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Clathrate hydrate crystallization in calcium sulfate solutions

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► **To cite this version:**

Jérôme Douzet, Juan David Alzate-Niño, Fernando Pereira, Daniel Garcia, Baptiste Bouillot, et al.. Clathrate hydrate crystallization in calcium sulfate solutions. 16ème Congrès de la Société Française de Génie des Procédés (SFGP 2017 NANCY), Jul 2017, Nancy, France. Ed. SFGP, Paris, France, Livre des résumés SFGP 2017, 110, 2017, Récents Progrès en Génie des Procédés. hal-01664071

HAL Id: hal-01664071

<https://hal.science/hal-01664071v1>

Submitted on 14 Dec 2017

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CLATHRATE HYDRATE CRYSTALLIZATION IN CALCIUM SULFATE SOLUTIONS

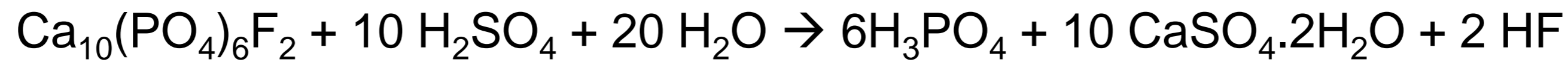


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Context

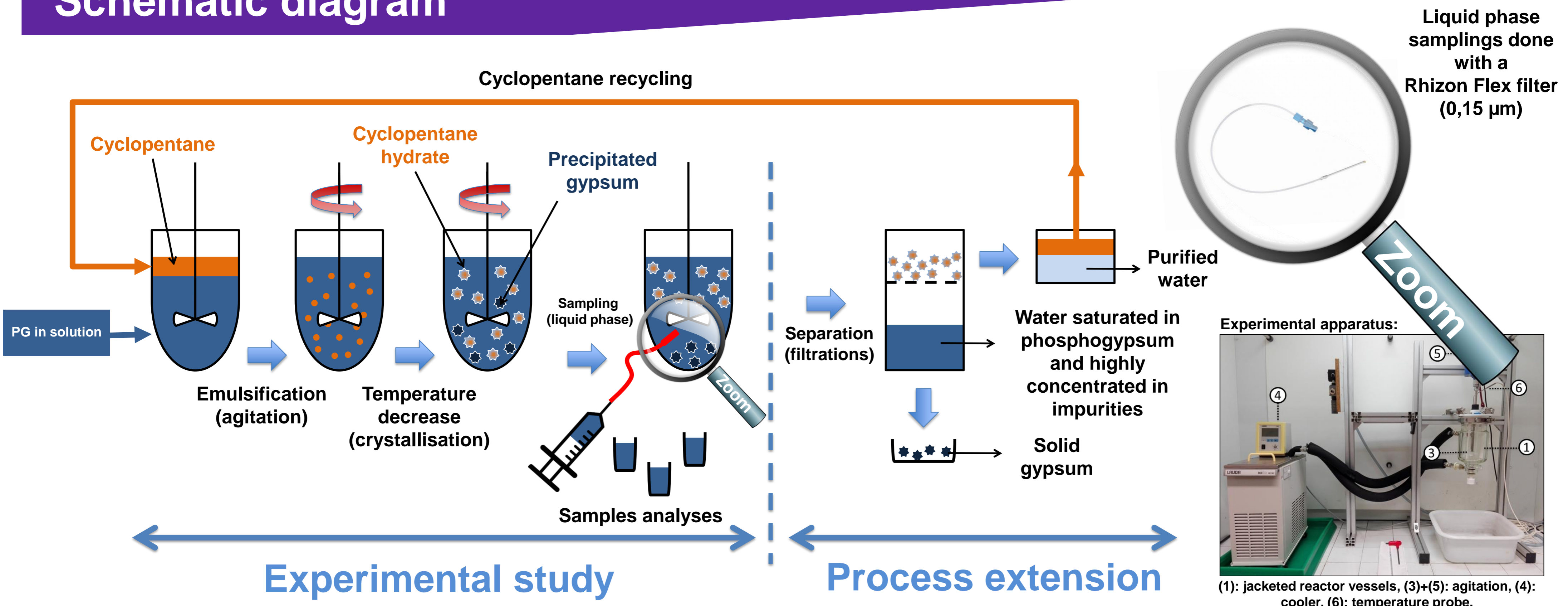
The industrial standard method for "Phosphate Rock" (PR) processing is a sulphuric acid wet digestion technique (due to its favourable economics), which produces "phosphoric acid" (PA) [H₃PO₄] and the waste product "PhosphoGypsum" (PG) [CaSO₄.2H₂O], as shown in the formula below:



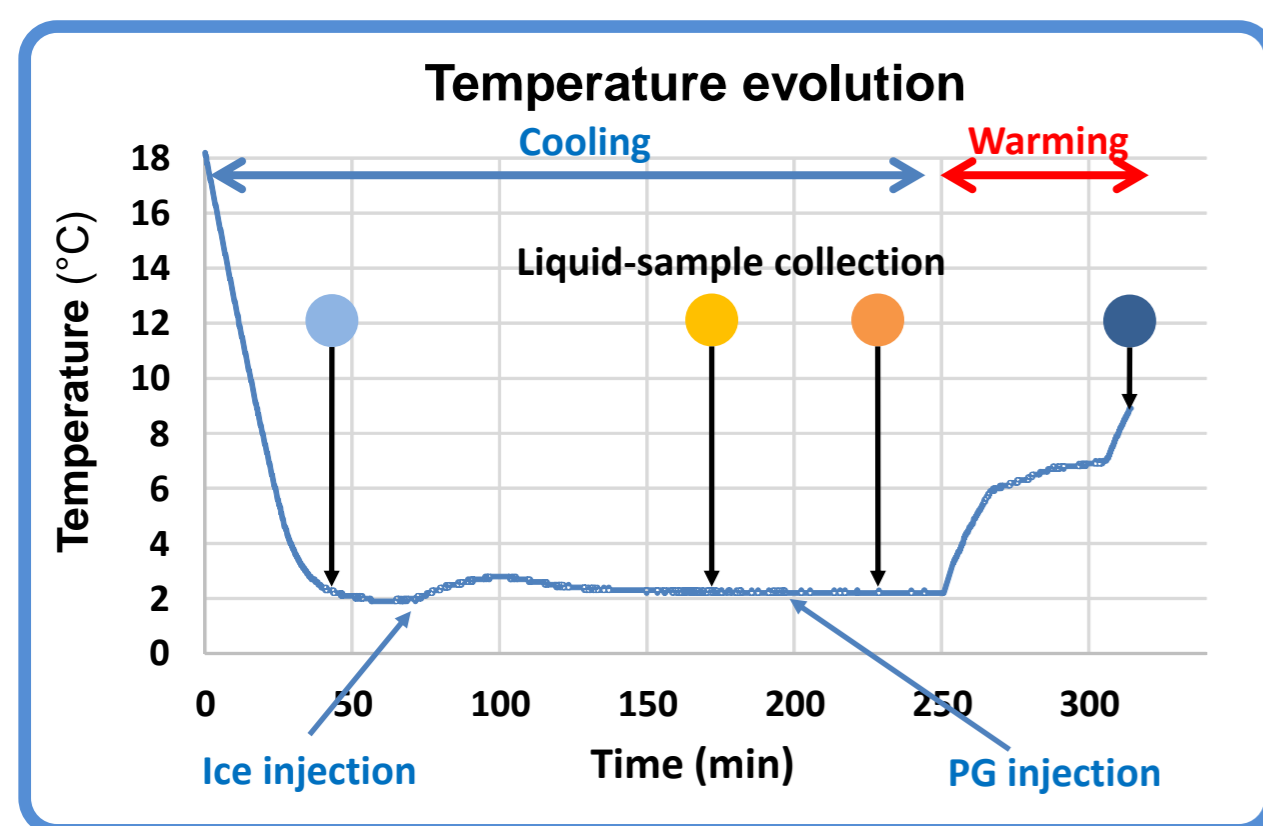
Large volumes of waste are produced using this reaction, which results in 5 tons of PG for every ton of PA generated. This "by-product", about 250 million tons per year, is today mostly disposed as a slurry into extensive tailings deposits. The significant legacy of existing PG waste piles means that methods must be developed to remediate these potential sources of air, soil and groundwater pollution. The only feasible way to do this is to transform that waste into a useable product that has a value, thus creating a favourable economic environment for investment and implementation. This requires PG purification.

PG is both a hazardous waste and a potential resource if its valuable compounds can be economically recovered. A practical goal in selecting a chemical route will be to separate the components as efficiently as possible from the each other with the final goal of near "zero waste", at the minimum cost. Instead of reprocessing PG stocks using another acid, we explore the washing route (*i.e.*, very dilute aqueous solution at moderate temperature). The goal in this case is to selectively dissolve the gypsum end-member in order to fractionate the phosphorous and the metals (light REEs, U, *etc.*) either in the water phase or in a solid residue. Since gypsum is not very soluble (2.4 g/l) in water, this option requires large amounts of water, thus driving an effort to improve the water-recycling technology. Cyclopentane (C₅H₁₀) forms hydrate at atmospheric pressure and at approximately 7 °C. It is an organic compound not miscible in water and in consequence easy to separate from water. Water is sequestered upon cyclopentane hydrate crystallization and purified after hydrate melting.

Schematic diagram

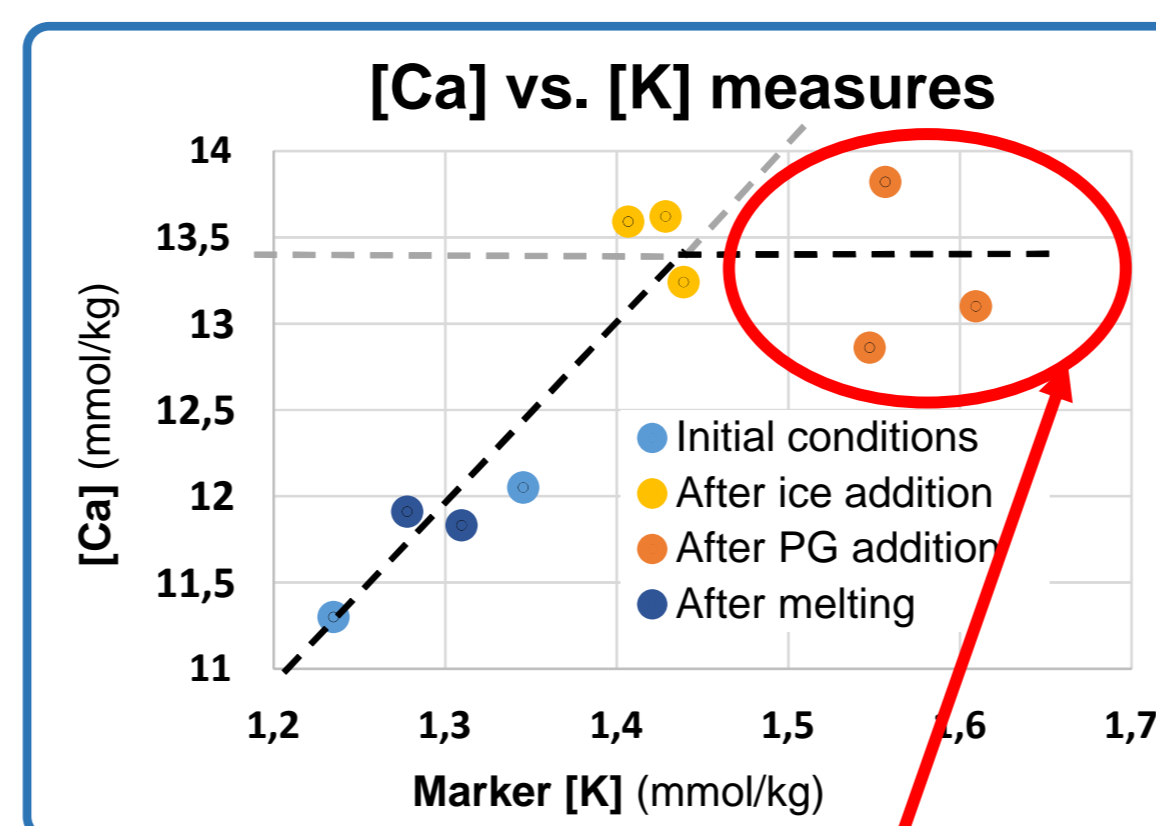


Experimental results



Ice injection allows to cause hydrates crystallisation

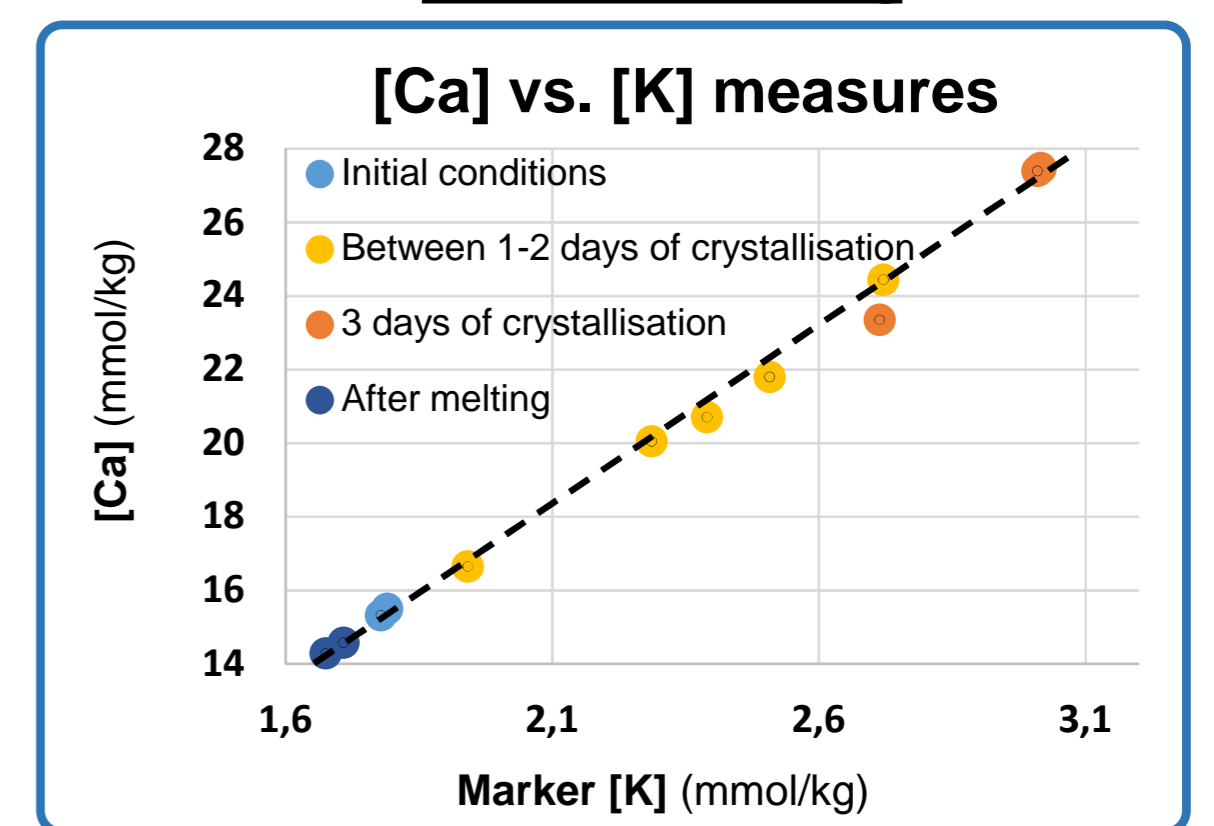
PG injection allows to cause gypsum precipitation



ICP/AES measures



Experimental testing of hydrates crystallisation without PG sowing



Ionic Chromatography measures



Conclusions

* The Ca concentration in the liquid phase no longer increases after PG injection → gypsum precipitation.

* The fact of non injecting PG shows that the Ca can be over-concentrated without causing gypsum precipitation.

