# REVIEWING DETACHMENT PROCESSES IN CRYSTALLISATION FOULING: IMPLICATIONS FOR ACCURATE PREDICTIONS

\*I.A. Løge<sup>1</sup>, and B.U. Anabaraonye<sup>2</sup>

<sup>1</sup> Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads 2800 Kongens Lyngby, Denmark, isacl@kt.dtu.dk

<sup>2</sup> Danish Offshore Technology Centre, Technical University of Denmark, Elektrovej, 2800 Kongens Lyngby, Denmark

# 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 <sup>1</sup>. 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 rates <sup>2</sup>.

Most implementations of the detachment term  $(m_d)$  in the literature are based on the interaction between the strength of the foulants  $(\sigma)$ , and the stress exerted on them  $(\tau)^3$ .

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

This model has been expanded to include properties such as density  $(\rho_f)$ , intercrystalline adhesion (*P*), particle size  $(d_p)$ , temperature change  $\Delta T$ , density of the liquid  $(\rho)$ , thickness of the fouling layer  $(x_{\theta})$  and the velocity of the liquid (*w*) <sup>4</sup>:

$$\dot{m_d} = \frac{\kappa_2}{P} \rho_f (1 + \delta \Delta T) d_p (\rho^2 \eta g)^{\frac{1}{3}} x_\theta w^2$$
(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-off <sup>5</sup>, supersaturation-induced crystal resilience <sup>6,7</sup>, and composite fouling <sup>8,9</sup>.

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<sup>10–14</sup>.

#### Surface Morphology

The physical structure of a surface, or its morphology, also plays a crucial role in fouling <sup>5,15–</sup><sup>18</sup>. Surfaces with rough textures can provide more nucleation sites for foulant deposition <sup>19</sup>, 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 <sup>20</sup> and enhanced advection (fluid movement that can carry foulants to the surface) <sup>5</sup>. Other studies have found that changes in roughness had minimal impact on deposition rates, suggesting that other factors might be at play <sup>21,22</sup>.

## **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 <sup>23</sup>, and need to be better understood. The presence of multiple foulants can alter the adhesion strength and detachment rates of the fouling layer <sup>8</sup>. 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<sup>8</sup>. 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 <sup>24</sup>. The interaction between particulates and crystals canaffects deposition rates based on size, composition, and shear stress <sup>25</sup>. Currently, one model accounts for particulate fouling <sup>26</sup>, 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 <sup>27–29</sup>. 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 <sup>10,30–32</sup>. 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 <sup>5</sup>.

## **Decreased Deposition at Higher Flow Rates**

Studies also show that increased flow velocities can reduce overall deposition rates <sup>33–39</sup>. 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 <sup>40,41</sup>, 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 <sup>42</sup>. 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 <sup>43</sup>. Techniques include employing magnetic slippery surfaces <sup>44</sup>, low-surface energy coatings, and altering wetting behaviour <sup>45</sup> 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 <sup>46</sup>. 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 <sup>44</sup>.

#### **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 <sup>47,48</sup>.
- Vibration-Induced Shear Stress: Applying vibratory shear-enhanced processes (VSEP) to systems such as membranes can effectively mitigate fouling, especially in handling softer foulants <sup>49</sup>.
- **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 BaSO<sub>4</sub> <sup>50</sup>.

# 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.

# REFERENCES

- 1. EPSTEIN, N. Thinking about Heat Transfer Fouling: A  $5 \times 5$  Matrix. *Heat Transf. Eng.* **4**, 43–56 (1983).
- Løge, I. A. *et al.* Scale attachment and detachment: The role of hydrodynamics and surface morphology. *Chem. Eng. J.* 430, 132583 (2022).
- Taborek, J., Aoki, T., Ritter, R. B., Palen, J. W. & Knudsen, J. G. Fouling: The Major Unresolved Problem in Heat Transfer. in *Chemical Engineering Progress* 59-- 67 (1972).
- 4. Bohnet, M. Fouling of heat transfer surfaces. *Chem. Eng. Technol.* **10**, 113–125 (1987).
- Løge, I. A. *et al.* Scale attachment and detachment: The role of hydrodynamics and surface morphology. *Chem. Eng. J.* 430, 132583 (2021).
- Løge, I. A., Anabaraonye, B. U., Bovet, N. & Fosbøl, P. L. Crystal Nucleation and Growth: Supersaturation and Crystal Resilience Determine Stickability. *Cryst. Growth Des.* 23, 2619–2627 (2023).
- Løge, I., Dragani, T. & Anabaraonye, B. Decoupling Inhibitor Mechanisms in Surface and Bulk Processes: Studies of BaSO<sub>4</sub>. Cryst. Growth Des. 23, 8518–8526.
- Løge, I. A., Anabaraonye, B. U. & Fosbøl, P. L. Growth mechanisms for composite fouling: The impact of substrates on detachment processes. *Chem. Eng. J.* 446, 137008 (2022).
- Løge, I. A., Anabaraonye, B. U. & Loldrup Fosbøl, P. Characterizing the Effect of Scale Inhibitors on Surfaces. in SPE International Conference on Oilfield Chemistry (2023). doi:10.2118/213830-MS.
- Al-Hadhrami, L. M. & Quddus, A. Role of solution hydrodynamics on the deposition of CaSo4 scale on copper substrate. *Desalin. Water Treat.* 21, 238–246 (2010).
- Quddus, A. & Al-Hadhrami, L. M. Impact of solution hydrodynamics on the deposition of CaSO4 on brass. *Desalin. Water Treat.* 50, 285–293 (2012).
- 12. Quddus, A. Effect of hydrodynamics on the deposition of CaSO4 scale on stainless steel. *Desalination* **142**, 57–63 (2002).
- Al-Hadhrami, L. M., Quddus, A. & Al-Otaibi, D. A. Calcium sulfate scale deposition on coated carbon steel and titanium. *Desalin. Water Treat.* 51, 2521– 2528 (2013).
- Quddus, A. & Al-Hadhrami, L. M. Hydrodynamically deposited CaCO3 and CaSO4 scales. *Desalination* 246, 526–533 (2009).

- Kazi, S. N., Duffy, G. G. & Chen, X. D. Mineral scale formation and mitigation on metals and a polymeric heat exchanger surface. *Appl. Therm. Eng.* **30**, 2236–2242 (2010).
- 16. Al-gailani, A. *et al.* Role of temperature , roughness and pressure in crystallization fouling from potable water on aluminium surface. *Therm. Sci. Eng. Prog.* **23**, 100911 (2021).
- Berce, J., Zupancic, M., Moze, M. & Golobic, I. A Review of Crystallization Fouling in Heat Exchangers. *PROCESSES* 9, (2021).
- Doyle, J. D., Oldring, K., Churchley, J. & Parsons, S. A. Struvite formation and the fouling propensity of different materials. *J. Mol. Liq.* 36, 3971–3978 (2002).
- Keysar, S., Semiat, R., Hasson, D. & Yahalom, J. Effect of Surface Roughness on the Morphology of Calcite Crystallizing on Mild Steel. *J. Colloid Interface Sci.* 162, 311–319 (1994).
- Wu, Z., Davidson, J. H. & Francis, L. F. Effect of water chemistry on calcium carbonate deposition on metal and polymer surfaces. J. Colloid Interface Sci. 343, 176– 187 (2010).
- Jin, H. Q., Athreya, H., Wang, S. & Nawaz, K. Experimental study of crystallization fouling by calcium carbonate: Effects of surface structure and material. *Desalination* 532, 115754 (2022).
- Vazirian, M. M., Charpentier, T. V. J., de Oliveira Penna, M. & Neville, A. Surface inorganic scale formation in oil and gas industry: As adhesion and deposition processes. J. Pet. Sci. Eng. 137, 22–32 (2016).
- 23. Yang, Y. *et al.* Characterization, formation and development of scales on L80 steel tube resulting from seawater injection treatment. *J. Pet. Sci. Eng.* **193**, 107433 (2020).
- Wang, Y. *et al.* Interaction between particulate fouling and precipitation fouling: Sticking probability and deposit bond strength. *Int. J. Heat Mass Transf.* 144, 118700 (2019).
- 25. Andritsos, N. & Karabelas, A. J. Calcium carbonate scaling in a plate heat exchanger in the presence of particles. *Int. J. Heat Mass Transf.* **46**, 4613–4627 (2003).
- Sheikholeslami, R. Calcium sulfate fouling

   precipitation or particulate: A proposed composite model. *Heat Transf. Eng.* 21, 24–33 (2000).
- Thompson, J. *et al.* RO membrane mineral scaling in the presence of a biofilm. *J. Memb. Sci.* 415–416, 181–191 (2012).

- Sheikholaslami, R. Composite fouling inorganic and biological: A review. *Environ. Prog.* 18, 113–122 (1999).
- 29. Stotzky, G. Influence of clay minerals on microorganisms: III. Effect of particle size, cation exchange capacity and surface area on bacteria. *Can. J. Microbiol.* **12**, (1966).
- Hoang, T. A., Ang, M. & Rohl, A. L. Effects of Process Parameters on Gypsum Scale Formation in Pipes. *Chem. Eng. Technol.* 34, 1003–1009 (2011).
- Muryanto, S., Bayuseno, A. P., Ma'mun, H., Usamah, M. & Jotho. Calcium Carbonate Scale Formation in Pipes: Effect of Flow Rates, Temperature, and Malic Acid as Additives on the Mass and Morphology of the Scale. *Procedia Chem.* 9, 69–76 (2014).
- Bogacz, W. *et al.* Impact of roughness, wettability and hydrodynamic conditions on the incrustation on stainless steel surfaces. *Appl. Therm. Eng.* **112**, 352–361 (2017).
- Alahmad, M. Factors affecting scale formation in sea water environments - An experimental approach. *Chem. Eng. Technol.* 31, 149–156 (2008).
- Lee, S. & Lee, C. H. Effect of operating conditions on CaSO4 scale formation mechanism in nanofiltration for water softening. *Water Res.* 34, 3854–3866 (2000).
- Mwaba, M. G., Rindt, C. C. M., Van Steenhoven, A. A. & Vorstman, M. A. G. Experimental investigation of CaSO 4 crystallization on a flat plate. *Heat Transf. Eng.* 27, 42–54 (2006).
- 36. Li, W., Su, X., Palazzolo, A., Ahmed, S. & Thomas, E. Reverse osmosis membrane, seawater desalination with vibration assisted reduced inorganic fouling. *Desalination* 417, 102–114 (2017).
- Dong, L., Crittenden, B. D. & Yang, M. Fouling Characteristics of Water–CaSO4 Solution under Surface Crystallization and Bulk Precipitation. *Int. J. Heat Mass Transf.* 180, 121812 (2021).
- Kho, T., Zettler, H. U., Müller-Steinhagen, H. & Hughes, D. Effect of flow distribution on scale formation in plate and frame heat exchangers. *Chem. Eng. Res. Des.* **75**, 635– 640 (1997).
- Khormali, A. & Ahmadi, S. Prediction of barium sulfate precipitation in dynamic tube blocking tests and its inhibition for waterflooding application using response surface methodology. J. Pet. Explor. Prod. Technol. (2023) doi:10.1007/s13202-023-01679-2.
- 40. Løge, I. A. *et al.* Revealing the complex

spatiotemporal nature of crystal growth in a steel pipe: Initiation, expansion, and densification. *Chem. Eng. J.* **466**, 143157 (2023).

- Godinho, J. R. A., Gerke, K. M., Stack, A. G. & Lee, P. D. The dynamic nature of crystal growth in pores OPEN. *Nat. Publ. Gr.* (2016) doi:10.1038/srep33086.
- Appelquist Løge, I., U. Anabaraonye, B., Bovet, N. & Loldrup Fosbøl, P. Crystal Nucleation and Growth: Supersaturation and Crystal Resilience Determine Stickability. *Cryst. Growth & amp; Des.* 23, 2619–2627 (2023).
- Eroini, V., Neville, A., Kapur, N. & Euvrard, M. Preventing Scale Formation Using Modified Surfaces. in *Corrosion* 1– 15 (2011).
- 44. Masoudi, A., Irajizad, P., Farokhnia, N., Kashyap, V. & Ghasemi, H. Antiscaling Magnetic Slippery Surfaces. *ACS Appl. Mater. Interfaces* 9, 21025–21033 (2017).
- Mousavi, S. M. A. & Pitchumani, R. Temperature-dependent dynamic fouling on superhydrophobic and slippery nonwetting copper surfaces. *Chem. Eng. J.* 431, 133960 (2022).
- Villegas, M., Zhang, Y., Abu Jarad, N., Soleymani, L. & Didar, T. F. Liquid-Infused Surfaces: A Review of Theory, Design, and Applications. ACS Nano 13, 8517–8536 (2019).
- Hasan, B. O., Nathan, G. J., Ashman, P. J., Craig, R. A. & Kelso, R. M. The use of turbulence generators to mitigate crystallization fouling under cross flow conditions. *Desalination* 288, 108–117 (2012).
- 48. Crittenden, B. D. *et al.* Crystallization fouling with enhanced heat transfer surfaces. *Heat Transf. Eng.* **36**, 741–749 (2015).
- Shi, W. & Benjamin, M. M. Fouling of RO membranes in a vibratory shear enhanced filtration process (VSEP) system. *J. Memb. Sci.* 331, 11–20 (2009).
- Bukharin, N., El Hassan, M., Omelyanyuk, M. & Nobes, D. Applications of cavitating jets to radioactive scale cleaning in pipes. *Energy Reports* 6, 1237–1243 (2020).