

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



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### 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 CO<sub>2</sub> and produce final materials with similar civil engineering uses to those proposed for current phosphogypsum wastes. This work offers new methods for jointly managing specific industrial wastes oriented to more sustainable industrial processes and controlling CO<sub>2</sub> emissions.

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## 1. Introduction

The anthropogenic emissions of greenhouse gases, especially CO<sub>2</sub>, 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 CO<sub>2</sub> concentrations, considering that the colossal

magnitude of global CO<sub>2</sub> 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 CO<sub>2</sub>/yr, could achieve stabilisation of atmospheric CO<sub>2</sub> 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 CO<sub>2</sub> 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

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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 designing 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 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 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 hydro-grossular 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

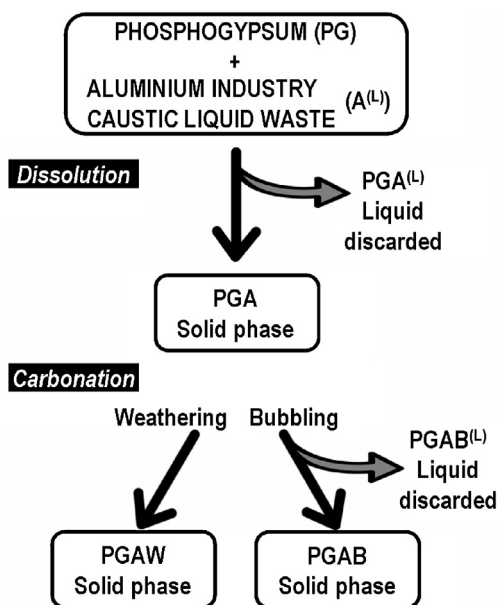


Fig. 1. Experimental methodology of the synthesis of the carbon sequestration agent and the two carbon capture procedures.

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