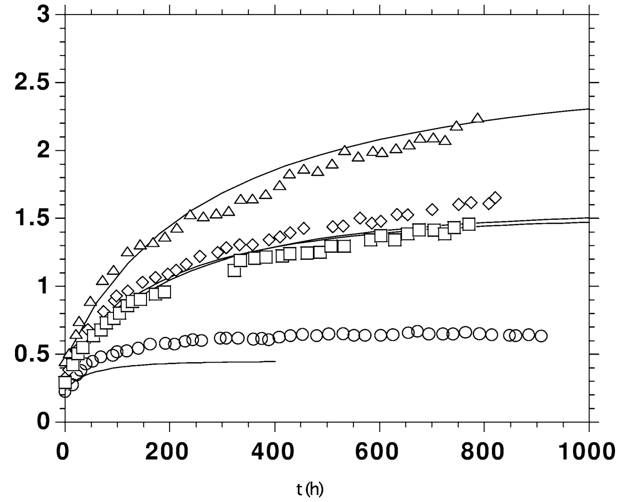


Fig. 13. Comparison of data on $CaCO_3$ fouling by Hasson [30] with model [19] predictions. High-R_f curve $u = 39$ cm·s^{-1}; low-R_f curve $u = 125$ cm·s^{-1}.

7. Comprehensive modeling of precipitation and fouling in pipe flow

In preceding sections, the focus was mainly on elementary processes contributing to scale formation. However, supersaturation triggers several precipitation-related phenomena that may occur along the flow path. The interaction between fluid dynamics and physicochemical processes (i.e., nucleation, particle growth, agglomeration) leads to an axial variation of bulk fluid properties and of ionic and particulate deposition rates at the pipe wall. Fig. 14 provides an overview of the various processes that may be classified into two main categories, i.e., *ionic* and *particulate* processes. In the case of sparingly soluble compounds, such as calcium salts, the rates of most of these individual processes tend to be of the same order of magnitude. Therefore, the respective processes may occur concurrently, creating very serious difficulties in studying separately each one of them as well as in modeling and predicting the outcome of their complicated interaction

Significant efforts have been made in this Laboratory to simulate such complicated systems [31,32]. Simple plug flow hydrodynamics is combined with rather comprehensive modeling of physicochemical phenomena. A population balance type of formulation is employed for modelling the particulate processes involved. Using modern and optimized (for such problems) computational techniques, efficient numerical algorithms have been obtained to cope with these demanding tasks. The methodology and the tools developed are appropriate for simulating precipitation phenomena, with emphasis on pipe wall fouling in turbulent flow. The usefulness of those tools is twofold: (a) to predict the axial

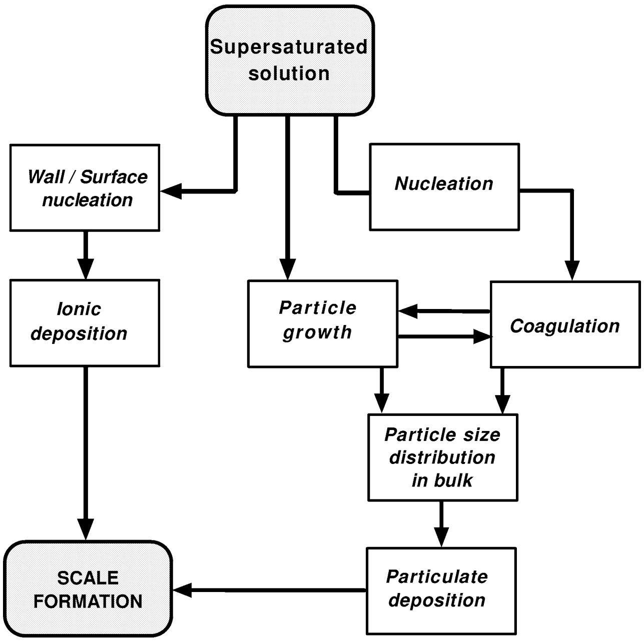


Fig. 14. Physical processes occurring in pipe flow of supersaturated solutions.

and/or temporal variation of scale and fluid characteristics, and (b) to provide a reliable computational framework for estimating those system parameters that cannot be determined with reliability by simplified experimental or other procedures. Although satisfactory results have been obtained so far with these tools, further improvements are required.

8. Concluding remarks

The supersaturation ratio S is clearly the most important parameter affecting the scale growth process. In the case of $CaCO_3$ deposition/precipitation, a critical supersaturation ratio ($S_c \sim 7$) appears to represent a significant transition from one type of scale growth process to another. The main features of each regime may be summarized as follows:

$\underline{S < 7}$ An induction period is observed in the scale growth process, which tends to increase with decreasing S. This is a direct consequence of the fact that (at such small supersaturation) only heterogeneous wall nucleation takes place, at relatively small rates. Furthermore, “surface reaction” appears to control the initial growth of nuclei/crystallites which are isolated and distributed on the substrate. Under these conditions, individual crystal growth, and in particular substrate surface coverage are relatively slow. The controlling process here (i.e., surface reaction) implies that there is no effect of flow velocity on the intrinsic deposition rate. There is some experimental evidence in support of this observation, although this issue requires clarification. Nevertheless, velocity may still play a role in the overall scale growth process. The crystals growing in isolation during the induction period (as shown in Fig. 3) are subjected to significant drag forces at high velocities, and might be detached if crystal/substrate adhesion forces are not strong enough. It will be pointed out, parenthetically, that creating conditions promoting such an occurrence (through modification of crystal morphology or weakening of substrate/crystal adhesion), thus lengthening the induction period, seems to be one of the main approaches to mitigate scaling. It will be also noted that most of the experimental work on pure $CaCO_3$ scaling reported so far shows that, after surface coverage has taken place, a rather compact and tenacious scale layer develops which is difficult to be affected by flow induced forces.

$\underline{S > 7}$ In this range, the rate of nucleation is fairly large and the substrate is rapidly covered by deposited mass. Thus, there is no induction period. The effect of flow velocity on deposition rate is quite strong ($d \propto U^{0.8}$) suggesting that convective diffusion controls. Another significant velocity effect is also observed. At small velocities prismatic outgrowths of calcite are evident; but at relatively high velocities the developing scale is quite compact and tenacious, its top surface exhibiting rounded cups (e.g., Fig. 8). There is no obvious explanation for this intriguing effect. It will be added that in this range of conditions ($S > 7$) bulk precipitation phenomena (nucleation, crystal growth, agglomeration) appear to take place along the flow path and to be intensified with increasing supersaturation.

At and above critical supersaturation, very significant enhancement of scaling rate is measured with the addition of a small amount of $CaCO_3$ particles. This effect is very strong at the smallest velocities tested, being reduced with increasing velocity. Colloidal particles of a different type (SiO_2) have practically no influence on $CaCO_3$ scale formation. This strong synergistic effect of added $CaCO_3$ particles definitely needs clarification. In fact, a common argument in the literature, contrary to the above results, is that the presence of particulates may have a negative overall effect in scale growth, adversely affecting scale coherence and facilitating solids detachment. This issue has obviously significant practical implications.

To summarize, significant knowledge gaps exist, with regard to scale formation, at two levels, i.e., elementary mechanisms/processes promoting scaling and interaction of such processes which take place concurrently. One of the most important aspects demanding attention appears to be that of *attachment* of nuclei/crystals on the substrate. The influence of the ionic environment and of the substrate properties on the adhesion forces between particles and substrate (inadequately understood and insufficiently tested so far) should be given priority in R & D efforts. Similarly, the conditions for attachment and/or incorporation of the (ever present in real systems) dispersed colloidal particles onto the developing scale, and their effect on scale coherence, seems to be an issue that requires clarification. Understanding and possibly controlling particle/substrate adhesion forces, and the effect of dispersed matter on scale properties, may be essential for tackling key issues such as the extent of *induction period* and the occurrence of *asymptotic* thermal fouling resistance (i.e., the condition of zero net deposition rate). Quantifying the influence of fluid dynamics on other elementary processes (i.e., nuclei and crystal growth, detachment effects) appears to be another significant issue that should be given high priority. Finally, better understanding of the effect of fluid properties (chemical composition, pH, temperature) on crystal/particle morphology seems to be a pre-requisite to developing effective scale mitigation procedures.

Modelling elementary processes as well as the entire flow system evolution can lead to improved predictive capabilities and, more important, can provide reliable methods/framework for interpreting experimental data and for process parameter estimation.

It is finally pointed out that this brief review of scale formation is restricted to a single depositing species ($CaCO_3$) in an attempt to focus on key issues requiring special attention in future research activities. Aside from that restriction, this paper is also incomplete in other respects, with several significant contributions to this field not included. In particular, the somewhat different scale characteristics [33] due to precipitation (or co-precipitation) of other compounds (e.g., $CaSO_4$) are not treated here despite their importance. Nevertheless, it is clear that considerable research work is still required to better understand scale formation even in simplified cases.

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