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Transforming phosphogypsum waste into products with market value

Ron Zevenhoven¹, Victor Morales-Floréz^{2,3}, Alberto J. Santos⁴ and Luis Esquivias^{2,3}

¹ Åbo Akademi University, Thermal and Flow Engineering Laboratory, 20500 Åbo/Turku, Finland

² University of Seville, Department of Condensed Matter, 41012 Seville, Spain

³ Institute of Materials Science of Seville, ICMS (CSIC/US), 41092 Seville, Spain

⁴ University of Cádiz, Department Earth Sciences, 11510 Puerto Real, Spain

Speaker: Ron Zevenhoven

Corresponding author: Ron Zevenhoven, ron.zevenhoven@abo.fi

Abstract

Vast amounts of phosphogypsum (PG) which is a by-product of phosphorous acid production from apatite rock using sulphuric acid, are deposited in large piles at many locations worldwide. PG materials are added at rates of the order of megatonnes (Mt) per annum. Recognising these PG piles to be a problem and a threat to the environment resulted in the development of technologies aiming at transforming these piles into useful products. The sheer amounts of PG material to be processed and the available markets for products make it necessary to use a portfolio of approaches.

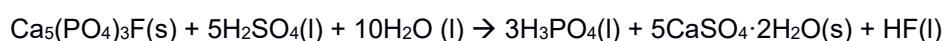
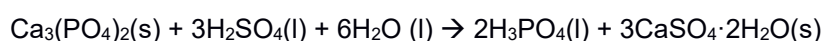
Researchers from Spain and Finland have investigated methods for converting PG into a precipitated calcium carbonate (PCC) and other products. While process conditions and equipment can be practically identical (similar near ambient temperatures and pressures, in aqueous solutions), the use of either ammonia and CO₂, or sodium hydroxide in the conversion processes can result in ammonium sulphate and calcium carbonate, or sodium sulphate and calcium hydroxide, which can bind CO₂, subsequently. Thereby, besides PG valorisation, large amounts of CO₂ can be also fixed into carbonates, thus, contributing to carbon emissions control strategies. Other waste streams have been successfully tested as possible reactants for converting PG such as soda-rich liquid waste from the aluminium industry. Important is the presence of rare earth elements and radionuclides in the PG, requiring special treatment while recovering materials with large market value. Aiming at products with high purity, the removal of phosphorus from PCC product may be necessary.

This paper summarises the work and findings that led to a joint approach towards processing 120 Mt of PG deposited at the salt marshes on the Tinto – Odiel estuary at Huelva, Spain, which was declared a UNESCO Biosphere in 1983. The various process routes are outlined and the quality/purity and amounts of products obtained are quantified. Finally, some projections on development towards large-scale implementation and commercialisation are given.

Keywords: phosphogypsum, waste processing, precipitated calcium carbonate (PCC), valuable sulphate product, carbon dioxide

1 Introduction

The production of phosphoric acid, H₃PO₄, from apatite or fluoroapatite rock can be summarised through the following chemical reactions



This results in large amounts of gypsum by-product, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, known as phosphogypsum (PG). Estimates for annually produced amounts worldwide are in the order of 250 megatonnes (Mt). Most of this PG is deposited in large stockpiles around the world. The amounts used in agriculture or construction, adding up to $\sim 15\%$, are limited due to the high concentrations of pollutants and sometimes also high levels of radioactivity. Radiation doses resulting from using PG are, however, negligible compared to doses from natural sources (Saadaoui et al., 2017). Overall, PG receives increasing attention as a source of raw materials, including rare earth elements, REEs. Being a calcium-based industrial by-product, PG is interesting from a carbon-capture and utilisation, CCU, viewpoint as well: one tonne of PG can react with ~ 250 kg CO_2 to produce a calcium carbonate, CaCO_3 , with significant market value, besides other products. This has the potential to bind up to ~ 75 Mt CO_2 annually (Mattila and Zevenhoven, 2015).

Thus, PG processing that results in calcium carbonate combines the urgent challenges of reducing solid waste amounts and lowering CO_2 emissions to the atmosphere while producing materials with market value. Finland and Spain are or have been stockpiling significant amounts of PG. Researchers in Huelva, Seville and Cádiz, in southern Spain, have suggested process routes for converting the feedstock into materials with market value, by primarily using other industrial by-products as reactants. Special attention goes to the U-Th series radionuclides found in PG deposited at Huelva. In Finland, research in Turku has resulted in a process route to obtain precipitated calcium carbonate, PCC. These activities are described below, driven by a need to implement a portfolio of methods with different feedstocks and resulting products in order to avoid flooding the market by a single products stream.

2 Phosphogypsum processing in Spain and Finland

2.1 Phosphogypsum stockpiles

The situation in Spain, at the south coast city of Huelva, with a ~ 120 Mt deposit area very close to the city at the salt marshes on the Tinto – Marismas del Odiel estuary calls for urgent action. The Marismas del Odiel estuary was declared a UNESCO Biosphere in 1983. Between 1968 and 2010, besides PG from the Huelva's fertilizer industrial facility, smaller amounts of other industrial wastes and by-products have been deposited in this area as well, see Figure 1 (left). One risk to consider is the seismic activity, fearing a repetition of what is known as the Great Lisbon 1755 earthquake and tsunami; another hazard is the high radioactivity level of the deposited material which may be transferred to the surrounding hydrosphere.



Figure 1: Deposits of phosphogypsum: at Huelva, Spain, covering ~ 1200 ha (left)¹ and near Siilinjärvi, Finland, covering ~ 60 ha (right)²

¹ Source picture: <http://www.huelvahoy.com/wp-content/uploads/2016/07/Fosfoyesos-en-Huelva.jpg>

² Source picture: http://media.tivi.fi/ponlItplv-1463133534/incoming/dqetp0-kipsikasa.jpg/alternates/LANDSCAPE_640/kipsikasa.jpg

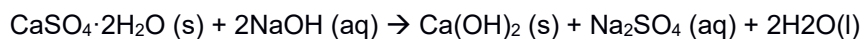
Because of the concentrations of As and Cd, the Huelva PG is a hazardous waste according to European Standards (Macias et al., 2017).

In Finland, a small and a larger deposit exist at Uusikaupunki (now closed) and Siilinjärvi (in operation since 1979, adding ~ 1.5 Mt PG annually to an existing stockpile of ~ 55 Mt), respectively. For the latter see Figure 1 (right). However, it is not considered necessary to take similar measures in Finland as planned in Spain.

2.2 Process concepts work in Spain

Two process concepts developed in Spain base on the use of either alkaline soda (NaOH) or an aluminium-rich liquid waste for converting Huelva PG (> 95%-wt gypsum) into calcium carbonate PCC, and other products. Both concepts make use of aqueous solutions and operate at or near to ambient temperatures and pressures.

The first process concept, shown in Figure 2 (left), has been developed the furthest and has been patented under the name of 'Captura CO₂' (Captura CO₂, 2017). Through this process, PG is dissolved in aqueous solution of NaOH, reacting to dissolved Na₂SO₄ and a precipitate of slaked lime, Ca(OH)₂, two products that can be separated by filtration (see the equation below representing the transformation):



Using CO₂, the slaked lime can be carbonated to produce calcium carbonate (CaCO₃) (possibly via weathering under atmospheric CO₂) while solid Na₂SO₄ can be obtained by evaporating the water. Trace elements (e.g. Cr, Ni, Pb, As, Cd) and radionuclides such as Th, U end up primarily in the ~ 90%-wt pure carbonate while high purity Na₂SO₄ is obtained. This process route can convert 120 Mt PG with 55.2 Mt NaOH and 30 Mt CO₂ into valuable products. More detail is given by Cárdenas-Escudero et al. (2011) and Contreras et al. (2015).

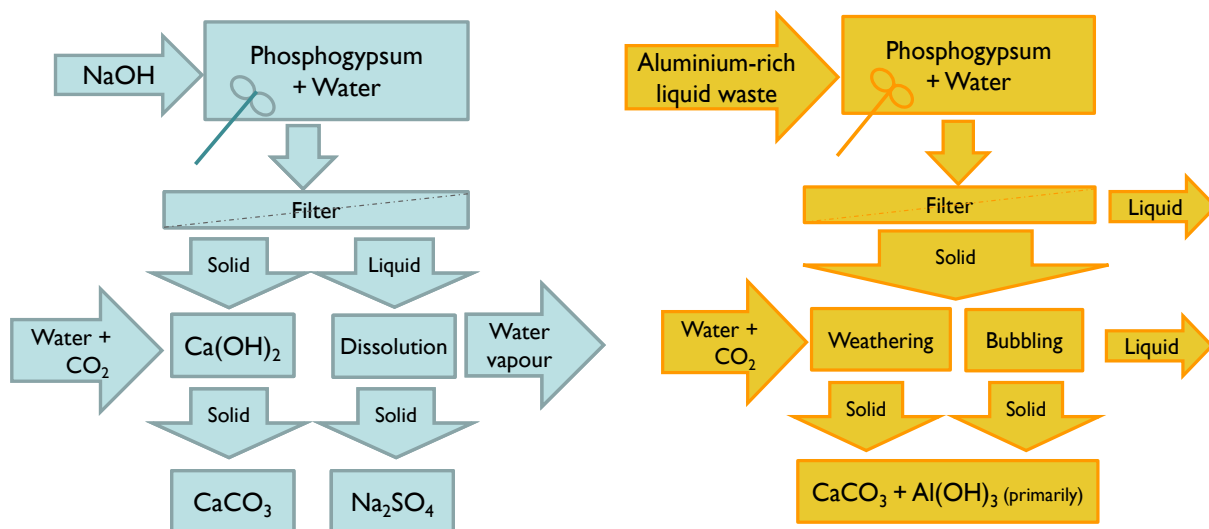
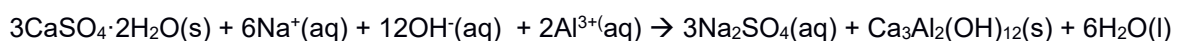


Figure 2: Process concepts for PG conversion using alkaline soda (left) and aluminium-rich alkaline waste (right), respectively.

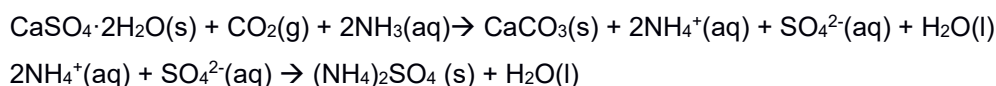
The second concept developed more recently in Spain uses an alkaline soda-rich waste stream from the aluminium anodising industry. As an intermediate, katoite or Ca₃Al₂(OH)₁₂ is formed, which can be carbonated with pure CO₂ or via weathering with atmospheric CO₂:



Again, trace elements end up mainly in the CaCO_3 product. This process route can convert 120 Mt PG into 73 Mt katoite that can further react with 20 Mt CO_2 into valuable products. It is worth noting that available amounts of the aluminium-rich alkaline waste to be used in this process are limited. More detail is given by Romero-Hermida et al. (2017).

2.3 Process concepts work in Finland

Fearing a limited market for Na_2SO_4 in Finland, a process concept using PG (from Siilinjärvi, > 97%-wt gypsum) aims at producing PCC and ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$. The latter finds a large market as fertilizer. (It can be also used as a flux salt for extraction of magnesium from silicate rock as the first step of CO_2 mineral sequestration, for example as in the so-called “ÅA routes” (e.g Zevenhoven et al., 2017) that bind CO_2 in magnesium (hydro) carbonates. Note, though, that in these “ÅA routes” the ammonium sulphate is eventually recovered and recycled.) Ammonia (NH_3) is used as reactant besides CO_2 , in a process that uses aqueous solutions and operate at or near ambient temperatures and pressures:



For 120 Mt PG, their reaction with 31 Mt CO_2 and 24 Mt NH_3 would produce 92 Mt ammonium sulphate, 68 Mt PCC and 14 Mt water.³

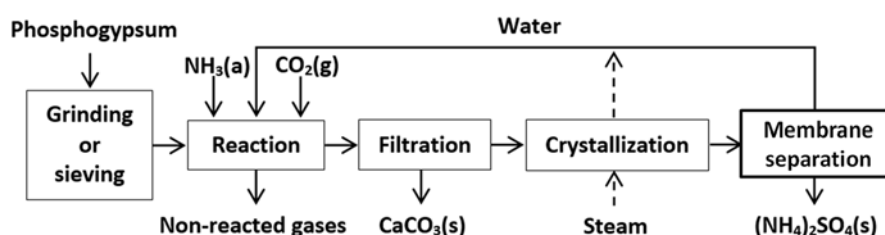


Figure 3: Process schematic for PG conversion using carbon dioxide and ammonia (adapted after Mattila and Zevenhoven, 2015)

Specific for the work in Finland, see Figure 3, is the possibility to produce a PCC with a pre-selected crystallinity. At ambient conditions $\sim 20^\circ\text{C}$ typically spherical vaterite is obtained; longer reaction times (and some excess of CO_2 feed) results in rhombohedral crystals, while scalenohedral PCC is obtained via a slight temperature increase to $\sim 45^\circ\text{C}$ – see Figure 4.

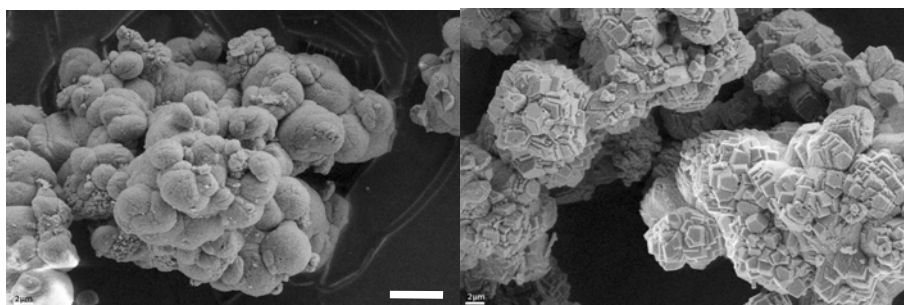


Figure 4: Spherical vaterite (left) and rhombohedral calcite (right) produced from PG (Mattila and Zevenhoven, 2015). Note the white scale bar that stands for 2 microns in both images.

³ This can be compared to a current annual production of 0.4-0.5 Mt NH_3 in Spain – see <http://empresite.eleconomista.es/Actividad/AMONIACO/>

Neutral pH values were obtained by controlled feed of CO₂ and ammonia which also minimises losses of free, dissolved ammonia. PG conversion levels > 95% and PCC purities > 90%-wt were obtained, with trace elements including several REEs (Nd, Ce) and lanthanides (La, Pr, Sm, Gd) transferred largely into the PCC. More detail is given by Mattila and Zevenhoven (2015).

For the recovery of ammonium sulphate, membrane separation methods are being tested (in conjunction with work on magnesium silicate rock carbonation) – see e.g. Koivisto and Zevenhoven (2017). This work on PG carbonation builds on experiences with the (patented) slag2pcc concept that is being developed in Finland for production of PCC from steel converter slag (Mattila and Zevenhoven, 2014, Said et al., 2016). Note that converting gypsum using ammonia and carbon dioxide is a conventional method for large-scale production of ammonium sulphate.

2.4 The way forward

With several process route options including the Captura CO₂ concept, development and scale-up of a process unit is the next step, to be soon followed by a unit that can process several Mt of PG annually - for a scale of 4 Mt PG per year this implies 500 t/h ~ 140 kg/s. Experience with scale-up of the slag2pcc process in Finland will be of use in Spain, Huelva, for PG processing. One hurdle to take into account is finding the amount of (cheap) needed waste or chemicals that contain the NaOH or other alkalinity needed. Flooding the market with cheap products can be avoided by using several different routes which all operate at or near ambient conditions using aqueous solutions: presumably a single process unit can handle different chemical feedstocks besides PG.

Processing solid waste stockpiles will nonetheless have an impact on the environment. By-products and wastes will be generated that must be disposed of: for example, the radionuclides that may be obtained from the PG in a concentrated form. A good overview on the environmental footprint of the suggested processes can be obtained using a life cycle assessment (LCA), showing the impact of seemingly harmless features like water use (e.g. Mattila et al., 2014). Especially for rare earth metals and radionuclides, separation methods must be studied in more detail. Also, recovery of small amounts (< 1%-wt) of phosphorous from the PG deserves attention. For recovery of dissolved salts from water, membrane methods can be considered, being (much) more energy efficient than methods such as solvent evaporation.

3 Conclusions

Phosphogypsum can be processed using routes that bind CO₂ while transforming (large amounts of stockpiled) solid waste into valuable carbonate and sulphate materials. This gives several windows of opportunity for processing the 120 Mt PG stockpiled in Huelva, Spain. Several process concepts using different reactants, preferably alkaline industrial wastes and by-products open up routes to various valuable products, lowering the risks of flooding markets with low-value material.

Precipitated calcium carbonate (PCC) with a chosen size, quality and morphology can be produced through several process routes, paying attention to the reduction and control of impurities. Especially for rare earth metals and radionuclides, separation must be studied in more detail. Also, the recovery of small amounts (< 1%-wt) of phosphorous from the PG deserves attention. A next step is a project framework (for example funded through the European Commission Horizon 2020 program) for development and scale-up of a process unit to be able to process larger amounts of Mt PG annually.

Abbreviations

CCU	Carbon capture and utilisation
LCA	Life cycle assessment
Mt	Megatonnes, Million tonnes
PCC	Precipitated calcium carbonate
PG	Phosphogypsum
REE	Rare earth element

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