

## **New method for carbon dioxide mineralization based on phosphogypsum and aluminium-rich industrial wastes resulting in valuable carbonated by-products**

I. Romero-Hermida,<sup>1</sup> A. Santos,<sup>2</sup> R. Pérez-López,<sup>3</sup> R. García-Tenorio,<sup>4</sup> L. Esquivias,<sup>5,6</sup> V. Morales-Flórez,<sup>5,6,\*</sup>

1 Departamento de Química-Física, Facultad de Ciencias, Universidad de Cádiz, Av. República Saharaui s/n, 11510 Puerto Real, Spain

2 Departamento de Ciencias de la Tierra, CASEM, Universidad de Cádiz, Av. República Saharaui s/n, 11510 Puerto Real, Spain

3 Departamento de Ciencias de la Tierra, Facultad de Ciencias Experimentales, Universidad de Huelva, Campus 'El Carmen' s/n, 21071 Huelva, Spain

4 Departamento de Física Aplicada, ETS Arquitectura, Universidad de Sevilla, Av. Reina Mercedes, s/n, 41012, Seville, Spain

5 Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Sevilla, Av. Reina Mercedes, s/n, 41012, Seville, Spain

6 Instituto de Ciencia de Materiales de Sevilla (CSIC/US), Av. Américo Vespucio, 49, 41092, Seville, Spain

\* Corresponding Author: V. Morales-Florez. Tel: +34 954 550 946. Fax: +34 954 552 870.

E-mail address: vmorales@us.es

## ABSTRACT

A new carbon mineralization method was designed based on a sequestration agent synthesised exclusively from industrial wastes. Phosphogypsum waste from the fertiliser industry was dissolved into caustic aqueous waste from the aluminium anodising industry. The resulting precipitate consisted of katoite ( $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , a Si-free hydrogrossular solid solution end-member of the Al-containing hydrogarnet) and thenardite ( $\text{Na}_2\text{SO}_4$ ); the latter easily removed by rinsing with water. The carbonation performance of this katoite-rich sequestration agent was evaluated using two different methods: by bubbling in aqueous media, and by weathering. Both procedures yielded high carbonation efficiencies (80% and 100%, respectively), and resulted in a solid precipitate composed primarily of calcite ( $\text{CaCO}_3$ ) and aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ). Priority attention was given to the transfer of trace elements and radionuclides of the uranium series typically present in the phosphogypsum. Results confirmed that the traces were transferred to resulting final solid carbonate at concentrations similar to those present in the raw phosphogypsum. In conclusion, these carbonated minerals would trap substantial amounts of  $\text{CO}_2$  and produce final materials with similar civil engineering uses to those proposed for current phosphogypsum wastes. This work offers new methods for jointly manage specific industrial wastes oriented to more sustainable industrial processes and to control  $\text{CO}_2$  emissions.

## KEYWORDS

Carbon sequestration · Industrial waste · phosphogypsum · aluminum industry · katoite

### 1. Introduction

The anthropogenic emissions of greenhouse gases, especially  $\text{CO}_2$ , are among the most hazardous actions that impact the Earth's climate and ecosystems, which have the potential to cause serious, negative impacts on human welfare [1–3]. These threats are motivating large research efforts on both carbon sequestration technologies and strategies to reduce these emissions. Nevertheless, it is unlikely that a single strategy achieves the necessary decrease in  $\text{CO}_2$  concentrations, considering the colossal magnitude of global  $\text{CO}_2$  emissions is currently 38 Gt/yr [4]. It has been suggested that seven emission reducing activities or “stabilization wedges”, each capable of decreasing emissions by 3.7 Gt  $\text{CO}_2$ /yr, could achieve stabilisation of atmospheric  $\text{CO}_2$  concentrations at ~500 parts per million (ppm) [5]. One of these wedges is based on carbon capture and geological storage (CCS). However, this technology could be more broadly interpreted to include carbon mineralisation [4] (also known as mineral sequestration). This process, which captures  $\text{CO}_2$  as a solid carbonate phase [6,7], considers as sequestration agents not only natural minerals from geological formations but also other feedstocks [8-10].

In the last years, the research on carbon mineralization focused mainly on three aspects: decreasing the energy requirements, enhancing the slow kinetics, and searching for alternative feedstocks as sequestration agents [11]. Precisely, the “accelerated carbonation” [12,13] involves examining industrial

wastes containing substantial quantities of available carbonation reactants, predominantly calcium and magnesium oxides, as alternative feedstock. Currently, the carbonation of wastes is already being recognised as a potential CO<sub>2</sub> sink [8,14–17], and several wastes have been proposed for reducing the energy requirements and to design cost-effective methods. Furthermore, the economic viability of the process could be improved, considering that the carbonation by-products are carbonate minerals that could be sold, as well as the financial advantages over carbon taxes [18–20]. Consequently, carbon capture, storage and utilization (CCSU) technologies are nowadays being developed to convert the CO<sub>2</sub> emissions in an opportunity [21,22].

It has been shown that the microstructure and high reactive surface area of the sequestration agent implies high mineralisation kinetics and full carbonation efficiency. This facilitates dissolution and, furthermore, the “passivating layer” caused by the surface precipitation of secondary phases such as carbonates or silica is avoided [23,24]. Additionally, comminution or other pre-treatments to increase kinetics and efficiency through the microstructure may not be necessary, as many wastes are produced with a particle size suitable for rapid and efficient carbonation [25–27].

Criteria similar to that applied to the selection of natural minerals for carbon mineralization are also used to select of alkaline wastes, namely, a substantial content in alkaline earth metals such as calcium and magnesium, a high degree of alkalinity, or the proximity to CO<sub>2</sub> sources [4,8,11,14,16]. For example, suitable mineral feedstock for carbon sequestration has been found in phosphogypsum (PG) waste stockpiles derived from the fertiliser industry [28–30]. These wastes have been considered for a two-step (“indirect”) mineralisation process under atmospheric conditions. According to this strategy, in our previous work [28] the PG is first transformed into a carbon sequestration agent (calcium hydroxide) by alkaline dissolution with soda (reagent grade). Then, this agent rapidly and completely reacts with CO<sub>2</sub> giving carbonates. In south-west Spain, there are 120 Mt of PG stockpiled in waste from the activity of the fertiliser industry for decades, and a similar amount is produced annually in different parts of the world. Thus, 30 Mt of CO<sub>2</sub> could potentially be sequestered using this PG feedstock upon a simple engineering implementation. In addition, some of the environmental issues associated with these wastes (e.g. mobility of the heavy metals or radionuclides) would ultimately be resolved in this methodology, as these traces would remain immobilised in the final carbonate [28,29].

Previous to this research, only alkaline reagent-grade solutions had been studied for PG carbonation [28,31]. However, alkaline industrial liquid wastes should be considered in order to not penalize the economic aspects of this two-step mineralisation process. One of these is the caustic liquid waste of the aluminium industry. Aluminium finishing plants primarily produce different effluents from the anodising and etching sections. Anodising is usually performed in sulphuric acid and etching is performed in sodium hydroxide solutions with concentrations ranging between 50 and 200 g/L. Typically, alkaline waste streams from the etching operation are treated by mixing them with the acid wastewaters from the anodising step. However, this neutralization process requires the incorporation of an additional

neutralising agent (NaOH or lime) due to the overall acid balance. Nevertheless, various methods to recover and recycle etching solutions have been proposed [32], such as that based on dawsonite synthesis [33].

In this work we have evaluated the viability of the indirect PG carbonation by caustic dissolution with liquid wastes of the aluminium anodising industry. Previously reported procedures based on PG [28,29,34] considered the use of a pure soda reagent, so costs and energy consumption of its production suppose an important drawback for its viability. The current study proposes a new management strategy for PG and waste streams of the aluminium anodising industry with two environmental objectives: (1) to synthesise katoite (member of the isomorphous hydrogrossular series [35-37]) by recycling both PG and aluminium wastes and (2) to explore the potential of katoite as a CO<sub>2</sub> sequestration agent by aqueous carbonation. In addition, special attention was paid to the transfer of hazardous traces (heavy metals or radionuclides) typically present in PG wastes, throughout the methodology.

## **2. Experimental procedure**

The main steps of the experimental procedure are summarised in Fig. 1.

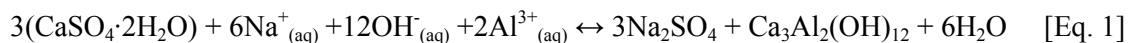
### *2.1. Starting materials*

5 kg of raw phosphogypsum ('PG') were supplied by Fertiberia (Huelva, Spain). The PG was homogenised, ground and oven-dried at 40 °C in order to preserve the structural water of gypsum. The caustic liquid Na-Al waste was supplied by Verinsur SA (Jerez de la Frontera, Spain). This waste was derived from the finishing process of the aluminium industry, and, regarding the supplier, ca. 200 t are produced annually. It is a transparent solution with pH ~14 and contains a small amount of reddish precipitate. In this work, the raw waste was filtered and the reddish precipitate was discarded. In addition, the filtered liquid was dried to evaporation at 110 °C (in a hot plate) and the dried precipitate ('A<sup>(S)</sup>') was analysed.

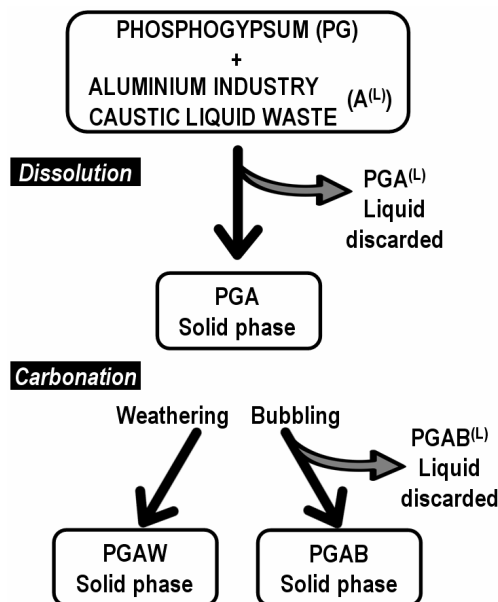
### *2.2. Synthesis of the carbon sequestration agent*

The sequestration agent was synthesised by alkaline dissolution of the PG using the Na-Al-rich liquid waste. The process started by the addition of 12.5 g of phosphogypsum in 25.0 mL of liquid waste upon magnetic stirring in a closed beaker for 3 h under room conditions. During the process, the pH remained at 12.0. A precipitate was formed ('PGA'), which was separated by centrifuging for 5 min at 3000 rpm. Then, it was put inside a stove at 80 °C to quickly dry the sample in order to avoid non-controlled carbonation by weathering or further hydration. The corresponding supernatant 'PGA<sup>(L)</sup>' was not considered for the carbon sequestration procedure.

Based on the chemical composition of the residues (see section 3.1), this specific mass ratio corresponded to a stoichiometric molar ratio of Ca:Al = 1.5, targeting the following chemical reaction:



Other molar ratios, as well as the addition of extra distilled water, were studied. Only the conditions that yielded the best results have been presented.



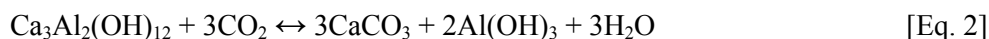
**Fig. 1.** Experimental methodology of the synthesis of the carbon sequestration agent and the two carbon capture procedures.

### 2.3. Carbon sequestration procedures

Two procedures were considered to evaluate the carbon capture efficiency of the new sequestration agent, PGA: (1) bubbling pure  $\text{CO}_2$  into an aqueous suspension of the sequestration agent, and (2) using the “weathering pools” [25].

#### 2.3.1. Bubbling

This procedure started with the dispersion of 2 g of the PGA sample in 40 mL of distilled water. The dispersion was then subjected to a continuous pure  $\text{CO}_2$  flux ( $\sim 1$  bar,  $20 \text{ cm}^3/\text{s}$ ) under magnetic stirring and room conditions, for 90 min. Under this flux, the pH rapidly decreased to 6.7. The expected carbonation reaction is:



This procedure resulted in a new solid-liquid suspension, which was separated by centrifugation (3000 rpm, 5 min) into a solid and liquid phases, hereafter referred to as ‘PGAB’ and ‘PGAB<sup>(L)</sup>’, respectively. The solid phase was analysed, and the liquid phase was discarded. This step was repeated four times to check reproducibility.

### 2.3.2. Weathering

The carbonation of the sample PGA was also studied using the atmospheric CO<sub>2</sub> by the weathering pools procedure [25]. The weathering pools consist of very shallow, flat, ponds on which a thin film of the sequestration agent is spread. In this work, 11 g of sample PGA were spread over a flat surface of 20x20 cm<sup>2</sup>. Distilled water (20 mL) was initially added, and the carbonation of the sample occurred during drying under room conditions. Distilled water (20 mL) was added every two weeks to enhance the capture performance. Typically, the complete process took up to 2 months. The final solid obtained is hereafter referred to as 'PGAW'.

### 2.4. Characterisation techniques

Chemical analyses were made by X-ray fluorescence (AXIOS Panalytical, with an Rh tube) using the semi-quantitative method for major elements, and pseudo-total acid-digestion followed by analysis with inductively coupled plasma mass-spectrometry (ICP-MS; HP-4500 instrument) for trace elements. The chemical analyses of the liquid waste were performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Horiba-Jobin-Yvon, Ultima 2). Activity concentrations of radionuclides belonging to the uranium series were determined in the raw materials and in the various solid and liquid fractions obtained by  $\alpha$ -particle spectrometry with 450 mm<sup>2</sup> PIPIS detectors. Previously, the isotopes were sequentially isolated using a validated radiochemical procedure based on extraction chromatographic resins (UTEVA resins, Triskem Int.) and on the preparation of the counting source by electrodeposition [38].

Crystalline phases of the samples were identified by X-ray diffraction (XRD) (BRUKER D8-Advance, Cu-K $\alpha$  radiation,  $\lambda_{\alpha 1}$ =0.154 nm), from 10.00° to 70.00° ( $\Delta(2\theta) = 0.015^\circ$ , counting time = 80 s). Sample morphology was characterised by scanning electron microscopy (SEM-FEG, Hitachi S5200) using an acceleration voltage of 5 kV. Particle size was estimated by laser diffraction using a Mastersizer 2000 system. Nitrogen physisorption experiments (ASAP 2420) were performed at 77.35 K to reveal nanostructural features. Samples were degasified at 150 °C for 2 h prior to the experiment.

The carbonation degree of the samples was estimated by thermogravimetric analyses (TGA) in an STD Q600 experimental device. The experiments were conducted under a nitrogen flux of 100.0 mL/min, from an initial ambient temperature up to 1000 °C, at 10 °C/min. As a reference, note that for a pure calcite sample the stoichiometric weight loss due to decarbonation is 44%, over the range 550–900 °C. To compare the experimental results with this theoretical maximum, the mass of the samples from the TGA experiments was normalised to the weight of the dehydrated sample (at T = 120 °C). Table S1 (Supplementary Material) summarizes the samples and techniques considered in this work.

### 3. Results and discussion

#### 3.1. Characterisation of the starting materials

XRD confirmed that gypsum was the only crystalline phase present in the raw sample PG (Fig. 2). Laser diffraction revealed a typical grain size of 40  $\mu\text{m}$  with > 90% below 110  $\mu\text{m}$  (Fig. S1, Supplementary Material). The caustic liquid waste had a density of 1.32  $\text{g}/\text{cm}^3$ , pH  $\sim 14$ , and a composition of  $[\text{Na}] = 110 \pm 2 \text{ g}/\text{L}$  ( $4.78 \pm 0.09 \text{ M}$ ) and  $[\text{Al}] = 52 \pm 2 \text{ g}/\text{L}$  ( $1.93 \pm 0.07 \text{ M}$ ). In the precipitate,  $\text{A}^{(\text{S})}$ , hydrated sodium carbonate (PDF: 01-070-0845,  $\text{Na}_2\text{CO}_3(\text{H}_2\text{O})$ ) and gibbsite (PDF: 00-012-0460,  $\text{Al}(\text{OH})_3$ ) were identified (Fig. 2). The presence of  $\text{Na}_2\text{CO}_3$  is due to the carbonation of the sodium by atmospheric  $\text{CO}_2$  during the drying process itself. But the  $\text{Na}_2\text{CO}_3$  is a very soluble phase that does not guarantee the permanent fixation of the  $\text{CO}_2$  (in comparison to  $\text{CaCO}_3$ ), so this particular carbonation was not considered as part of the carbon sequestration potentialities of the method.

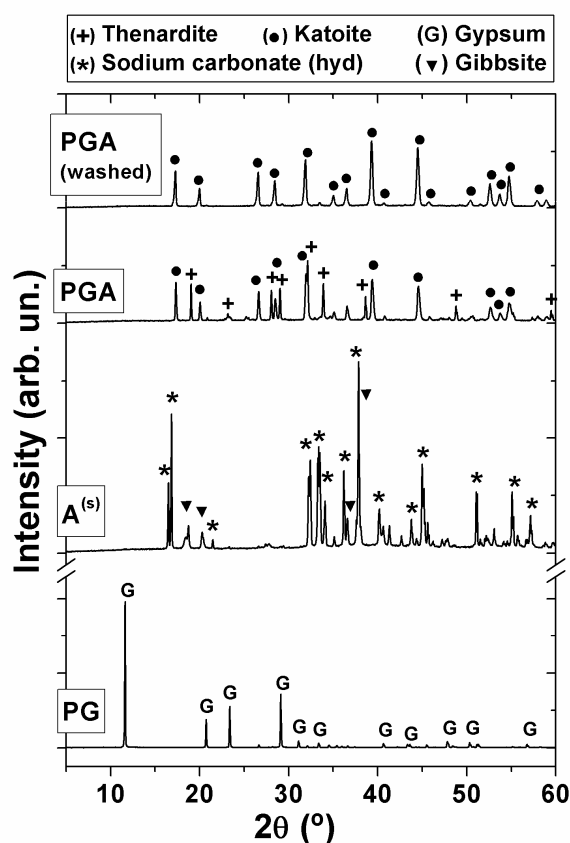


Fig. 2. X-ray diffraction patterns of samples ‘PG’, ‘ $\text{A}^{(\text{S})}$ ’, and ‘PGA’, as-synthesised and washed. Maximum intensities reached 44860 counts for PG, 8110 for  $\text{A}^{(\text{S})}$ , 2860 for PGA, and 3650 for PGA (washed).

The major elements of the starting materials obtained from XRF are shown in Table 1. Sample PG was mainly composed of Ca and S, in a molar ratio very close to unity (0.993), as expected for gypsum, and an 18.4 wt.% of loss of ignition (LOI) due to the gypsum dehydration, which departs from stoichiometric values due to the presence of some major impurities inherited from the industrial process

such as SiO<sub>2</sub> (2.52 wt.%) and P<sub>2</sub>O<sub>5</sub> (0.65 wt.%). Thus, the PG sample was composed of gypsum with purity > 96%. These results are similar to other analyses of samples from the same stockpiled PG [28,29]. On the other hand, the solid precipitate from the liquid waste (sample A<sup>(S)</sup>) was composed of mainly Al and Na (>99 wt.%), while major detected impurities were Ca, S, Si, Fe, and K. The presence of trace elements and radionuclides in the PG is discussed in sections 3.4 and 3.5, respectively.

### 3.2. Carbon sequestration agent

The dissolution of the PG with the liquid waste generated a solid precipitate, PGA, and the corresponding supernatant, PGA<sup>(L)</sup>, which was discarded. Chemical analysis of the discarded liquid revealed the presence of Na ([Na] = 91 ± 6 g/L), S ([S] = 39.6 ± 0.4 g/L), Al ([Al] = 23 ± 2 g/L) and negligible Ca ([Ca] < 0.1 mg/L) amount. The density of the supernatant was 1.34 ± 0.1 g/cm<sup>3</sup>. The constituent crystalline phases of PGA were identified by XRD (Fig. 2), and the two observed phases were hydrogrossularite (PDF: 00-002-1124, Ca<sub>3</sub>Al<sub>2</sub>(OH)<sub>12</sub>, katoite\*) and thenardite (PDF: 01-074-2036, Na<sub>2</sub>SO<sub>4</sub>, sodium sulphate). No residual gypsum was detected. In accordance with this, the chemical composition of PGA (Table 1) revealed Ca, Al, S and Na as the major components, in relative molar ratios Ca:Al and Na:S equal to those of the katoite (which was the target ratio of the experimental procedure) and thenardite, respectively.

**Table 1**

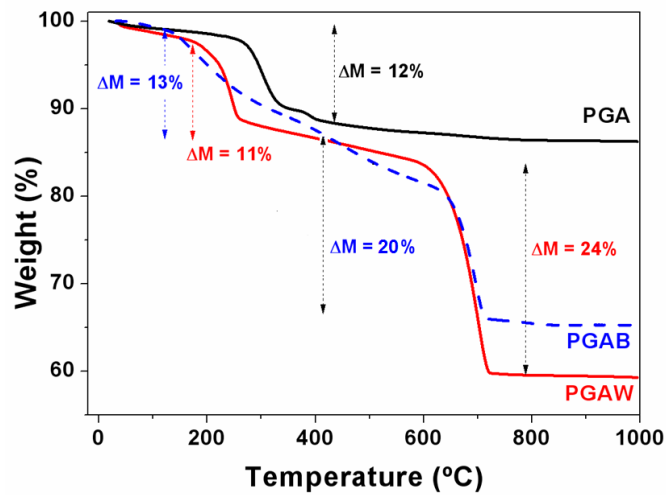
Major elements of the various solids obtained from the experimental procedure. LOI: Loss of ignition at 1000 °C; n. d.: not detected.

Major elements (wt. %)	Raw materials		Dissolution	Carbonation
	PG	A <sup>(S)</sup>	PGA	PGAB
CaO	32 ± 1	0.15 ± 0.01	21 ± 1	32 ± 2
Al <sub>2</sub> O <sub>3</sub>	0.20 ± 0.01	32.3 ± 0.6	12.7 ± 0.2	14.5 ± 0.3
SO <sub>3</sub>	46 ± 3	0.07 ± 0.01	27 ± 2	14.4 ± 0.9
Na <sub>2</sub> O	0.01 ± 0.01	46 ± 2	20.5 ± 0.7	2.29 ± 0.08
SiO <sub>2</sub>	2.52 ± 0.03	0.06 ± 0.01	1.81 ± 0.02	2.66 ± 0.03
P <sub>2</sub> O <sub>5</sub>	0.65 ± 0.02	n. d.	0.38 ± 0.01	0.47 ± 0.01
K <sub>2</sub> O	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.01
Fe <sub>2</sub> O <sub>3</sub>	n. d.	0.03 ± 0.01	n. d.	0.01 ± 0.01
LOI	18.4 ± 0.4	21.4 ± 0.2	16.4 ± 0.2	33 ± 1
	<b>Molar ratio Ca:Al</b>		1.51	2.01
	<b>Molar ratio Ca:S</b>		1.11	3.43
	<b>Molar ratio Na:S</b>		1.96	0.41

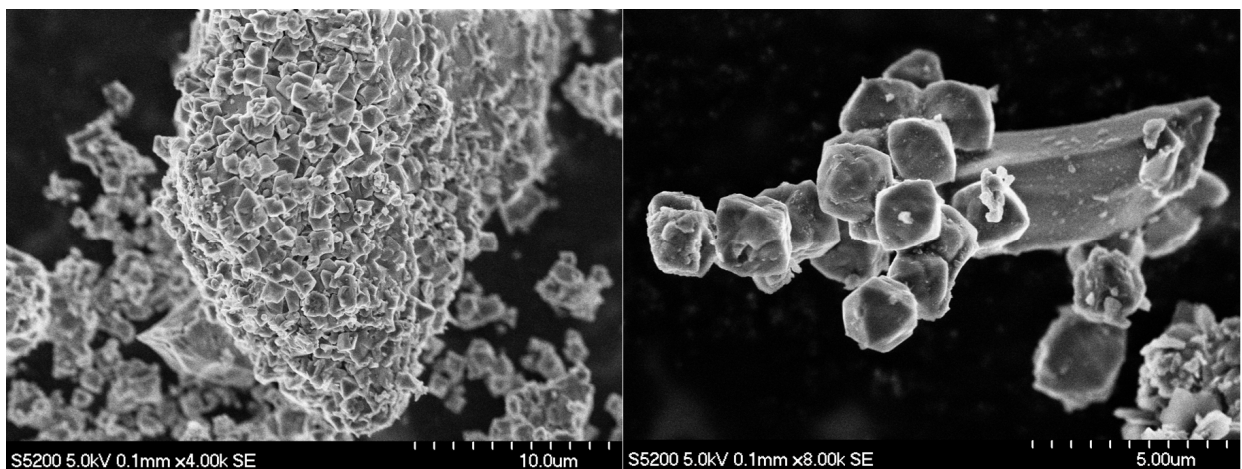
\* This nomenclature was approved by the Commission of the International Mineralogical Association.



Katoite is included in a group of minerals known as hydrogarnet ( $\text{Ca}_3(\text{Al,Fe})_2(\text{SiO}_4)_y(\text{OH})_{4(3-y)}$ ;  $0 < y < 3$ ), where the  $\text{SiO}_4^{4-}$  tetrahedra are partially or completely replaced by  $\text{OH}^-$ . The Al-containing hydrogarnet includes the hydrogrossular solid solution ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_y(\text{OH})_{4(3-y)}$ ,  $0 < y < 3$ ), being the katoite the Si-free end-member ( $\text{C}_3\text{AH}_6$  in cement notation<sup>†</sup>) [36,39]. Thenardite is highly soluble in water under room conditions, so gentle rinsing with pure water led to the separation of the thenardite and katoite (“PGA washed” in Fig. 2;  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ) within a purity of 95% (XRF, see Table S2, Supplementary Material). TGA analysis (Fig. 3) confirmed that a weight loss of 12 wt.% occurred in a two-step process between 250 °C and 400 °C, which can be explained in terms of the reported two-step katoite dehydration [40]. No other substantial weight losses were detected in the TGA. The morphology of the thenardite and katoite present in PGA was observed by SEM. In Fig. 4, micron-sized octahedral habit of the katoite was easily recognised, as reported previously [41,42]. In addition, elongated-shaped thenardite crystals could be readily observed.



**Fig. 3.** TGA experiments of the sequestration agent PGA, and carbonated samples PGAB and PGAW.



**Fig. 4.** SEM images of sample PGA, where ~2 micron sized katoite octahedra and elongated-shaped thenardite crystals were readily identified.

<sup>†</sup> Cement short-hand notation: C=CaO, A=Al<sub>2</sub>O<sub>3</sub> and H=H<sub>2</sub>O.

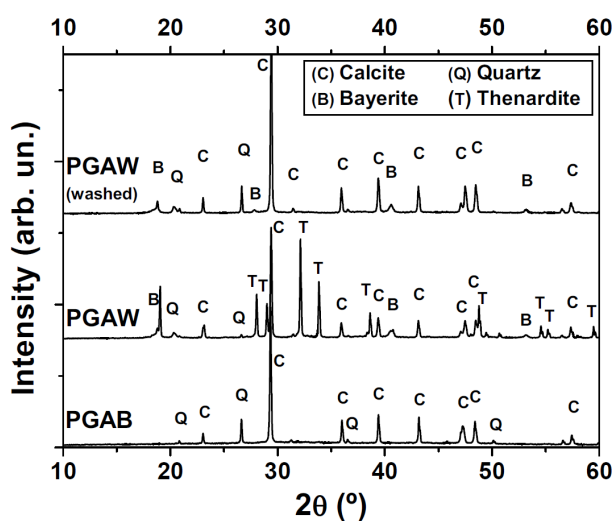
### 3.3 Carbon sequestration experiments

The carbonation performance of the synthesised sequestration agent, PGA, was tested by two different methods: bubbling CO<sub>2</sub> into an aqueous suspension of PGA, and weathering.

#### 3.3.1. Bubbling

The carbonation by bubbling resulted in a new precipitate, PGAB, and the corresponding supernatant PGAB<sup>(L)</sup>. The PGAB<sup>(L)</sup> presented a density of  $1.00 \pm 0.1$  g/cm<sup>3</sup>, and substantial S ([S] =  $1.200 \pm 0.006$  g/L) and Na ([Na] =  $0.763 \pm 0.008$  g/L) contents by the dissolution of the thenardite from the sample PGA, and low Al and Ca contents ([Al] =  $6.2 \pm 0.3$  mg/L; [Ca] =  $0.227 \pm 0.006$  g/L). XRD analysis of PGAB is plotted in Fig. 5. The crystalline phases were almost exclusively comprised of calcium carbonate (PDF: 01-083-1762, CaCO<sub>3</sub>, calcite), although some impurities of quartz from the raw PG could be seen. Thenardite was not present, confirming its complete dissolution during the carbonation process (pH ~ 6.7). Nevertheless, XRF analysis (Table 1) revealed the presence of substantial contents of amorphous phases, containing mainly Al and S, and, to a lesser extent, Na.

Finally, the TGA analysis (Fig. 3) revealed three separate weight losses in the PGAB. First, a soft weight loss of 13% centred around 200 °C that could be explained in terms of the dehydration of hydrated amorphous phases, containing mainly Al or S, and probably some Ca. Second, a small weight loss between 400 °C and 600 °C can be seen, which could be associated with the decarbonation of poorly crystallised carbonates or scarcely detected CaCO<sub>3</sub> polymorphs as vaterite or aragonite. The presence of these carbonates has been observed in several PGAB samples (in Fig. S2, Supplementary Material, vaterite is clearly identified). Third, a well-defined weight loss at 700 °C due to decarbonation of the calcite present in PGAB, as revealed by XRD. In summary, a weight loss of 20% is due to the release of CO<sub>2</sub> from carbonates within a total of 33%, in full agreement with the LOI from XRF.



**Fig. 5.** XRD patterns of samples PGAB, PGAW and PGAW (washed). As a reference, maximum intensities reached 8800 counts for PGAB, 6519 for PGAW, and 11500 for PGAW (washed).

### 3.3.2. Mass balance

In Table 2, mass balances and transfer factors are summarised; some estimations of the discrepancies respect to the expected values are also provided. In a typical experiment of PG dissolution for carbon sequestration by bubbling, 12.50 g of PG was dissolved in 25 mL of alkaline waste (33.00 g, density = 1.32 g/cm<sup>3</sup>). We have studied this procedure, instead the weathering, because its simpler industrial implementation, and because it allows the easy reutilization of the final carbonate products for civil engineering purposes. The dissolution reaction yielded 17.0 g of PGA, containing most of the Ca content of the system: 90% of the CaO was transferred from PG to PGA, which was the ultimate objective of the process, as CaO is the chemically active carbon sequestration specie. Additionally, the Al<sub>2</sub>O<sub>3</sub> was almost completely transferred to PGA.

**Table 2**

Mass balance and transfer factors ( $\eta$ ) of the chemical species throughout the process. Uncertainties are given as standard deviation of the mean. “Discr.” stands for absolute values of discrepancy between the total values. (\*) Mass data of the carbonation experiments consider the addition of demineralised water (see section 2.3 for details). Discrepancies of carbonated species are only related to species contained in the PGA sample, given PGA<sup>(L)</sup> was discarded. (-) No data. Digits in the first column are restricted to the minimum precision of each sample series.

Mass of the chemical species present in the samples (g)	Total mass of the sample	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SO <sub>3</sub>	CaO
<i>Raw materials</i>					
<b>PG</b>	12.50	0.025 ± 0.001	(1.25 ± 0.01)10 <sup>-3</sup>	5.75 ± 0.06	4.00 ± 0.06
<b>A<sup>(L)</sup></b>	33.00	2.44 ± 0.06	3.960 ± 0.005	-	-
<b>Total mass involved</b>	45.50	2.47 ± 0.06	3.961 ± 0.005	5.75 ± 0.06	4.00 ± 0.06
<i>Dissolution</i>					
<b>PGA</b>	17.0	2.16 ± 0.03	3.5 ± 0.1	4.6 ± 0.3	3.6 ± 0.2
Transfer factor		$\eta = 87 \%$	$\eta = 88 \%$	$\eta = 80 \%$	$\eta = 90 \%$
<b>PGA<sup>(L)</sup></b>	26.80	0.88 ± 0.02	2.44 ± 0.04	1.98 ± 0.01	≤ 10 <sup>-3</sup>
<b>Total mass involved</b>	43.8	3.04 ± 0.05	5.9 ± 0.1	6.6 ± 0.3	3.6 ± 0.2
Discrepancy	4 %	23 %	50 %	14 %	10 %
<i>Carbonation*</i>					
<b>PGAB</b>	9.8	1.43 ± 0.03	0.22 ± 0.01	1.42 ± 0.09	3.1 ± 0.2
Transfer factor		$\eta = 66 \%$	$\eta = 6 \%$	$\eta = 31 \%$	$\eta = 86 \%$
<b>PGAB<sup>(L)</sup></b>	297.12	(3.4 ± 0.1)10 <sup>-3</sup>	1.97 ± 0.03	3.59 ± 0.04	0.09 ± 0.01
<b>Total mass involved</b>	306.9	1.43 ± 0.03	2.19 ± 0.04	5.0 ± 0.1	3.2 ± 0.2
Discrepancy	14 %	34 %	38 %	13 %	11 %

Regarding the quantification of the crystalline phases (Fig. 2), the 12 wt.% drop measured in the TGA analysis of PGA (Fig. 3) could be attributed to katoite dehydration. This water amount corresponds stoichiometrically to 11.3 wt.%  $\text{Al}_2\text{O}_3$  and 18.7 wt.% CaO from katoite. Therefore, the  $\text{Al}_2\text{O}_3$  and CaO (XRF, Table 1) almost completely form katoite. The small excess of CaO and  $\text{Al}_2\text{O}_3$  suggest that there could be some minor Ca-Al minerals or amorphous compounds. Based in these results and considering the Na and S contents, PGA could be described as approximately 45 wt.% katoite, 45 wt.% thenardite, and 10 wt.% amorphous or minor crystalline phases.

Regarding the PGAB sample, the almost exclusively presence of calcite and the absence of other Ca-rich crystalline phases (as katoite) suggested a good carbon sequestration efficiency. The high transfer rate (ca. 80%) of CaO from PG to the final carbonate showed that was an efficient route of using the Ca content of PG wastes for carbon sequestration. Na and S were almost completely removed from PGAB due to the aqueous carbonation whereas Al kept an important presence in the carbonate (ca. 60% of transference).

The amounts of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  released during TGA (13 wt.% and 20 wt.%, respectively; Fig. 3), and the stoichiometry of the carbonation reaction proposed for the katoite (Eq. 2), suggested that all the released water could come from amorphous aluminium hydroxides, and the aqueous carbonation process implied dissolution of the thenardite. To resolve the presence of amorphous phases, PGAB was heated at 800 °C for 2 h and then analysed by XRD (Fig. S3, Supplementary Material). The heated sample contained crystalline sulphates and oxides of Ca, Al and Na, confirming the presence of Al, Na and S as amorphous phases in the PGAB sample. Furthermore, the weight loss due to the  $\text{CO}_2$  corresponded to carbonation of 80% of the total CaO content. Therefore, an 80% carbonation efficiency was achieved based on the simple carbonation method performed under room conditions. Extending the carbonation time did not substantially enhance this efficiency.

As an estimation of the up-scaled carbonation process, the bubbling method would allow capturing 0.16 kg of  $\text{CO}_2$  per kg of PG, considering transfer factors of CaO and limited carbonation efficiency, involving a fixation power of 16%. These fixation power values are comparable or even higher than those from municipal solid waste bottom-ash (2.3%), carbon fly ash (2.6%) or paper mill waste (21.8%) [26]. Moreover, the treatment of 1 kg of PG would recycle then 2.6 kg of caustic liquid waste derived from the aluminium industry and ca. 1 kg of  $\text{Na}_2\text{SO}_4$  could be recovered. Considering the amount of accumulated PG stockpiles from south-west Spain (120 Mt), it would be possible to obtain 73 Mt of katoite, capturing ca. 20 Mt of  $\text{CO}_2$  and producing 94 Mt of carbonated material. Finally, considering the estimation of 2.11 t of emitted  $\text{CO}_2$  per each tonne of anodised aluminium [43], 20 t of Al could be anodised without associated  $\text{CO}_2$  emissions, solely by recycling the annual production of Al-rich waste from our supplier. Finally, regarding the costs of this technology, it should be remarked that starting materials may be easily achievable as it consists of industrial by-products or wastes, transferring the heaviest part of the total costs to transportation.

### 3.3.3. Weathering

In this work, the efficiency of an additional carbonation procedure was tested. Sample PGAW was obtained by the carbon sequestration experiments by the weathering pools method [25]. The XRD analysis (Fig. 5) revealed the presence of calcium carbonate (calcite), a substantial amount of remaining thenardite, aluminium hydroxide (PDF: 01-074-1119, Al(OH)<sub>3</sub>, bayerite), and traces of quartz. TGA analysis of PGAW (Fig. 3) resulted in an 11% weight loss from 200 °C to 250 °C, which can be explained in terms of bayerite dehydration, and a 24% weight loss at 700 °C, corresponding to the release of CO<sub>2</sub> from calcite. No significant differences are expected regarding its chemical composition. This result confirms that the weathering procedure achieved full of carbonation (100% efficiency). Considering the relevance of specific surface area in the weathering kinetics [23], nitrogen physisorption analysis of the PGA sample revealed a very low specific surface area (0.32 m<sup>2</sup>/g), which explains the extensive time required for full carbonation. Finally, the XRD pattern of sample PGAW (washed) shown in Fig. 5 reaffirmed that the thenardite present in PGAW could be readily removed.

### 3.4 Minor potentially toxic elements

The transfer of trace elements was calculated based on the total mass of the solid precipitates of the dissolution and carbonation reactions (samples PGA and PGAB, respectively). The fates of the toxic components and minor elements are listed in Table 3. Percentages were calculated according to the initial concentration in the raw PG. As a general consideration, Cr, Sr, Cd, Ba, Pb and Th were fully transferred from PG to PGA, while a substantial part of the U was transferred to the residual liquid phase PGA<sup>(L)</sup>. The contents of V and As in PGA were also raised by contributions from the liquid caustic Al-rich precursor (transfer factors > 100%).

**Table 3**

*Contents of trace elements analysed by ICP-MS. Transfer factors are obtained with reference to contents of PG sample. \* Transfer factors higher than 100% involve contributions from the caustic waste.*

<b>Trace elements (mg kg<sup>-1</sup>)</b>	<b>V</b>	<b>Cr</b>	<b>As</b>	<b>Sr</b>	<b>Cd</b>	<b>Ba</b>	<b>Pb</b>	<b>Th</b>	<b>U</b>
<i>Raw materials</i>									
<b>PG</b>	2.88	6.27	-	360	1.75	37.0	1.84	1.14	5.21
<i>Dissolution</i>									
<b>PGA</b>	8.05	5.32	1.82	248	1.13	27.2	1.51	0.81	2.46
Transfer factor, $\eta$ (%)	358*	109		88	82	94	105	91	60
<i>Carbonation</i>									
<b>PGAB</b>	5.80	6.71	1.43	345	1.58	36.0	1.64	1.13	2.89
Transfer factor, $\eta$ (%)	50	87	54	95	97	91	75	97	81

The transfer of the trace elements through the carbonation reaction was expected to be similar to previously reported procedures [28,29]. Indeed, it can be seen that Sr, Cd, Ba, and Th were almost completely transferred from PGA to the solid precipitate PGAB, and to a lesser extent, Cr, Pb and U. Only, V and As were substantially shared between solid PGAB and liquid phase PGAB<sup>(L)</sup>. It could, therefore, be concluded that the toxic trace elements present in the original PG were generally transferred to the solid precipitated phases and finally trapped in the final carbonate. The trace elements from liquid caustic waste, V and As were almost equally distributed between solid and liquid phases. It is noteworthy that, based on the proposed method, the contaminants will be fixed into less soluble phases, specially the final carbonated product, improving its fixation and suggesting a reduction of the risk of release to the environment through dissolution or lixiviation, as it can occur in their current state within the phosphogypsum stockpiles [44].

### *3.5 Radioactive species*

In this work, there was particular emphasis on researching the route followed by several radionuclides of the uranium series, which are present in the PG wastes at concentrations slightly higher than that in undisturbed soils and sediments. Consequently, potential radiological problems associated with the application of the proposed sequestration process could be assessed, and eventually discarded. The radiometric determinations associated with the raw materials and different phases of the process are compiled in Table 4. The U and Th radionuclides ratify the conclusions obtained from their ICP-MS determinations (see previous section). Almost all the Th originally associated with the raw PG was transferred into the final solid product, while the majority of U was also transferred to the same final product. A fraction of the U was transferred to the liquid phases but in concentrations low enough to affirm that no radiological issues would be associated with their management. Based on the results obtained for Sr by ICP-MS, and the similar chemical behaviour of Sr and Ra (both elements from the column IIa in the periodic table), it could be expected that the majority of <sup>226</sup>Ra (another member of the uranium series) would also be associated with the final solid product. Finally, the <sup>234</sup>U/<sup>238</sup>U ratio is close to unity, indicating that the secular equilibrium present in the original phosphate rock was maintained during the formation of the PG and subsequently along the carbon sequestration process.

Knowing the mass relation between the raw PG and the final carbonated phase PGAB, it could be also be affirmed that the concentrations of U, Th and Ra in the solid phases generated in the proposed sequestration processes would be similar to those originally found in the PG. Consequently, from a radiological point of view, most of the uses that have been recognised by the international community for the valorisation of PG (soil amendment, construction material, road basement, etc.) could be considered for this new solid material [26,45–47]. In this sense, at concentration levels found in the PG for the radionuclides of the uranium series (< 1 Bq/g), it is now internationally recognised that the valorisation of PG can be performed safely without the need for radiological regulation.

**Table 4**  
Summary of average activity concentrations of radionuclides.  
Uncertainties are given as standard deviation of the mean.

<b>Concentration (mBq/g)</b> <i>(Transfer factor, <math>\eta</math>)</i>	$^{234}\text{U}$	$^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}$
<i>Raw materials</i>				
<b>PG</b>	69 ± 4	67 ± 4	1.03 ± 0.08	534 ± 19
<b>A<sup>(L)</sup></b>	1.5 ± 0.2	1.1 ± 0.1	1.2 ± 0.2	2.2 ± 0.3
<i>Dissolution</i>				
<b>PGA</b>	42 ± 10 <i>(78 %)</i>	54 ± 4 <i>(102 %)</i>	0.8 ± 0.2	401 ± 98 <i>(101 %)</i>
<b>PGA<sup>(L)</sup></b>	8.8 ± 0.2 <i>(26 %)</i>	8.5 ± 0.2 <i>(26 %)</i>	1.04 ± 0.09	0.81 ± 0.09 <i>(0.3 %)</i>
<i>Carbonation</i>				
<b>PGAB</b>	69 ± 10 <i>(95 %)</i>	70 ± 4 <i>(75 %)</i>	0.9 ± 0.2	847 ± 35 <i>(122 %)</i>
<b>PGAB<sup>(L)</sup></b>	0.16 ± 0.05 <i>(7 %)</i>	0.14 ± 0.04 <i>(5 %)</i>	1.1 ± 0.4	0.15 ± 0.05 <i>(0.6 %)</i>

#### 4. Conclusions

A new experimental method to recycle industrial wastes for carbon sequestration technologies has been successfully proven. Specifically, the study showed how the phosphogypsum stockpiles could be treated by alkaline dissolution with the liquid waste of the aluminium anodising industry to obtain a Ca-rich precipitate, which, if insistently washed with pure water gives katoite at 95 % purity. The high carbon sequestration efficiency of this Ca-rich mineral was verified by two simple procedures: bubbling pure CO<sub>2</sub> into an aqueous suspension, achieving 80 % carbonation efficiency in a few hours; and the "weathering pools" method, which allowed 100 % efficiency in two months. Implementing these methods to the phosphogypsum stockpiles of south-west Spain (around 120 Mt) would give 73 Mt of katoite, which could capture 20 Mt of CO<sub>2</sub> and produce 94 Mt of carbonated material. It is noteworthy that neither of the considered industrial wastes can permanently capture CO<sub>2</sub> by themselves so this technology encompasses a new method of recycling wastes for carbon sequestration purposes, which will also influence their respective carbon emission balances.

Additionally, the majority of hazardous trace elements and radionuclides included in the starting industrial wastes were transferred into the solid phases at each step of the procedure. Thus, these contaminants will be finally fixed into a less soluble carbonate phase. In addition, hazardous traces

present in the final carbonate by-product were low enough to enable their use in selected applications in civil engineering similar to those currently proposed for phosphogypsum.

In summary, the procedure presented in this work represents an environmental proposal to jointly manage the controversial phosphogypsum stockpiles and the aluminium industry caustic waste, enabling an efficient carbon dioxide sequestration technology.

## Acknowledgements

This work was supported by the Spanish Government through the research project MAT2013-42934-R and the Andalusia Government through the research project P12-RNM-2260. IR-H wants to especially thank the funding support of the project MAT2013-42934-R. RP-L also thanks the Spanish Ministry of Science and Innovation and the ‘Ramón y Cajal Subprogramme’ (MICINN-RYC 2011), and VM-F thanks the funding action of ‘V Plan Propio de la Universidad de Sevilla’. The technical staff of the CITIUS-Universidad de Sevilla are acknowledged for their kind help with the analyses of the samples. The authors also thank VERINSUR for supplying the aluminium industry waste, and FERTIBERIA, for supplying phosphogypsum. Creators and owners of *www.citethisforme.com* are also acknowledged. J.M. González Leal from Universidad de Cádiz is also acknowledged for his help in Raman analyses.

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## New method for carbon dioxide mineralization based on phosphogypsum and aluminium-rich industrial wastes resulting in valuable carbonated by-products

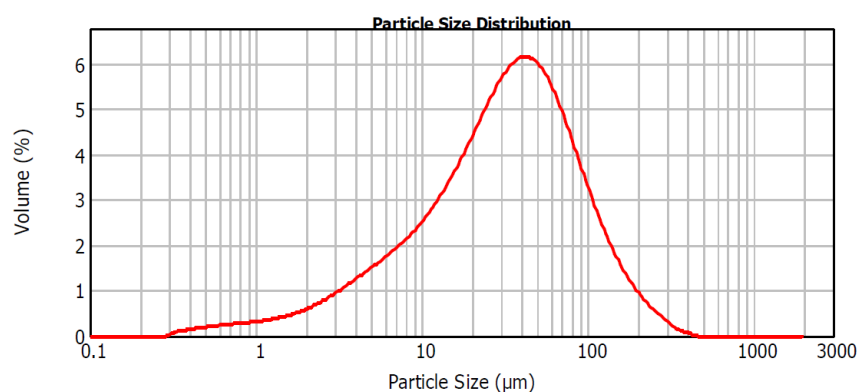
I. Romero-Hermida,<sup>1</sup> A. Santos,<sup>2</sup> R. Pérez-López,<sup>3</sup> R. García-Tenorio,<sup>4</sup> L. Esquivias,<sup>5,6</sup> V. Morales-Flórez,<sup>5,6,\*</sup>

\* Corresponding Author: V. Morales-Florez. Tel: +34 954 550 946. Fax: +34 954 552 870.

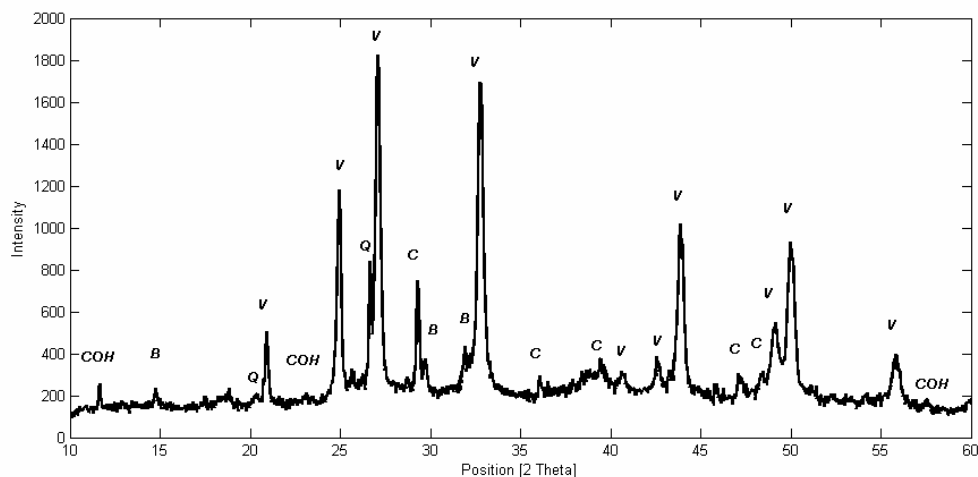
E-mail address: vmorales@us.es

### SUPPLEMENTARY MATERIAL

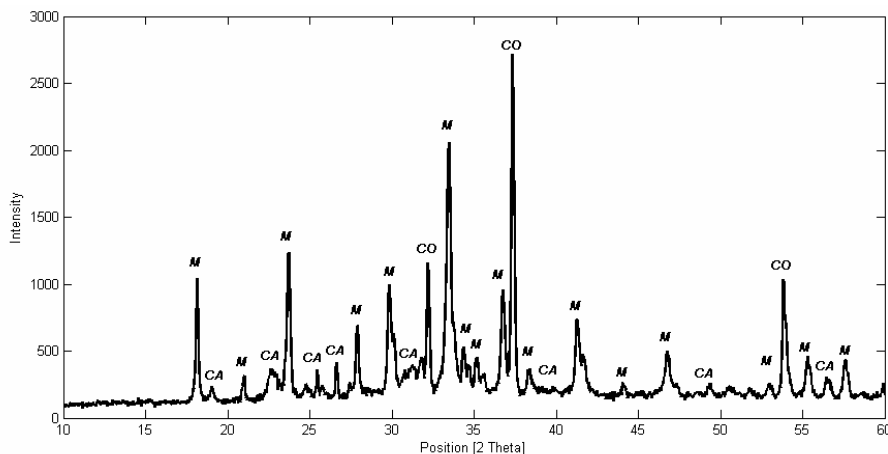
**Figure S1.** Particle size distribution of the sample PG



**Figure S2.** XRD pattern of a poorly carbonated PGAB sample, where the polymorphs of calcium carbonate are identified as V: vaterite (PDF: 00-024-0030), Q: quartz alpha (PDF: 01-089-8936), C: calcite (PDF: 01-086-2340). Other crystalline phases are also identified: B: bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , PDF: 00-041-0224), COH: calcium aluminum oxide carbonate hydrate ( $\text{Ca}_4\text{Al}_2\text{CO}_9 \cdot 11\text{H}_2\text{O}$ , PDF: 00-014-0083).



**Figure S3.** XRD pattern of sample PGAB heated at 800 °C. CO: Calcium Oxide (CaO, PDF: 00-043-1001); M: Mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, PDF: 00-009-0413); CA: Calcium Aluminum Oxide Sulfate (Ca<sub>4</sub>Al<sub>6</sub>O<sub>12</sub>SO<sub>4</sub>, PDF: 00-042-1478).



**Table S1:** Description and sample identifiers used in this work. Summary of the experimental techniques. X-ray diffraction (XRD), X-ray fluorescence (XRF), total acid digestion followed by inductively coupled plasma mass-spectrometry (ICP-MS), inductively coupled plasma (ICP), scanning electron microscopy (SEM-FEG), laser diffraction, N<sub>2</sub> physisorption, thermogravimetric analyses (TGA), and  $\alpha$ -Spectrometry ( $\alpha$ SP).

Sample	Sample characteristic	Technique
PG	Original phosphogypsum sample	XRD, XRF, ICP-MS, laser diffraction, $\alpha$ SP
A <sup>(L)</sup>	Na-Al-rich caustic liquid waste	ICP-AES, $\alpha$ SP
A <sup>(S)</sup>	Solid precipitate from the liquid waste	XRD, XRF
PGA	Carbon sequestration agent	XRD, XRF, TGA, SEM, ICP-MS, $\alpha$ SP, N <sub>2</sub> physisorption
PGA <sup>(L)</sup>	Liquid phase (supernatant of PGA)	ICP-AES, $\alpha$ SP
PGAB	PGA carbonated (by bubbling CO <sub>2</sub> )	XRD, XRF, ICP-MS, $\alpha$ SP
PGAB <sup>(L)</sup>	Liquid phase (supernatant of PGAB)	ICP-AES, $\alpha$ SP
PGAW	Weathered PGA sample	XRD, TGA

**Table S2.** Chemical composition of sample “PGA washed”. LOI: Loss of ignition at 1000 °C.

<b>Major elements (wt. %)</b>	<i>Raw material</i>
	<b>PGA washed</b>
<b>CaO</b>	47.5
<b>Al<sub>2</sub>O<sub>3</sub></b>	18.9
<b>SO<sub>3</sub></b>	4.8
<b>Na<sub>2</sub>O</b>	0.3
<b>SiO<sub>2</sub></b>	1.2
<b>P<sub>2</sub>O<sub>5</sub></b>	0.6
<b>F<sub>2</sub>O</b>	0.9
<b>LOI</b>	25.8