

# CLATHRATE HYDRATE CRYSTALLIZATION IN CALCIUM SULFATE SOLUTIONS

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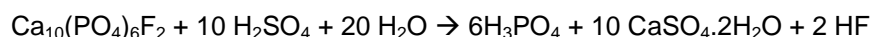
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## Abstract

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) [H<sub>3</sub>PO<sub>4</sub>] and the waste product "phosphogypsum" (PG) [CaSO<sub>4</sub>.2H<sub>2</sub>O], 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. There are three main and potentially valuable end-members in PG:

- calcium sulphate, hydrous (gypsum end-member) ;
- calcium phosphate, mostly substituted to calcium sulphate (brushite end-member) ;
- "Critical Raw Materials" (CRMs) [like "Rare Earth Elements" (REEs)], radioactive elements (e.g., U), toxic metals (e.g., Cd, etc.) collectively referred to as the metallic end-member.

A practical goal in selecting a chemical route will be to separate the three 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 (C<sub>5</sub>H<sub>10</sub>) forms hydrate at atmospheric pressure and at approximately 7 °C [1]. 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.

A schematic method of extracting gypsum from water by a co-crystallization with cyclopentane hydrates is given in Figure 1. The experiments are performed in a cooled and stirred classical double-jacketed vessel containing one liter of saturated gypsum solution by focusing on the feasibility of co-crystallization of gypsum and cyclopentane hydrates. The main results show that it is possible to sequester water in cyclopentane hydrate without precipitating gypsum, thus producing a solution substantially oversaturated with respect to gypsum. During the hydrate crystallization, the concentration of calcium increased over the solubility of gypsum without precipitation up to approximately the twice of the theoretical solubility. Conversely, it can be observed that in the

supersaturation conditions, the addition of gypsum seeds to the vessel allows to precipitate the excess concentration and to reach the equilibrium solubility in the liquid.

The poster will propose to give a brief report on the principal results obtained.

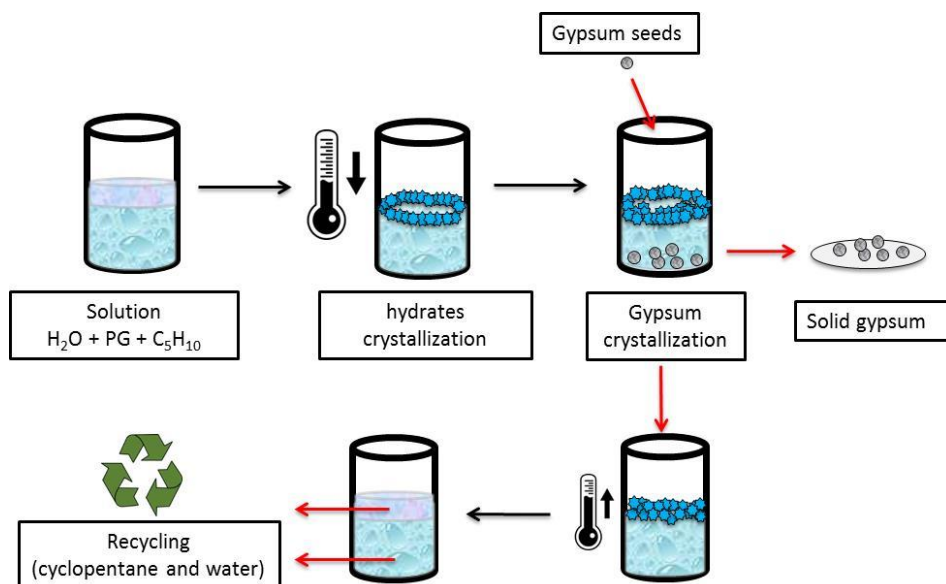


Figure 1. Schematic diagram of co-crystallization of hydrates and gypsum. Recycling of cyclopentane and water.

#### References:

- [1]. Nakajima M, Ohmura R, H. Mori Y. Clathrate hydrate formation from cyclopentane in water emulsions. Ind. Eng. Chem. Res. 2008, 47:8933-8939.