REVIEWING DETACHMENT PROCESSES IN CRYSTALLISATION FOULING: IMPLICATIONS FOR ACCURATE PREDICTIONS

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ABSTRACT

Crystallisation fouling is detrimental to many industrial processes. The persistence of fouling is determined by the balance of attachment and detachment processes. In most prediction models, however, detachment processes are either ignored or oversimplified.

In this work, we present a review of detachment processes in crystallisation fouling models. We show that experimental studies strongly suggest that detachment processes must be considered. Next, we review the properties of the fouling interface and discuss the influence of surface morphology and composition.

We also evaluate the influence of fluid flow properties on fouling rates, and address the contradictory observations in the literature. Finally, we show how detachment processes can be intentionally enhanced as part of fouling mitigation protocols.

We conclude that new prediction models must account for detachment processes or ensure that they are negligible under the process conditions that are being simulated.

INTRODUCTION

Fouling can be understood through five distinct subprocesses: initiation, transport, attachment, detachment, and ageing ¹. While initiation, transport, and attachment are commonly incorporated into models, detachment and ageing are often neglected. It has been shown that an incorrect understanding of the detachment term can lead to inaccurate predictions of the net deposition rates².

Most implementations of the detachment term (\dot{m}_d) in the literature are based on the interaction between the strength of the foulants (σ) , and the stress exerted on them $(\tau)^3$.

$$
m_d = C \frac{\tau}{\sigma} \tag{1}
$$

This model has been expanded to include properties such as density (ρ_f) , intercrystalline adhesion (P), particle size (d_n) , temperature change ΔT , density of the liquid (ρ), thickness of the fouling layer (x_a) and the velocity of the liquid (w) 4 :

$$
\dot{m_d} = \frac{k_2}{p} \rho_f (1 + \delta \Delta T) d_p (\rho^2 \eta g)^{\frac{1}{3}} x_\theta w^2
$$
 (2)

Where K_2 is a constant. The assumptions in the model, however, do not fully capture the complexities found in published experimental studies. These complexities include the dynamic effect of break-off⁵, supersaturation-induced crystal resilience $6,7$, and composite fouling $8,9$.

Existing models often do not account for properties such as crystal shape, surface roughness, and the adhesive strength of the foulant. Furthermore, a proper understanding the influence of shear forces arising from a process stream is limited.

THE FOULING INTERFACE

Surfaces play an important role in crystallisation fouling, as both their composition and morphology determine the affinity for fouling.

Substrate-Foulant Interaction

The interaction between the substrate (the surface being fouled) and foulants (the materials deposited on the surface) is multifaceted, involving both morphological (shape and structure) and energetic (forces and energies) aspects. These interactions are crucial to the detachment rate because they influence how strongly foulants adhere to the surface and their resilience against detachment processes.

Substrate Composition

The chemical composition of a surface significantly impacts its interaction with foulants. This composition determines the surface energy, which affects wetting properties and the adhesion forces between the surface and foulants. High adhesion forces mean foulants are more likely to remain attached, making the surface more prone to fouling. Studies have shown that surface compositions can significantly influence fouling dynamics 10–14 .

Surface Morphology

The physical structure of a surface, or its morphology, also plays a crucial role in fouling 5,15– 18 . Surfaces with rough textures can provide more nucleation sites for foulant deposition 19 , leading to increased fouling. However, the relationship between surface roughness and fouling is complex, with studies showing varying effects. While some studies show that increased surface roughness leads to more fouling due to the increased availability of nucleation sites ²⁰ and enhanced advection (fluid movement that can carry foulants to the surface) 5 . Other studies have found that changes in roughness had minimal impact on deposition rates, suggesting that other factors might be at play $2^{1,22}$.

Composite Fouling

Beyond the initial layer of deposition, the interactions between subsequent layers of foulants can significantly influence the overall fouling process. Multicomponent fouling layers are prevalent in industrial settings 23 , and need to be better understood. The presence of multiple foulants can alter the adhesion strength and detachment rates of the fouling layer ⁸. For example, the sequence in which different foulants deposit can affect the overall adhesion of the layer, with certain combinations leading to enhanced deposition rates or increased detachment ⁸. Experimental studies have shown that mixed foulants can interact in ways that significantly alter fouling dynamics, underscoring the need for models that can account for these complex interactions. When crystallisation fouling and particulate fouling interact, fouling is influenced by dispersed particles acting as nucleation points ²⁴. The interaction between particulates and crystals canaffects deposition rates based on size, composition, and shear stress 25 . Currently, one model accounts for particulate fouling 26 , however, it overlooks the impact of embedded particles on adhesion strength. Additionally, the interaction between biofilms and crystallisation fouling is complex, with biofilms potentially enhancing surface interaction with crystals $27-29$. To our knowledge, no modelling attempts have been made to account for this effect. Understanding these fouling mechanisms is crucial to optimizing industrial processes and mitigating fouling-related problems.

SHEAR FORCES EXERTED THROUGH FLOW

Flow properties play a pivotal role in crystallisation fouling, as the forces exerted by the moving fluid on the fouled surface influence the detachment rates of foulants.

Increased Deposition at Higher Flow Rates

Experimental evidence indicates that an increase in flow velocity can lead to a higher rate of fouling deposition $10,30-32$. This increase is primarily attributed to the increased transport of reactive substances to the surface, especially in systems where transport is the limiting factor. It is worth mentioning that this effect depends on the properties of the crystals being formed and the distribution of shear stress across the surface ⁵.

Decreased Deposition at Higher Flow Rates

Studies also show that increased flow velocities can reduce overall deposition rates $33-39$. This reduction is attributed to an increase in shear forces that promote detachment of foulants from the surface. This reduction often exhibits an asymptotic behaviour 40,41, indicating a balance between deposition and detachment forces at certain flow rates.

PROMOTING DETACHMENT

Detachment processes can be effectively promoted in industrial settings by adjusting process parameters ⁴². This requires understanding the strength of the foulant and applying sufficient external shear forces to overcome it. We explore strategies to reduce adhesion strength and increase external forces to mitigate fouling.

Engineered Surface Adhesion

Modifying the adhesion properties of a surface presents a proactive strategy to combat fouling 43 . Techniques include employing magnetic slippery surfaces ⁴⁴, low-surface energy coatings, and altering wetting behaviour 45 to reduce adhesion of foulants to the surface. Liquid-infused surfaces (LIS) offer excellent antifouling properties by enhancing the ability of surfaces to repel foulants, although their durability under operational conditions can be a concern ⁴⁶. Advances in surface engineering, such as robust ferromagnetic coatings, have demonstrated significant reductions in fouling by lowering adhesion strength, enabling easier detachment at lower shear stresses 44 .

Shear Stress Modification

Increasing shear stress is an effective method to promote the detachment of fouling deposits. This can be achieved through design modifications that create flow constrictions, alter linear velocities, or modify the solution's inherent shear stress. Techniques include:

- **Flow Field Alteration**: The introduction of baffles or orifices can isolate and improve linear shear force, significantly reducing fouling $47,48$.
- **Vibration-Induced Shear Stress**: Applying vibratory shear-enhanced processes (VSEP) to systems such as membranes can effectively mitigate fouling, especially in handling softer foulants⁴⁹.
- **High-Pressure Injections**: Employing high-pressure liquid injections or gas bursts can alter surface shear stresses, proving effective in removing even tenacious scales such as $BaSO₄$ ⁵⁰.

Practical Considerations for Industrial Application

Although engineered surfaces and shear stress modifications offer promising avenues for fouling mitigation, their application must be tailored to the specific industrial context. Factors such as the nature of the foulant, operational conditions, and economic considerations are crucial in determining the most effective strategy. For instance, vibrationinduced shear stresses may be effective for soft scales, while harder scales might require more aggressive interventions like high-pressure liquid scouring.

Additionally, the integration of these strategies requires evaluating their potential impact on system efficiency and maintenance requirements. The choice between surface engineering and shear stress modification will depend on the expected lifespan of the modification, the ease of implementation, and the overall cost-effectiveness of the solution.

CONCLUSION

We have presented an overview of the critical aspects of crystallisation fouling detachment, covering interactions at the surface level, the effects of flow dynamics, and the strategies for promoting detachment processes.

We explored substrate-foulant interactions and the importance of surface properties, such as composition and morphology, and demonstrated the need for precision in the design and selection of materials. We showed how flow velocity can affect fouling rates and how it can be used to mitigate fouling.

We conclude that future models could improve accuracy through updating the detachment term.

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