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SEMI-BATCH CRYSTALLIZATION OF GYPSUM FROM CALCITE AND SULFURIC ACID

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One of the most important environmental issues for decades to come is the treatment of industrial wastewaters containing salts (sulfates, chlorides, sodium, magnesium ...) which can lead to strong perturbations affecting the fauna and flora when highly concentrated at the discharge point.
Different processes used to separate the dissolved salts from the liquid matrix may be encountered depending on the nature and the composition of the effluent. One major objective in the R&D sectors of water and environment is to optimize such processes, while another is to promote the treated wastewaters by recycling the cleared liquid phase or reusing some compounds they contain in other production processes. The latter is of great interest, both to limit the amount of waste and to save natural resources including rare metals but also less noble materials whose amount consumed each year is very important, but the one available not unlimited.
Gypsum, the most important raw material of plaster's industry, is a rather interesting example from this point of view as world's known resources are estimated at 2.34 billion tons, which roughly represents 25 years of operation. The industry of plaster will therefore meet in the coming decades a decrease in resources for the commodity, especially in some countries where gypsum deposits will eventually become out of reach or completely depleted.

This study thereby focuses on the precipitation of gypsum in a semi-batch laboratory-scale installation modeling the neutralization of a sulphuric acid solution by injection of a diluted limestone suspension. The generation of the supersaturation of the calcium sulphate is then obtained through the gradual dissolution of calcite particles providing accumulation of calcium ions in the solution.
Particular attention is paid to the direct conversion of calcite into gypsum beginning with the rapid formation of an overlayer of gypsum instantaneously nucleated on the surface of calcite particles (see figure 1) and delaying the dissolution process as previously mentioned by Booth *et al*[1]. This phenomenon is of first importance with regards to the process as it highly impacts both of the size and shape of the precipitated gypsum crystals through the kinetic control it exerts on the liberation of calcium ions in solution.
Effects of temperature (20°C, 40°C and 60°C), concentration of sulphate (0.15M, 0.30M and 0.60M), mean particle size of calcite powder (25µm, 35µm and 55µm) and inlet flow of calcite suspension (10ml/min, 5ml/min and 2.5ml/min) are investigated.

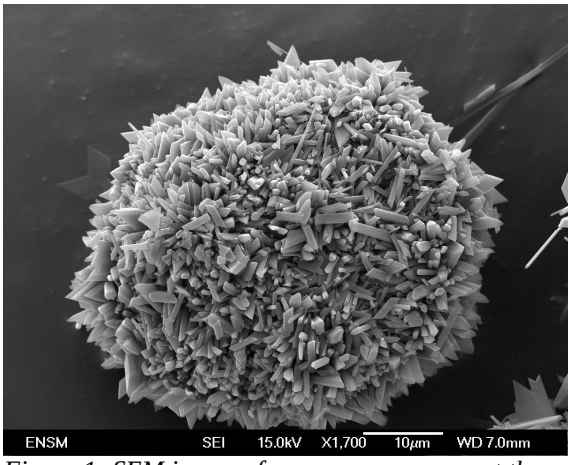

Figure 1: SEM image of gypsum overgrown at the surface of a calcite particle.

Figures 2 to 5 expose total calcium concentration vs. total sulphate concentration curves reflecting the generation of the supersaturation during the injection of the calcite suspension. Additional experimental measurements are conducted to get the concentration of calcium at different concentration of sulphate in conditions of equilibrium with gypsum. Final particle size distributions are also exposed aside.
Temperature has been found to increase the supersaturation while being decreased. At 20°C and 60°C, formation of gypsum occurs preferentially by precipitation onto the surface of calcite particles rather than from solution (Figure 2).
Acid concentration has been found to increase the supersaturation while being decreased. Starting with a high sulphate concentration provide a quasi-exclusive precipitation on the surface of calcite particles while starting with lower acid concentrations favours precipitation from solution (Figure 3).
The smaller the calcite particles, the higher the peak of supersaturation reached before precipitation occurs. The use of smaller particles of calcite in the feeding suspension also leads to a solid product in which the particles precipitated from the solution prevail (Figure 4).
The slower the inlet flow of suspension, the closer the supersaturation to equilibrium concentration. Decreasing the inlet flow results in favouring the precipitation of gypsum onto the surface of calcite particles (Figure 5).
The higher supersaturation level reached by decreasing calcite particle size finds its origin clearly in the increase in calcite reactive surface for a given mass of calcium carbonate which provides quicker liberation of calcium, and the lower supersaturation level reached by decreasing the inlet flow of suspension may find a reasonable explanation in a lower rate of injection of calcium towards the rate of dissolution of calcite. However, modifications of the behaviour of the mixture induced by temperature and acid concentration appear to be more difficult to explain without taking in account the conversion mechanism of calcite particles into gypsum.

The present study aims to purpose a reaction – diffusion mechanism for calcite particles based on calcium mass balance equation (1) which might explain the delaying role played by the gypsum layer in the liberation of calcium in solution.

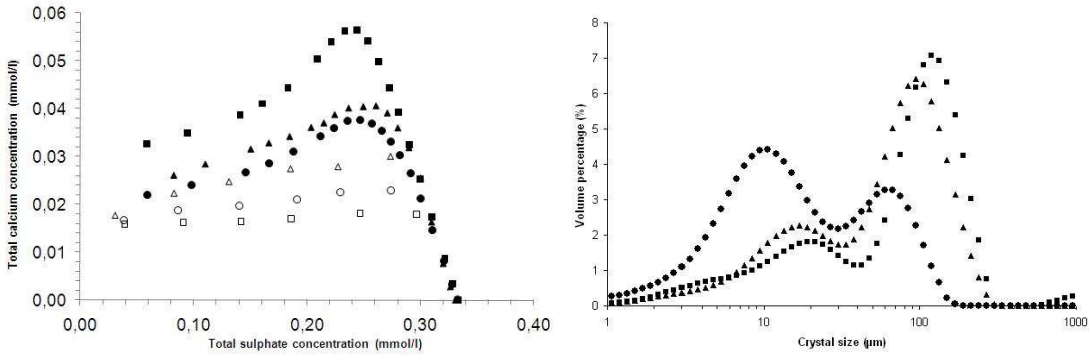

Figure 2: *Total calcium vs. Total sulphate concentrations measured by ICP-AES (on the left) and final particle size distribution measured by laser granulometer (on the right) in experiments conducted at 20°C (squares), 40°C (dots) and 60°C (triangles). Empty symbols represent concentrations measured in conditions of equilibrium with gypsum.*

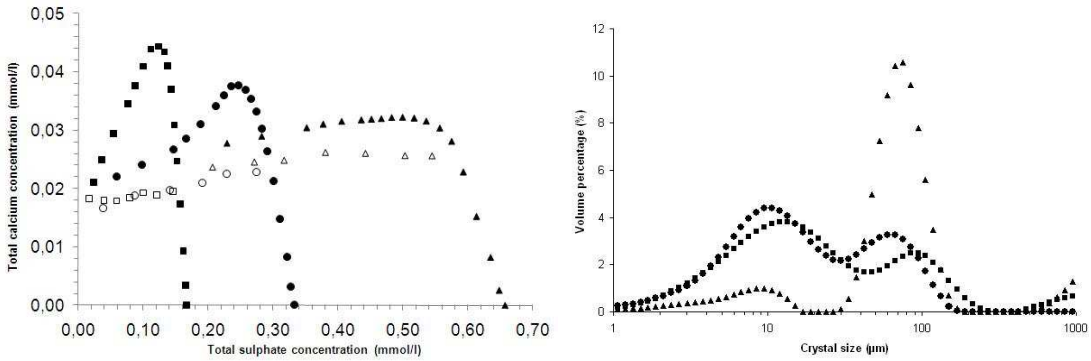

Figure 3: *Total calcium vs. Total sulphate concentrations measured by ICP-AES (on the left) and final particle size distribution measured by laser granulometer(on the right) in experiments conducted with 0.15M (squares), 0.30M (dots) and 0.6M (triangles) initial sulphate concentrations. Empty symbols represent concentrations measured in conditions of equilibrium with gypsum.*

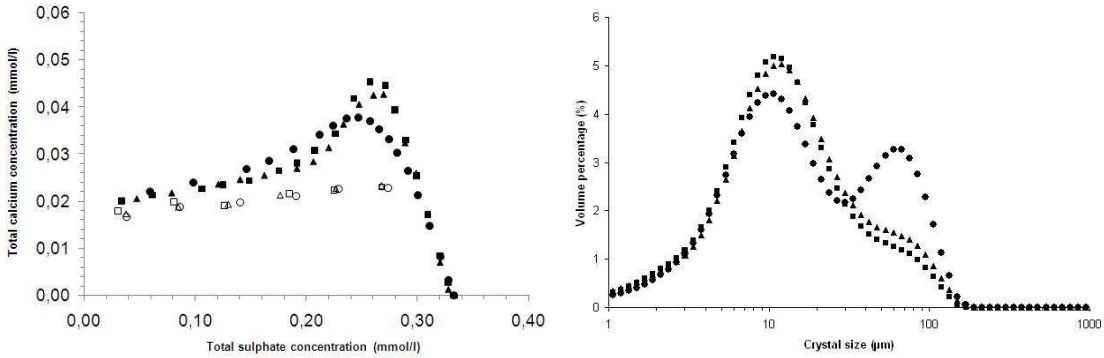

Figure 4: *Total calcium vs. Total sulphate concentrations measured by ICP-AES (on the left) and final particle size distribution measured by laser granulometer (on the right) in experiments conducted with 25µm (squares), 35µm (triangles) and 55µm (dots) mean particle size of calcite powder. Empty symbols represent concentrations measured in conditions of equilibrium with gypsum.*

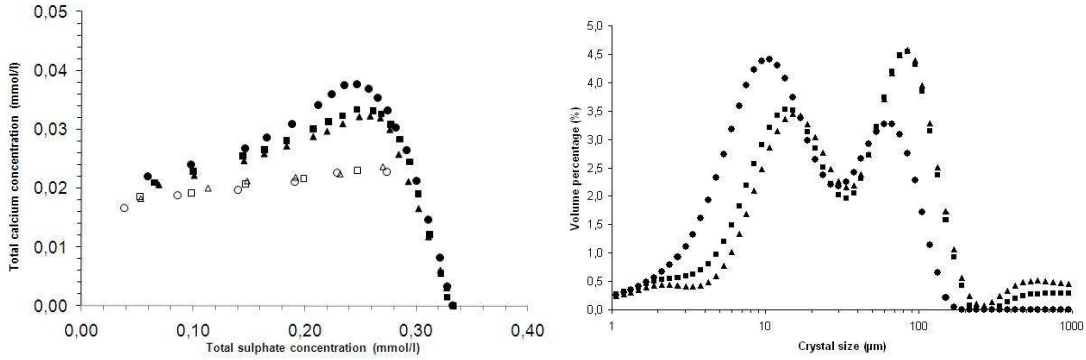

Figure 5: Total calcium vs. Total sulphate concentrations measured by ICP-AES (on the left) and final particle size distribution measured by laser granulometer(on the right) in experiments conducted with 10ml/min (dots), 5ml/min (squares) and 2.5ml/min (triangles) inlet flow of calcite suspension. Empty symbols represent concentrations measured in conditions of equilibrium with gypsum.

$$S_r.k_d.C^s_{H^+} = S_r.k_g.\left(C^s_{Ca^{2+}} - C^*_{Ca^{2+}}\right)^2 + S_r\frac{D^{eff}_{Ca^{2+}}}{e}\left(C^s_{Ca^{2+}} - C^b_{Ca^{2+}}\right) \quad (1)$$

S_r	Reactive surface	m^2
k_d	Rate constant for calcite dissolution	$m.s^{-1}$
$C^s_{H^+}$	Proton concentration at calcite/gypsum interface	$mol.m^{-3}$
k_g	Rate constant for gypsum precipitation	$m^4.s^{-1}.mol^{-1}$
$C^s_{Ca^{2+}}$	Calcium concentration at calcite/gypsum interface	$mol.m^{-3}$
$C^*_{Ca^{2+}}$	Calcium concentration at equilibrium with gypsum	$mol.m^{-3}$
$C^b_{Ca^{2+}}$	Calcium concentration in the bulk solution	$mol.m^{-3}$
$D^{eff}_{Ca^{2+}}$	Calcium coefficient for effective diffusion in gypsum layer	$m^2.s^{-1}$
e	thickness of the gypsum layer	m

Equation (1) is based on equality at calcite/gypsum layer interface between the fluxes of calcium liberated by the dissolution of calcite in one hand and consumed by gypsum precipitation and diffusion trough the gypsum layer in the other hand. The dissolution term in the left member is expressed as linear function of proton concentration as mentioned by Chou *et al*[2]. The first term of the second member shows the second order dependence of gypsum growth with absolute supersaturation in calcium as depicted in [3].

References:

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