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Technological Proposals for Recycling Industrial Wastes for Environmental Applications

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Abstract: A two-fold objective is proposed for this research: removing hazardous and unpleasant wastes and mitigating the emissions of green house gasses in the atmosphere. Thus, the first aim of this work is to identify, characterize and recycle industrial wastes with high contents of calcium or sodium. This involves synthesizing materials with the ability for CO₂ sequestration as preliminary work for designing industrial processes, which involve a reduction of CO₂ emissions. In this regard, phosphogypsum from the fertilizer industry and liquid wastes from the green olive and bauxite industries have been considered as precursors. Following a very simple procedure, Ca-bearing phosphogypsum wastes are mixed with Na-bearing liquid wastes in order to obtain a harmless liquid phase and an active solid phase, which may act as a carbon sequestration agent. In this way, wastes, which are unable to fix CO₂ by themselves, can be successfully turned into effective CO₂ sinks. The CO₂ sequestration efficiency and the CO₂ fixation power of the procedure based on these wastes are assessed.

Keywords: greenhouse gases; CO₂ sequestration; phosphogypsum; industrial waste

1. Introduction

Technological proposals to combat the rise in atmospheric carbon dioxide (CO₂) and its effects on climate change have been implemented in order to reduce anthropologically generated CO₂ [1]. To mitigate the harmful consequences caused by climate change, one of the challenges is to develop and improve technologies for energy production and to reduce the concentration of greenhouse gases in the atmosphere [2]. This reduction may be accomplished not only capturing the gases emitted but also by designing procedures with low emissions. Among the carbon capture and storage (CCS) technologies, mineral sequestration has been proposed to indefinitely convert CO₂ by carbonation reaction into an innocuous, stable and environmentally benign carbonate mineral [3,4]. The weakest points of the process are the low speed of the reaction and the costs. To this regard, the high potential of industrial alkalinity sources can contribute to reducing the costs as well as to avoiding the ecological impacts of mineral extraction on a massive scale [5,6].

On the other hand, lime production is typically a high CO₂ emission process. Quicklime is produced by calcination of limestone at about 1000 °C in a limekiln according to the reaction:



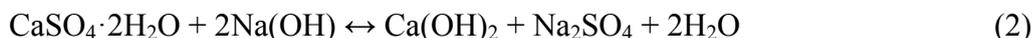
Therefore, 78.6 t of CO₂ is emitted per 100 t of quicklime produced. CO₂ emission comes not only from limestone calcination but also from the production of the power needed for heating the limekiln, usually obtained from fossil fuels. Depending on the type of kiln, the power consumption used to obtain a quicklime range from 3.7 to 7.5 GJ/t [7] also represents a high economic impact in terms of manufacturing cost (≈60% of the total). During the secondary processes of slaking and grinding, depending on the specific production method, lime factories cause emissions to the atmosphere, water and soil (as wastes). Additionally, the environment can be affected by noise and foul smells. Particles of NO_x, SO₂ and CO are other pollutants emitted to the atmosphere. Depending on the limestone and fuel employed, polychlorinated dibenzo-para-dioxins and dibenzofuranes, total organic carbon, metals and hydrochloric and hydrofluoric acid may also result.

The established best available techniques (BAT) conclusions under Directive 2010/75/EU of the European Parliament and of the Council on Industrial Emissions for the Production of Cement, Lime and Magnesium Oxide [8] suggest consumption levels and associated emissions to BAT. The BAT directive deals with clean technologies, emerging effluent treatments, recycling technologies and management strategies. In this paper, we propose a process for lime production that abides by this directive.

Beyond political norms, there is currently a growing general interest in and concern for environmental restoration that encourages the search for possible low-cost applications of industrial by-products. We have designed a procedure for recycling phosphogypsum (CaSO₄·*n*H₂O) waste from the manufacture of phosphoric acid (*i.e.*, H₃PO₄) for fertilizers [9]. This by-product comes through the chemical attack of phosphate rock ore (mainly apatite, Ca₅(PO₄)₃OH) with sulphuric acid (H₂SO₄). Phosphogypsum (PG) waste is usually slurred with water and then pumped out to a nearby disposal

area. In Spain, about 120 million tones have been stockpiled in an area of 1200 ha on the salt marshes associated with the right margin of the Tinto river less than 1 km away from the city centre of Huelva, Spain, a city with a population of 149,000 inhabitants.

The reported procedure starts with the dissolution of raw PG in a sodium hydroxide (Na(OH)) solution that results in the precipitation of a whitish solid phase and a supernatant liquid. The precipitate corresponds mostly to portlandite (calcium hydroxide, Ca(OH)₂), and subsequent evaporation of the supernatant liquid indicates that it mostly contains thenardite (sodium sulphate, Na₂SO₄), as expected from the reaction (Equation (2)):



These results confirm the efficiency of this reaction as a procedure to deal with raw PG waste and to obtain a roughly pure portlandite. In order to develop a viable technology for industrial sectors, the proposed CO₂ sequestration procedure [9] has been subjected to modifications with the aim of reducing cost and environmental impact. In this work, we have used commercial soda and soda derived from by-products of the marinating of green olives and the treatment of bauxite to obtain aluminum to treat the PG [10]. Finally, the precipitated solid phases from the proposed procedure will be considered for lime mortar manufacturing as a first approach to develop an application for the by-products.

2. Experimental Section

2.1. Original Samples

The wastes considered in this work were supplied by different industries from Andalusia, Spain. All the samples are listed in Table 1. All reactive-grade precursors have been used in this work with the aim of improving the viability of the studied techniques at an industrial level.

Table 1. Description and sample names used in this work.

Sample name	Sample characteristics
PG	Original phosphogypsum sample
PGTS	Solid phase from phosphogypsum + caustic soda for domestic use
PGOS	Solid phase from phosphogypsum + olive industry waste
PGOL	Liquid phase from phosphogypsum + olive industry waste
PGAS	Solid phase from phosphogypsum + aluminum industry waste
PGAS_CO ₂ w	Weathered sample PGAS
PGAS_CO ₂ b	Sample PGAS carbonated by bubbling CO ₂ in aqueous media
PGT_mortar	Mortar obtained from PGTS

2.1.1. Phosphogypsum Waste

The phosphogypsum samples (approximately 3 kg) were collected at different depths from bore-holes carried out using a soil sampling auger from the phosphogypsum stockpiles in Huelva in November 2009. In the laboratory, samples were oven-dried (80 °C) until completely dry and then milled and homogenized. Major components and traces are listed in Table 2. This waste has been deeply analyzed and its characteristics and properties can be consulted elsewhere [9].

Table 2. Major components and traces of the different mineral sources considered in this work, indicating the analytical technique. X-ray fluorescence (XRF) data were normalized to calcined mass. Uncertainties are given as standard deviations.

Technique	Posphogypsum waste [9]	Olive industry waste	Aluminum-rich waste
XRF (wt %)	[SO ₃] = 50.2%		[Na ₂ O] = 80.24%
	[CaO] = 44.7%		[Al ₂ O ₃] = 17.81%
	[Na ₂ O] = 1.2%	-	[Cl] = 1.23%
	[F] = 1.6%		[SiO ₂] = 0.52%
Chemical and elemental analyses		[Na] = 45.7 ± 0.1 mg/L	
		[Ca] = 17 ± 1 mg/L	[Na] = 148 ± 2 g/L
		[C] = 1.5 ± 0.1%	[Al] = 87.3 ± 1.4 g/L
		[N] ≤ 0.01%	

2.1.2. Low-Cost Soda Samples

Relevant properties of the considered wastes are listed in Table 2. The first low-cost soda source considered in this work consisted of sodium hydroxide (NaOH), also known as caustic soda flakes for domestic use (purity > 90%). The second soda source was a yellowish liquid waste (pH ~ 7.5) from the marinating of green olives, usually stocked in open-air reservoirs. Two liters were collected from one of these reservoirs at Arahal (Seville) for laboratory testing. Finally, the third soda source was the soda-rich liquid phase used for the treatment of bauxite in the aluminum industry. It consisted of a very basic dark reddish liquid phase (pH ~ 14) with a density of 1.35 g/cm³. This waste was supplied by Verinsur S.A. (Jerez de la Frontera, Spain). For characterization purposes, this waste was left to evaporate in a hot plate at 110 °C in order to analyze the solid precipitate. Afterwards, the sample was kept in a stove at 80 °C to prevent hydration and carbonation due to weathering.

2.2. Sample Preparation

The proposed methodology started with the dissolution of the raw phosphogypsum sample in a soda-rich solution prepared from the different wastes. The amount of phosphogypsum depended on the soda content of the prepared solution. In the case of the common soda, 83.12 g of soda were added to 3.5 L of water, and 140 g of phosphogypsum were subsequently added into the solution. The obtained solid phase from this procedure was labeled “PGTS”. In the case of the olive industry waste, 1.7 g of phosphogypsum were added directly to 100 mL of the liquid waste, and the solid and liquid phases were labeled as “PGOS” and “PGOL” respectively. When working with the aluminum waste, 8.75 g of phosphogypsum were added to 25 mL of liquid waste yielding the sample labeled as “PGAS”. Then, the systems were dispersed by magnetic stirring at room pressure and temperature for 3 h. The phosphogypsum dissolution resulted in the precipitation of a brownish solid phase and a supernatant liquid. Afterwards, samples were centrifuged for 5 min. at 3000 rpm for phase separation. The solid phase was dried at 80 °C in a stove and kept at 80 °C in the stove to prevent hydration and carbonation due to weathering. This phase was considered for manufacturing lime mortars (see Section 3.1.1 for details) and for CO₂ sequestration. The product liquid phase was discarded in all cases, but, when working with the olive industry waste, the drying was done on a hot plate at 110 °C just for characterization.

2.3. CO₂ Sequestration Experiments

The carbonation capacity of the solid phases obtained by the procedure explained previously was assessed in two different ways. Firstly, simple weathering experiments were conducted in small scale “weathering pools” [11], that is, spreading the aqueous suspension on a flat surface for drying under room conditions and letting the sample react with atmospheric CO₂. The carbonation of the solid phases occurred during drying under atmospheric conditions, typically taking from 3 days to one week.

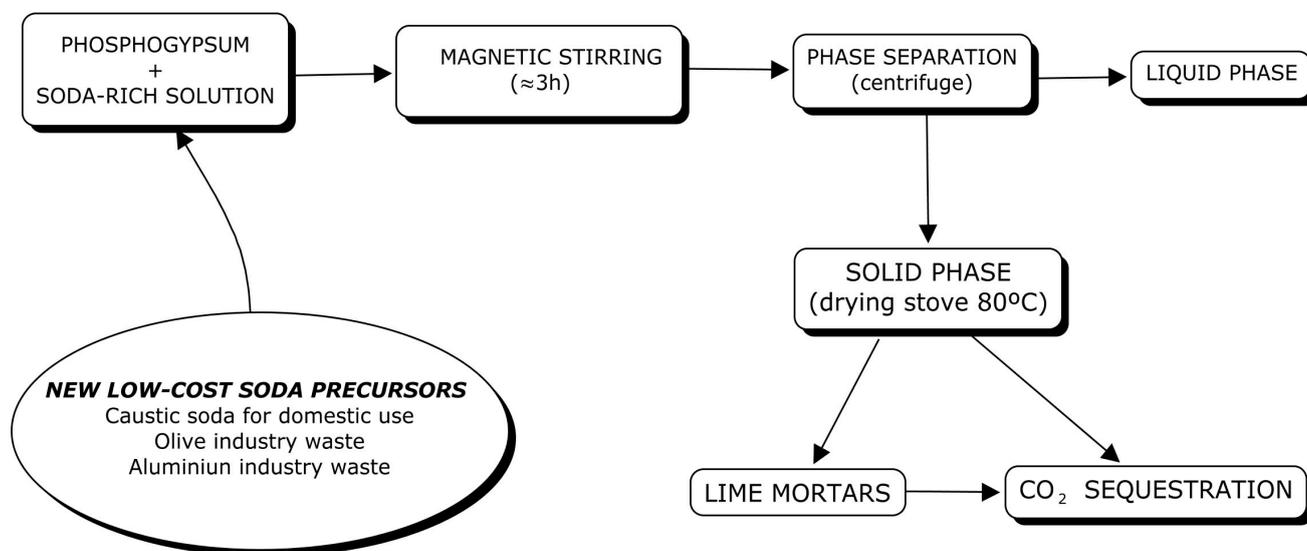
Secondly, 2 g of this precipitate were dispersed in 40 mL of high-purity water into a reactor, and a CO₂ flux (1 bar, 20 cm³/s) was bubbled through the suspension for 15 min. at room pressure and temperature. Afterwards, the sample was left to rest overnight in the CO₂-rich water. The resulting solid phase was separated by centrifugation and dried in air at 80 °C, and the supernatant discarded.

2.4. Characterization Techniques

Chemical characterization of the samples was performed by X-ray fluorescence (XRF) with an Axios Panalytical instrument (Almelo, The Netherlands,) for major elements and traces. Chemical analyses of the aqueous samples were performed by inductively coupled plasma (ICP-AES) on a Horiba Jobin Yvon (Kyoto, Japan) Ultima 2 and elemental analysis Leco (St. Joseph, MI, USA) CHNS-932. Crystalline phases of the samples were identified by X-ray diffraction (XRD) performed on a Bruker (Karlsruhe, Germany) D8 Advance and obtained with Cu-K α radiation ($\lambda_{\alpha 1} = 0.154$ nm). Data were collected in the interval $10^\circ < 2\theta < 60^\circ$ with a step size of $\Delta(2\theta) = 0.015^\circ$. Counts were measured by keeping a collection time of 0.1 s/step.

The experimental methods and materials explained in this section and the main goals of this work are summarized in Figure 1.

Figure 1. General scheme of the experimental procedure.



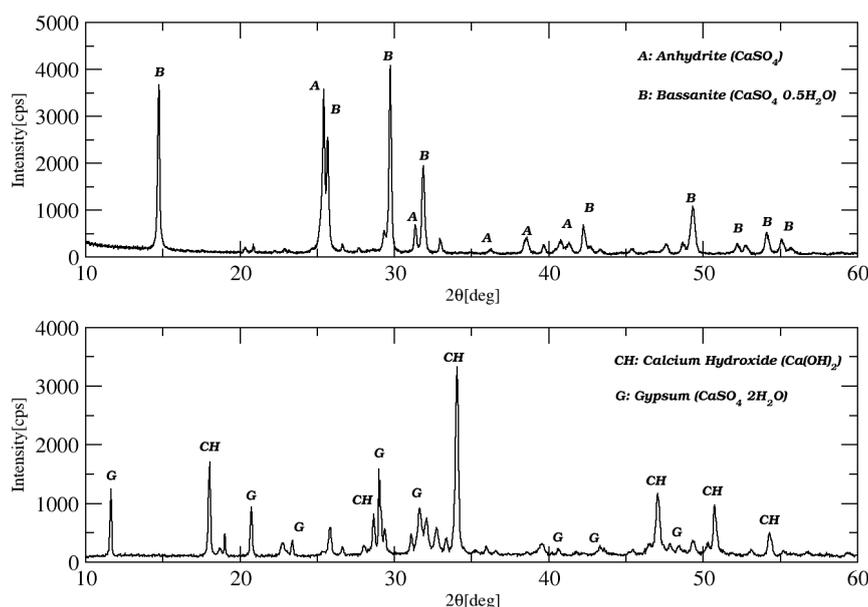
3. Results and Discussion

3.1. Phase Separation

3.1.1. Phosphogypsum and Caustic Soda

The analysis of the original raw phosphogypsum revealed the presence of hemi-hydrated and anhydrite calcium sulphates, that is, bassanite and anhydrite instead of the expected gypsum. In Figure 2, the X-ray diffraction pattern of the raw phosphogypsum is plotted, and major reflections identified. The milling process for homogenizing and refining the particle size, together with the drying process for a long time at 80 °C leads to the formation of the dehydrated phases [12,13]. This fact is supported by the sole presence of gypsum features in the XRD pattern of samples dried at 40 °C [9]. The exact nature of the wastes spread throughout 1200 ha in the phosphogypsum stockpiles remains unrevealed; so, different samples from different points could present different calcium sulphate phases. Actually, this important mapping of the complete stockpiles is still pending. The low water content in the calcium phase was considered for stoichiometric calculations on phase separation.

Figure 2. Original raw phosphogypsum sample (top), where anhydrite (PDF:00-006-0226) and bassanite (PDF:00-041-0224) are identified, and sample PGTS (bottom), where calcium hydroxide (PDF:01-084-1271) and gypsum (PDF:00-036-0432) are identified.



In Figure 2, bottom, the obtained solid phase, labeled as PGTS, was mainly composed of calcium hydroxide and gypsum. An analogous reaction to Equation (2) was mainly fulfilled in this simple system and calcium was mainly released from sulphate. Furthermore, the presence of gypsum (dihydrated calcium sulphate) reveals the hydration of the original sulphate phases due to the immersion in the soda-rich solution. In addition, minor reflections corresponding to calcite, coming very probably from weathering while handling the sample, and cesanite (calcium sodium hydroxide sulphate, Ca₂Na₃(SO₄)₃(OH)) and thenardite could be identified, but they are not labeled in the XRD plot. In summary, when caustic soda is used to attack the PG, the results clearly indicate the presence

of slaked lime (calcium hydroxide), as was expected. Thus, caustic soda for domestic use is adequate for our study.

The portlandite-rich sample, PGTS, was used for the preparation of traditional lime mortars by mixing them with dolomite (according to standard UNE-EN 13139 [14]) with grains <1 mm in a volume ratio of 1:2.5. The mixtures were kept in closed recipients to prevent direct exposure to air, up to the application of a plastering layer 0.5 cm thick with a trowel on an old wall, predominantly composed of sand. After several days, the sample showed a uniform, homogeneous and crack-free finish. Thus, ongoing work is being developed on this point in order to develop and characterize applications for the by-products of the introduced recycling procedure. There are several environmental benefits of these mortars obtained from industrial wastes. Among them, avoiding carbon emissions from both raw calcite decarbonation and powering for kiln heating is worth mentioning. These features would help to improve the sustainability of the construction industry. On the other side, it is well known that phosphogypsum waste can carry toxic metals and radioactive traces. Consequently, these contents should be controlled prior to any subsequent application of the derived construction materials [15].

Despite that caustic soda for domestic use is now proposed for a successful strategy in reducing costs, we take a step further towards using only industrial wastes for obtaining valuable products. We have tried to apply our finding to treat unwanted industrial wastes such as those from the marinating of green olives and the production of aluminum from bauxite. The results are shown in the following sections.

3.1.2. Phosphogypsum and Olive Industry Waste

The first attempt to design processes based only on industrial wastes consisted of using raw phosphogypsum waste and liquid waste from marinating green olives. In Figure 3, the XRD patterns from the solid phase (labeled PGOS) and the evaporated liquid phase (PGOL) are shown. According to our methodology, features of portlandite should have appeared in the diagram corresponding to PGOS (Figure 3, top). Instead, bassanite and anhydrite, both components of the original phosphogypsum waste, appeared. Moreover, the phase liquid PGOL contains halite (NaCl) in place of sodium sulphate (Na_2SO_4), indicating that olive industrial waste behaves differently than expected. The presence of halite in sample PGOL confirms that the measured content of Na in the liquid waste does not come from soda. This point is confirmed by a pH of slightly higher than 7.

3.1.3. Phosphogypsum and Aluminum-Rich Waste

The other residue assayed for this study was from the aluminum industry, a substance with a high Na content. The residue was examined by XRF and chemical analysis and its contents are shown in Table 2. As it can be seen, its Na content is very high (148 g/L), and $\text{pH} \approx 14$, indicating that the Na likely comes from soda. This idea is also supported by the obtained results from XRD (Figure 4, top). Two crystalline phases were identified, sodium carbonate (Na_2CO_3) and sodium aluminum oxide ($\text{Na}(\text{AlO}_2)$). The first one could be originated by chemical reaction between the soda and atmospheric CO_2 while drying the original liquid waste, and the second one corresponds to the expected oxide from waste drying.

Figure 3. XRD patterns from phosphogypsum and industry waste sample: sample PGOS (top), where anhydrite (PDF:01-086-2270) and bassanite (PDF:00-041-0224) are observed, and sample PGOL (bottom), where bassanite (PDF:00-041-0224) and halite (PDF:00-005-0628) are observed.

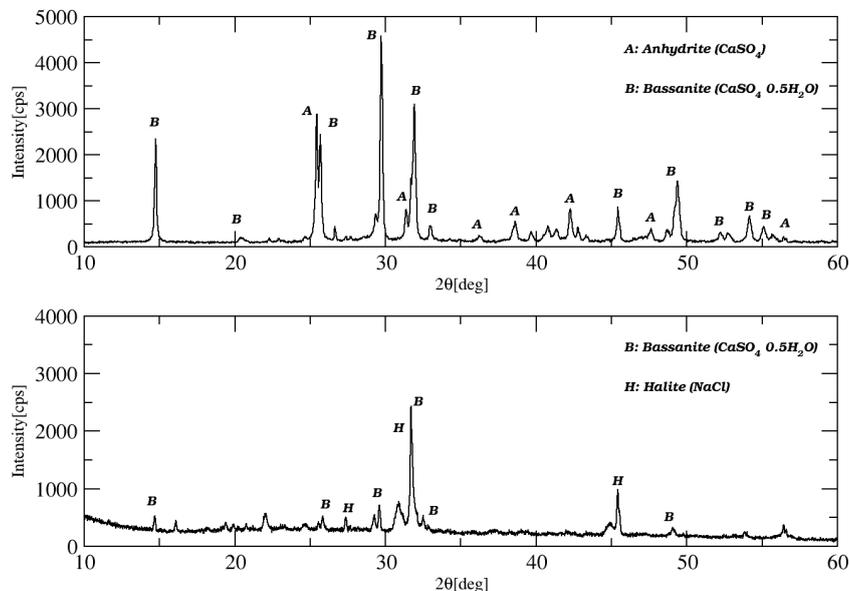
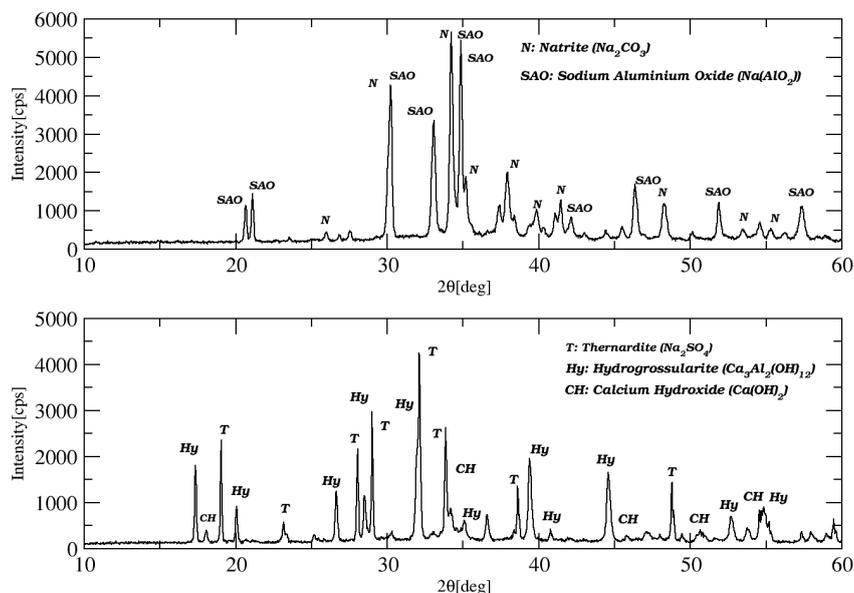
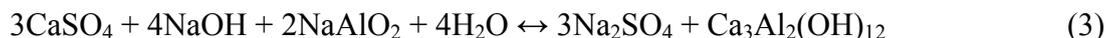


Figure 4. XRD patterns from the original aluminum-rich waste evaporate (top), where natrite (PDF:00-037-0451) and sodium aluminum oxide (PDF:01-083-0316) were identified, and sample PGAS (bottom) where hydrogrossularite (PDF:00-002-1124), portlandite (PDF:00-004-0733) and thenardite (PDF:00-037-1465) were identified.



The next step consisted of the formation solid phase accomplished by dispersion of phosphogypsum into the soda-rich solution from aluminum waste. The XRD analysis of the obtained solid phase (sample PGAS) is plotted in Figure 4, bottom (once the supernatant was discarded). The presence of thenardite, hydrogrossularite (Ca₃Al₂(OH)₁₂) and, as expected, calcium hydroxide (Ca(OH)₂) was verified. Differently from previous results with caustic soda (Figure 2), in this case two different

hydroxides precipitated. The precipitation of calcium hydroxide probably took place once the aluminum content was used up. Thus, due to the presence of high aluminum content in the suspension, the expected reaction Equation (2) occurred together with the process described by Equation (3):



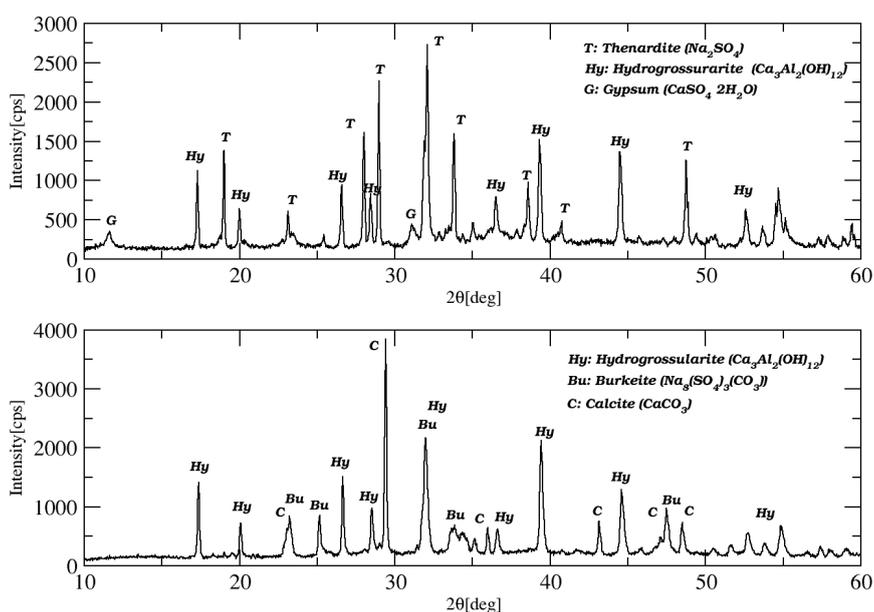
Finally, unlike the case of the olive industry waste, no remaining bassanite or anhydrite was detected, indicating that there is no phosphogypsum residue and, therefore, that the reaction was complete.

3.2. CO₂ Sequestration by Reusing Phosphogypsum and Aluminum-Rich Wastes

Two different procedures were considered for the study of the CO₂ sequestration efficiency of the obtained sample PGAS. Firstly, the sole effect of weathering the sample was estimated, and secondly, CO₂ was bubbled in a suspension of sample PGAS (see the experimental section for details).

The carbonation of the samples depended on the carbonation procedure. Thus, the weathered sample PGAS_CO₂w showed no carbon sequestration during drying (Figure 5, top) since any of the identified crystalline phases correspond to a carbonated phase. On the contrary, the sample PGAS_CO₂b (bubbled with CO₂ in aqueous media) presented two well defined carbonated crystalline phases (Figure 5, bottom), namely calcite and burkeite. Therefore, the weathering pools procedure, as mentioned above, does not work with this synthetic CO₂ sequestration agent from phosphogypsum and aluminum-rich waste. This is because the dissolution of sodium sulphate and portlandite and the subsequent precipitation of gypsum are favored, instead of the precipitation of carbonated phases. The carbonation of this sample by weathering pools should consider longer times, together with rewetting the sample, as explained in [11].

Figure 5. XRD patterns from sample PGAS_CO₂w (top), where thenardite (PDF:00-037-1465), hydrogrossularite (katoite, PDF:00-024-0217) and gypsum (PDF:01-076-1746) are clearly identified, and PGAS_CO₂b (bottom), with labeled peaks from calcite (PDF:00-005-0586), burkeite (PDF:01-085-1733) and hydrogrossularite (PDF:00-002-1124).



On the other hand, a promising procedure based on the recycling of these wastes and bubbling CO_2 in aqueous media under atmospheric conditions has been designed. The complete disappearance of calcium hydroxide observed in sample PGAS (Figure 4, bottom) and its substitution by calcite in sample PGAS_ CO_2 b (Figure 5, bottom) reveals a maximum efficiency of this synthetic portlandite. However, the presence of hydrogrossularite reveals an incomplete carbonation process, signifying that experimental conditions must be improved in order to achieve complete carbonation and to maximize the carbon sequestration efficiency of this technology. It must be remarked that this sequestration agent has been synthesized exclusively from industrial wastes and no chemical reagent has been used. In addition, the synthesis procedure is extremely simple, as it does not involve any complicated chemical or physical treatment, only stirring or centrifuging. So, the energy consumption of this procedure is very low in comparison with other proposed technologies [4,16,17].

Regarding the calcium and sodium contents of the industrial wastes used for obtaining sample PGAS, the combined fixation power was estimated to be 10%. This was estimated based on the hypothetical full efficiency of the carbon sequestration, according to the contents of the respective Ca and Na containing wastes (Table 2) and the density of the aluminum-rich liquid waste. This power is an interesting value if compared with other residues such as municipal solid waste bottom-ash (2.3%), carbon fly ash (2.6%), acetylene calcium-rich waste (7%) and paper mill waste (21%) [11].

Finally, the crystalline composition of sample PGAS_ CO_2 b suggests its possible applications to some mineral-demanding industrial sectors as the construction materials sector. Considering the 120 Mt of phosphogypsum waste stockpiled in the stacks, the production of 200 t/year of waste in the considered aluminum industry would enable the fixation by mineral sequestration of 21 t/year of CO_2 , yielding roughly 50 t/year of carbonates. The application of aluminum-rich compounds in cement [18] and mortar [19] syntheses is widely known, and, therefore, this carbonation by-product, and its non-carbonated counterpart PGAS as well, can be considered for synthesizing cements and mortars. In addition, environmental benefits will also involve avoiding mineral extraction on a massive scale. Successful results of this application will unquestionably enhance the technological viability of the proposed procedures of sample PGAS synthesis and carbonation.

4. Conclusions

The proposed routes for phase separation from phosphogypsum and low-cost soda sources have yielded different results. First of all, it was confirmed that common soda for domestic use, similar to reactive grade soda, is completely efficient for obtaining calcium hydroxide from phosphogypsum, and therefore, for producing materials with the ability for CO_2 sequestration by means of two low-cost precursors. On the contrary, the liquid waste from the green olive industry has been revealed as useless for phase separation.

On the other hand, the procedure from phosphogypsum and liquid waste from the treatment of bauxite in the aluminum industry is an efficient route for phase separation. Furthermore, the separated solid phase has verified its capacity for CO_2 sequestration. Phosphogypsum and aluminum industry waste have proven a fixation power of 10%, and the production of one aluminum industrial plant would allow sequestering 21 t/year of CO_2 . Thus, working only with industrial wastes, a CO_2 sequester is obtained, decreasing even more the costs of the complete process as compared to the costs of the

process using pure soda. In addition, recycling these industrial wastes will reduce their environmental impact and avoid unwished storage and socially unpleasant reservoirs. In summary, this procedure considers two different industrial wastes, which are unable to sequester CO₂, and through very simple procedures they become a CO₂ sink.

Finally, first trials for obtaining construction materials from these wastes have been performed and the promising results are being considered for future work on low-cost and environment-friendly construction materials.

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Author Contributions

All the authors were involved in laboratory work, sample characterization, writing and revising all parts of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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