Experimental report

11/07/2024

Proposal:	**9-10-1750**	**Council:**	10/2022
Title:	Thickness of foam thin films in forced drainage experiments: metal leaching application		
Research area:	Engineering		

This proposal is a new proposal

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Samples: D2O
cupper chloride
BrijO10, polyoxyethylene alkyl ether

Instrument	Requested days	Allocated days	From	To
D33	1	1	01/07/2023	02/07/2023
D22	1	0		

Abstract:

Metal leaching requiring an oxidizing gas is more efficient in foam than in solution. However, the control of the liquid in foam and especially in the thin film between bubbles through which the gas has to permeate is critical. During a metal leaching process using foam, this metastable soft structure that is foam swells and de-swells with an impact on its stability. Two different scales are affected: the foam liquid channels (sub-micron scale) and the inter-bubble thin film (10-100 nm). We have recently demonstrated that SANS technique is perfectly suitable to probe simultaneously these two scales within foam and to observe different kinetics of its structure evolution that brings a lot for the understanding for the process and finally its optimisation. The objective of this proposal is to probe by SANS technique a foam structure under controlled forced drainage conditions and this for the first time.

Thickness of foam thin films in forced drainage experiments: metal leaching application

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Context of the SANS study:

With the aim of developing green alternatives to hydrometallurgy, we are working on leaching aqueous foams, which could allow to drastically decrease the volume of effluents, as the leaching liquid phase represents less than 10 % of the total volume. We have established proof of concept that copper (Cu) can be oxidized by oxygen O_2 present in the gas bubbles, in the presence of chlorhydric acid HCl in the continuous phase (equation 1). These foams are stabilized by a non-ionic surfactant, polyoxyethylene alkyl ether.

$$2\,Cu + O_2 + 4\,H^+ \rightarrow 2\,Cu^{2+} + 2\,H_2O \quad \text{(Eq. 1)}$$

To study for the impact of foam structure, we elaborated a specific set-up allowing to change the liquid fraction within the foam through forced drainage (see Figure 1).

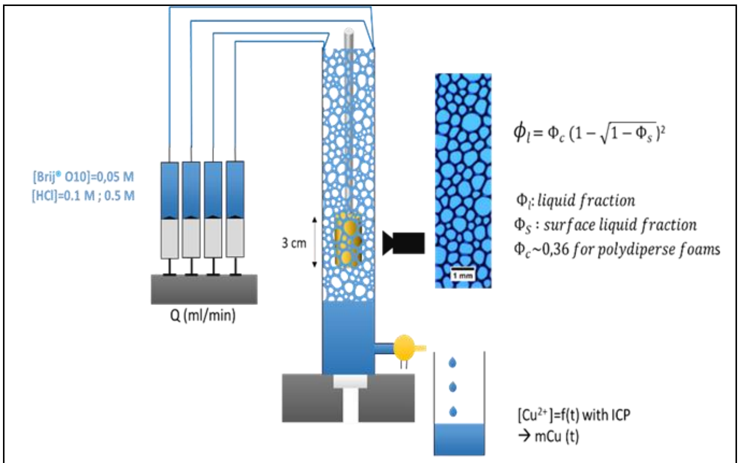

Figure 1. Forced drainage set-up

We have seen that the mass of dissolved copper presents a maximum with the flow rate, Q. We have attributed this behavior to the existence of two regimes in the transfer of reactants: at low flow rate, the reaction is limited by the quantity of H^+ ions, hence the higher the flow rate the higher the amount of Cu^{2+} produced. At high Q and ϕ_l, the reaction is probably limited by the quantity of O_2 in the system. We suggest that the diffusion of O_2 through the thin liquid films probably becomes slower with Q and ϕ_l because either of the decrease of the surface area of the thin film and/or because of the increase of the film thickness which reduces the permeability of the thin liquid films. [1]

The goal of this project is to determine how the foam structure controls the reactants transfer in the foam and hence the reaction kinetics.

Preliminary analysis and results obtained from SANS measurements:

Foam was formed by bubbling through a porous frit at a controlled flow rate and then let to freely drain during 60 minutes. Foaming solution was then reinjected at the top of the foam at various flow rate. Afterwards, the foam was let to freely drain a second time. We have performed SANS measurements every 3 minutes along the whole experiment. Herein we will present the results obtained for a flow rate of 0.4 mL/min imposed for 45 minutes.

Analysis of the SANS curves includes 3 major contributions:

- fit of the micelles signal, predominant in high-q region, obtained separately from other SANS measurements recorded in solution;

- fit of the films signal, predominant in mid-q region, based on reflectivity;
- fit of the Plateau borders signal, predominant in low-q region, based on a Porod contribution.

The curves obtained were individually fitted with the model developed (see reference [2] for first version of the model), as can be seen on Figure 2. Fitted parameters have a physical meaning such as thin films thickness, or specific surface of films, and the found values are discussed below.

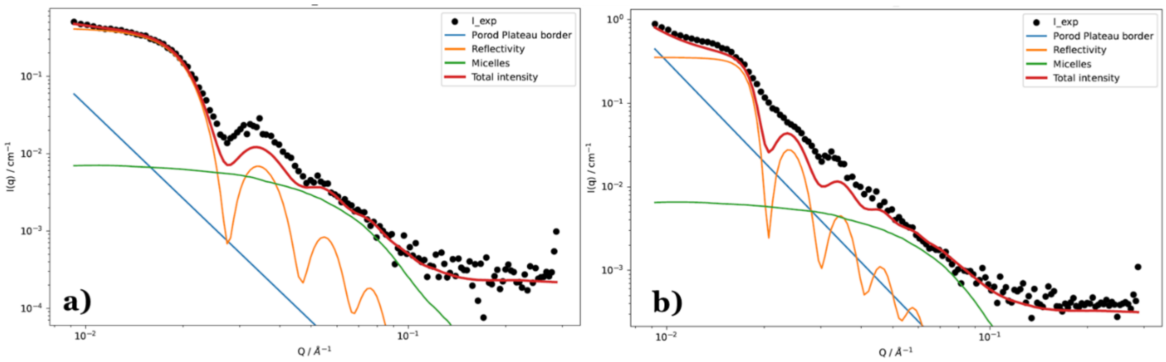

Figure 2. Examples of fitted SANS data acquired from the foam (a) after 60 min of free drainage succeeding to foaming (b) during forced drainage at a flowrate of 0.4 mL/min

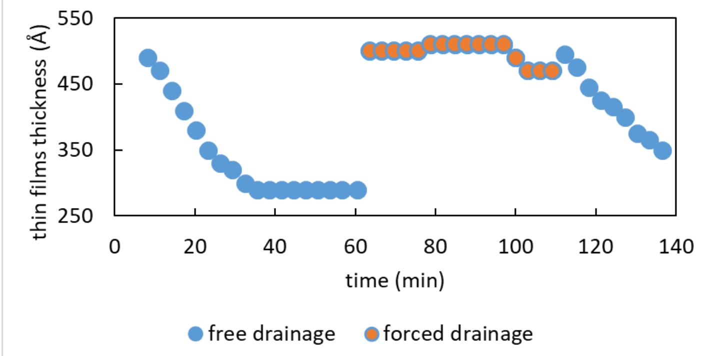

Figure 3. Evolution of thin films thickness across time determined from SANS measurements

One can see on Figure 3 that the thickness of foam films increases as soon as forced drainage begins. It decreases rapidly as forced drainage is stopped.

One can see on Figure 4 that Plateau borders specific surface increases during forced drainage and abruptly decreases as soon as forced drainage stops (see triangle shapes). This proves that they are filled with liquid during forced drainage, which cause a rise in size and thus exhibiting more surfaces for the same probed volume.

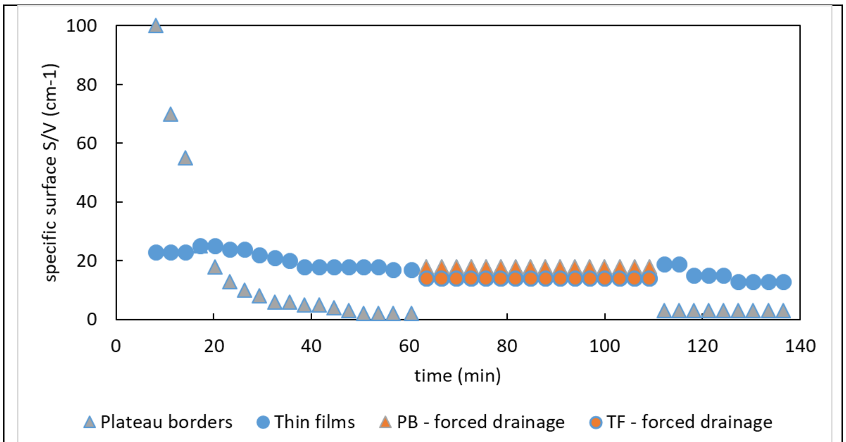

Figure 4. Evolution of specific surface of Plateau borders (PB) and thin films (TF) across time determined from SANS measurements

Interestingly, one can see on Figure 4 that films specific surface stays constant (see round shapes), i.e., that the total surface exhibited by films does not change within the probed volume, even during forced drainage. Thus, we infer that films keep their faceted shape.

Preliminary conclusion

Injecting liquid within the foam does not seem to play on the surface area of thin films but rather on their thickness. Analysis are still ongoing for other flowrates as well as on interpretation of the two phases of free drainage.

References

[1] Trinh P, Mikhailovskaya A, Lefèvre G, et al. Relation between oxidation kinetics and reactant transport in an aqueous foam. *J Colloid Interface Sci* 2023; 643: 267–275.

[2] Lamolinairie J, Dollet B, Bridot J-L, et al. Probing foams from the nanometer to the millimeter scale by coupling small-angle neutron scattering, imaging, and electrical conductivity measurements. *Soft Matter* 2022; 18: 8733–8747.