Procedure to use phosphogypsum industrial waste for mineral CO$_2$ sequestration

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Abstract

Industrial wet phosphoric acid production in Huelva (SW Spain) has led to the controversial stockpiling of waste phosphogypsum by-products, resulting in the release of significant quantities of toxic impurities in salt marshes in the Tinto river estuary. In the framework of the fight against global climate change and the effort to reduce carbon dioxide emissions, a simple and efficient procedure for CO_2 mineral sequestration is presented in this work, using phosphogypsum waste as a calcium source. Our results demonstrate the high efficiency of portlandite precipitation by phosphogypsum dissolution using an alkaline soda solution. Carbonation experiments performed at ambient pressure and temperature resulted in total conversion of the portlandite into carbonate. The fate of trace elements present in the phosphogypsum waste was also investigated, and trace impurities were found to be completely transferred to the final calcite. We believe that the procedure proposed here should be considered not only as a solution for reducing old stockpiles of phosphogypsum wastes, but also for future phosphoric acid and other gypsum-producing industrial processes, resulting in more sustainable production.

1. Introduction

The wet-acid process for manufacture of phosphoric acid (i.e. H_3PO_4) for fertilizers involves the chemical attack of phosphate rock ore (mainly apatite, $Ca_5(PO_4)_3OH$) with sulphuric acid (H_2SO_4), generating a gypsum by-product known as phosphogypsum ($CaSO_4 \cdot nH_2O$). The phosphogypsum waste is

usually slurried with water and then pumped out of the fertilizer industrial plant to nearby settling/disposal area, using a system of pipes. Recycling of phosphogypsum is limited by the high content of metallic impurities and radionuclides [1].

In Spain, the phosphoric acid production began in 1968 in an industrial complex located at the estuary formed by the union of the Tinto and Odiel river mouths (Huelva, SW Spain). The phosphogypsum has been stockpiled over an area of 1200 ha containing about 120 million tonnes on the salt marshes associated with the right margin of the Tinto river, less than 1 km away from the city centre. In fact, the area covered by the phosphogypsum stack is roughly similar to the surface area covered by the city of Huelva itself, with a population of 149.000. The proximity of the waste to the city has also aroused considerable controversy for its alleged implications for the health of the local population; however, most studies have concluded that populations living close to stacks are not exposed to any significant health risk (see for example [2]). Moreover, salt marshes on the Tinto-Odiel estuarine system hold an important part of Europe's ornithological biodiversity and they were declared UNESCO Biosphere Reserve in 1983 and RAMSAR-NATURA wetlands sites in 1989. Sudden changes in land-use and direct dumping of phosphogypsum on these salt marshes dramatically altered the visual landscape and degraded the marshland occupied by the stack. The high content of metals and U-Th series radionuclides in phosphogypsum and the impact of these wastes on the quality of sediments and waters of surrounding environmental receptors have been widely described [3-6].

After two decades of looking for sustainable solutions and alternatives to the stockpiling of wastes, the Huelva's fertilizer industrial complex ceased dumping of phosphogypsum over salt marshes in December 2010 following a decision of the Spanish Major National Court. Currently, the growing interest for the environmental restoration encourages the search of possible low-cost applications to phosphogypsum waste. Few investigations have been so far reported in the literature for this purpose; and up to now, the only reported use of this phosphogypsum waste is as an additive, in six doses of 20-25 t/ha, to improve fertility and reduce sodium saturation in an area of 140 km^2 of agricultural soils [7]. However, this practice was halted in 2001 due to public concern about safety. Thus, under the framework of the integrated waste management, it is crucial to find the best alternative use for the 120 million tonnes of discarded gypsum by-products without damaging the natural environment. The proposal discussed in this work concerns the utilization of this waste as CO_2 sequester agent.

Several carbon dioxide sequestration strategies are being studied worldwide to reduce anthropogenic greenhouse gas emissions, and hence, mitigate global warming. Mineral sequestration [8] is a promising approach to the problem of managing and capturing carbon dioxide permanently and safely, and has the potential to sequester CO_2 emissions directly from localised sources, mobile sources (e.g. transport), and even past CO_2 emissions. The mineral sequestration process involves a reaction where aqueous ions (mainly Ca and Mg from silicates [9] or hydroxides) react with CO_2 to form stable carbonate minerals and it has controlled the CO_2 content on the atmosphere for millennia. The costs associated with industrial scale mineral sequestration are a major

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drawback of this technology, but they could be significantly reduced by using industrial alkaline wastes as aqueous Ca and Mg sources ([10-14]).

In light of the above, the aim of the present study is to evaluate the use of phosphogypsum waste as a Ca source for carbon dioxide mineral sequestration. We believe that this new methodology is especially attractive and ecologically clean, since it has the potential to reduce two environmental problems simultaneously: 1) management of hazardous industrial waste; and 2) greenhouse gasses emissions.

2. Experimental procedure

Several samples (approx. 2 kg) were collected from the phosphogypsum stack in November of 2009 at different depths from bore-holes carried out using a soil sampling auger. In the laboratory, samples were oven-dried (40 ◦C) until complete dryness, ground and homogenised. The data relative to one representative sample of phosphogypsum are discussed in this paper.

The proposed methodology starts by the dissolution of the raw sample in an alkaline solution. The dissolution experiments were conducted in 20 mL of high-purity water where 5 g of phosphogypsum were dispersed by magnetic stirring at room pressure and temperature. Immediately after, 2.34 g of NaOH were added to reach a OH^-/Ca molar ratio of 2. The mixture was kept at room temperature for 3 h under constant stirring. The phosphogypsum dissolution resulted in the precipitation of a whitish solid phase and a supernatant liquid. Subsequent evaporation of the supernatant to dryness on a hot plate at 80ºC

yielded transparent salts, which were later characterized as a second solid phase.

The carbonation capacity and efficiency of the solid phase precipitated in the dissolution experiments were assessed by a simple carbonation experimental set-up: 2 g of this precipitate were dispersed in 40 ml of high-purity water under magnetic stirring into a reactor, and a CO_2 flux (1 bar, 20 cm^3/s) was bubbled through the suspension for 15 min at room pressure and temperature. Afterwards, the sample was left to rest overnight into the CO_2-rich water. The resulting solid phase was separated by centrifugation and dried in air at 80ºC, and the supernatant discarded. In figure 1, the entire experimental procedure is sketched.

Chemical characterization of the raw phosphogypsum and the solid products from dissolution and carbonation experiments was performed by X-ray fluorescence (XRF; AXIOS Panalytical instrument) 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. Crystalline phases of the samples were identified by X-ray diffraction (XRD) in a diffractometer (Philips X'Pert) with Cu-Kα radiation, from 5.00^o to 70.00^o with a step of 0.05^o and counting time of 80 s. The carbonation degree of the samples was studied by thermogravimetric analyses (TGA; STD Q600) carried out under a nitrogen flux of 100.0 ml/min, starting from ambient temperature and increasing by 10 ºC/min up to 1000 ºC.

3. Results and discussion

3.1 Analysis of the samples prior to CO_2 sequestration

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The XRD of the raw phosphogypsum sample is shown in figure 2. The diffraction pattern indicates that the sample is composed mainly of gypsum ($CaSO_4 \cdot 2H_2O$, PDF number: 99-101-0394), as expected [15]. After the dispersion of this sample in water and the addition of NaOH, the resulting whitish precipitate correspond mostly to portlandite (Calcium hydroxide, $Ca(OH)_2$, PDF number: 99-100-0115), as shown in the diffractogram of the figure 2 and as expected by reaction [α]:

$$CaSO_4 \cdot 2H_2O + 2\ NaOH \leftrightarrow Ca(OH)_2 + Na_2SO_4 + 2\ H_2O \qquad [α]$$
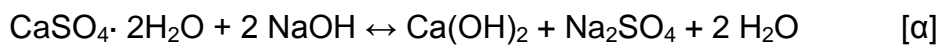
and considering the large difference between gypsum and portlandite's solubility constants, being the solubility constant of gypsum $K=3.14 \cdot 10^{-5}$ and that of the portlandite $K=5.02 \cdot 10^{-6}$ [16]. Finally, the diffractogram of the transparent salts precipitated by evaporation of the supernatant liquid (figure 2) indicates that is mostly composed of thenardite (Na_2SO_4, PDF number: 99-100-4889), again as expected regarding reaction [α]. These results confirm the efficiency of the reaction [α] as a procedure to deal the raw phosphogypsum waste and obtain a roughly pure portlandite.

Major element concentrations determined by XRF of the different solid phases from phosphogypsum dissolution were in agreement with the mineralogical composition estimated by XRD (Table 1). Raw phosphogypsum composition is clearly dominated by S (50.2 wt% as SO_3) and Ca (44.7 wt% as CaO). However, the calcium content of the gypsum was slightly higher than expected stoichiometrically, revealing the existence of other different calcium compounds poorly crystallized, not easily observable by XRD (Figure 2). Portlandite is manly composed of Ca (89 wt% as CaO); again, calcium content remains slightly higher than expected, so minor calcium compounds are carried

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in this portlandite phase as impurities, possibly calcium phosphate from original rock. Finally, the solid obtained from the supernatant evaporation is characterized by high contents of S (55.8 wt% as SO_3) and Na (42.7 wt% as Na_2O). Other major impurities of the starting phosphogypsum are F, Na, Cl, P, Si, Al and Mg, and to a lesser extent Fe, Sr and Y (Table 1). Excepting some of Cl, Si and Sr present in the sodium sulphate, the most of these impurities were also found in the resulting portlandite (Table 1).

The presence of potentially toxic trace elements in the raw phosphogypsum was analyzed by acid-digestion and ICP-MS (Table 2). The main trace elements identified were Cr, As, U, Ni, V, Se, Cd, Pb, Zn and Th, in order of abundance. The contents of these elements in the products from phosphogypsum dissolution, i.e. portlandite and sodium sulphate, are also shown in Table 2. All trace elements were present at ≤3.70 mg/kg within the phosphogypsum sample. These values are close to the average values analyzed in surface samples from the pile [6], supporting this sample as representative of the stack. The contents of trace elements are slightly inferior to those of phosphogypsum samples produced from other phosphate rock sources around the world [17] Most of these trace elements were below or near to the detection limit in the precipitated sodium sulphate. Based on reaction [α], a mass balance or transfer factor was calculated in order to determine the partitioning of trace elements during phosphogypsum dissolution and portlandite precipitation. Accordingly, approx. 100% for all trace elements are transferred from phosphogypsum to the resulting portlandite. Hence, no metals remained in the sodium sulphate solution resulting from the phosphogypsum dissolution.

3.2 Carbon dioxide capture efficiency

The XRD diffractogram of the carbonated portlandite resulting from the aqueous carbonation procedure is shown in Figure 3. It clearly indicates that total conversion of the original portlandite to calcite ($CaCO_3$, PDF number: 99-101-2108) was achieved. The carbonation reaction is as follow:

$$Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O \qquad [\beta]$$
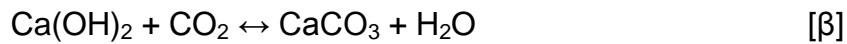
This point was confirmed by thermogravimetric analyses of the original and calcite samples. The analysis of the reference portlandite prior to the carbonation procedure confirmed that the purity of the portlandite was close to 90%. The measured weight loss due to dehydration was 22%, as estimated by XRD (see table 1). And the carbonated portlandite showed a 38.4% weight loss due to the release of the CO_2 at 700ºC (almost 40%, the maximum theoretical weight loss of pure calcite), indicating that all the calcium present in the sample, whether from portlandite or from other minor calcium compounds, was carbonated and revealing a extremely high carbonation efficiency of these wastes.

During the aqueous carbonation process, toxic trace elements initially contained in the portlandite are released into solution. Based on reaction [β] stoichiometry and the molecular weights, the concentration of trace metals in the final calcite implies a high transfer factor of around 100% for all elements (Table 2). Again, no metals were kept in the resulting water after the carbonation reaction, and all of them were transferred to the solid precipitate.

Metal uptake by calcite precipitation is responsible for trace element removal from solution through co-precipitation or adsorption on its surface. Divalent metals such as Ni, Cd, Pb and Zn can be easily removed from solution

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and incorporated into the structure of the calcite by co-precipitation [18]. Albeit, adsorption on the calcite surface could be also a significant mechanism for retention of metals as long as their concentrations in solution are lower than the limit of 10^{-5} M established by Zachara et al. [19], as is the case in our experiments of portlandite dissolution and carbonation. Nevertheless, whatever the scavenging process, calcite precipitation is a successful mechanism for reducing metal mobility in natural aqueous systems [20].

A sustainable and environmental-oriented procedure to manage of these wastes is inferred from these results. In a realistic and numerical approximation to quantities of phosphogypsum that are generated annually by the fertilizer industry of Huelva, the reagents to develop the proposed methodology are summarized as follows: to treat 2 Mt of phosphogypsum, 0.92 Mt of NaOH will be needed, and 0.4 Mt of H_2O from phosphogypsum, 1.64 Mt of Na_2SO_4 and 0.84 Mt of $Ca(OH)_2$ will be produced. This amount of $Ca(OH)_2$ could be used to subsequently capture 0.50 Mt of CO_2, yielding 1.16 Mt of $CaCO_3$. Based on these results, an estimation of the carbon capture capacity of the entire stockpiled phosphogypsum waste was made. 55.2 Mt of NaOH will be needed to treat 120 Mt of phosphogypsum, enabling capture 30 Mt of CO_2.

4. Conclusions

In this work, total conversion of phosphogypsum industrial waste into portlandite (calcium hydroxide) and sodium sulphate was confirmed, and the high carbon dioxide capture efficiency of the resulting portlandite was demonstrated. Portlandite was produced by dissolution of dihydrated calcium sulphate from the phosphogypsum and reaction with sodium hydroxide. The

main impurities contained in the phosphogypsum were transferred to the portlandite and, subsequently, to the final calcite after bubbling CO_2, with transfer factors close to 100%. The total and rapid conversion of portlandite into calcite demonstrated in this study makes the proposed methodology an attractive and ecological solution to two environmental problems: 1) the high amount of phosphogypsum waste generated by the fertilizer industry; and 2) the CO_2 emissions generated by the same industry.

Furthermore, mineral CO_2 sequestration using phosphogypsum by-products from the fertilizer industry of Huelva (Spain) is especially attractive since the waste disposal stockpiles are located about 60 km from the Iberian Pyrite Belt, the largest sulfide metallogenic province in the world. The intense mining activity in this region has produced a huge volume of sulphide-rich mining wastes [21]. The oxidation of these mining-wastes releases solutions with abnormally high acidity and metal concentrations [22]. Some restoration strategies using calcite have been tested in the field with satisfactory results to deal this environmental problem [23]. However, the calcite used in the treatment systems is associated with a high economic and environmental cost, since calcite is typically a resource and not a residue. Using the final calcite from dissolution and carbonation of the phosphogypsum would significantly reduce the costs of future remediation plans. The toxic metals contained in the final calcite may be released into solution during the treatment of acid mine waters, but this additional amount of toxic elements is negligible compared to that released by sulphide-rich wastes in acid discharges and the precipitation of metal hydroxides also depletes these elements by sorption process. .

Finally, the purity of the sodium sulphate by-product allows it to be commercialized, for example to detergent or paper industries. In summary, our results support the development of an economically viable technology of carbon dioxide sequestration based on the re-use of these phosphogypsum industrial wastes.

Acknowledgements

TABLES AND FIGURES CAPTIONS

Table 1. Major elements contents of the samples analyzed by X-ray fluorescence. Weight percentages are normalized to the mass without loss-of-ignition values (LOI).

Table 2. Contents of trace elements measured by analysis with inductively coupled plasma mass-spectrometry.

Figure 1. Flowchart of the experimental methodology.

Figure 2. Diffractograms of the raw phosphogypsum ($CaSO_4 \cdot 2H_2O$) from Huelva (Spain), of the solid filtered where portlandite ($Ca(OH)_2$) can be clearly

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observed, and the solid phase obtained from supernatant evaporation where the diffraction pattern of thenardite (Na_2SO_4) is clearly matched. Diffractograms were shifted for of clarity.

Figure 3. Diffractogram of the carbonated porlandite. No other phase than calcium carbonate is observed. Portlandite diffractogram has been repeated for comparison purposes only. Diffractograms were shifted for clarity.

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Tables

	PHOSPHOGYPSUM	PORTLANDITE	Na_2SO_4
Major elements (%)			
SO_3	50.2	4.28	55.8
CaO	44.7	89.4	1.04
F	1.56	1.61	n.d.[a]
Na_2O	1.16	2.12	42.7
Cl	0.72	0.04	0.23
P_2O_5	0.67	1.21	n.d.
SiO_2	0.43	0.64	0.16
Al_2O_3	0.24	0.27	n.d.
MgO	0.14	0.13	n.d.
Fe_2O_3	0.07	0.20	n.d.
SrO	0.07	0.06	0.02
Y_2O_3	0.02	0.04	n.d.
LOI [b]	21.2	14.3	27.9

Table 2

	PHOSPHOGYPSUM	Na_2SO_4	PORTLANDITE	CALCITE
Trace elements (mg kg^{-1})				
Cr	3.70	<l.d.	7.59	8.17
As	3.58	<l.d.	8.57	9.32
U	3.48	0.07	7.84	8.05
Ni	2.49	<l.d.	4.76	5.21
V	2.10	<l.d.	4.76	4.79
Se	1.97	<l.d.	5.04	6.04
Cd	1.34	0.02	2.34	2.51
Pb	1.20	<l.d.	2.47	2.56
Zn	0.92	<l.d.	2.02	2.98
Th	0.69	<l.d.	1.62	1.71

Table(s)

	PHOSPHOGYPSUM	Na_2SO_4	PORTLANDITE
Major elements (%)			
SO_3	50.2	55.8	4.28
CaO	44.7	1.04	89.4
F	1.56	n.d.[a]	1.61
Na_2O	1.16	42.7	2.12
Cl	0.72	0.23	0.04
P_2O_5	0.67	n.d.	1.21
SiO_2	0.43	0.16	0.64
Al_2O_3	0.24	n.d.	0.27
MgO	0.14	n.d.	0.13
Fe_2O_3	0.07	n.d.	0.20
SrO	0.07	0.02	0.06
Y_2O_3	0.02	n.d.	0.04
LOI [b]	21.2	27.9	14.3

(a) n.d.: not detected

(b) LOI: loss-of-ignition

Table 1. Major elements of the samples analyzed by X-ray fluorescence. Weight percentages are normalized to

the mass without loss-of-ignition values.

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	PHOSPHOGYPSUM	Na$_2$SO$_4$	PORTLANDITE	CALCITE
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Ni	2.49	<l.d.	4.76	5.21
V	2.10	<l.d.	4.76	4.79
Se	1.97	<l.d.	5.04	6.04
Cd	1.34	0.02	2.34	2.51
Pb	1.20	<l.d.	2.47	2.56
Zn	0.92	<l.d.	2.02	2.98
Th	0.69	<l.d.	1.62	1.71

(a) l.d.: limit of detection

Table 2. Contents of trace elements observed by analysis with inductively coupled plasma mass-spectrometry.
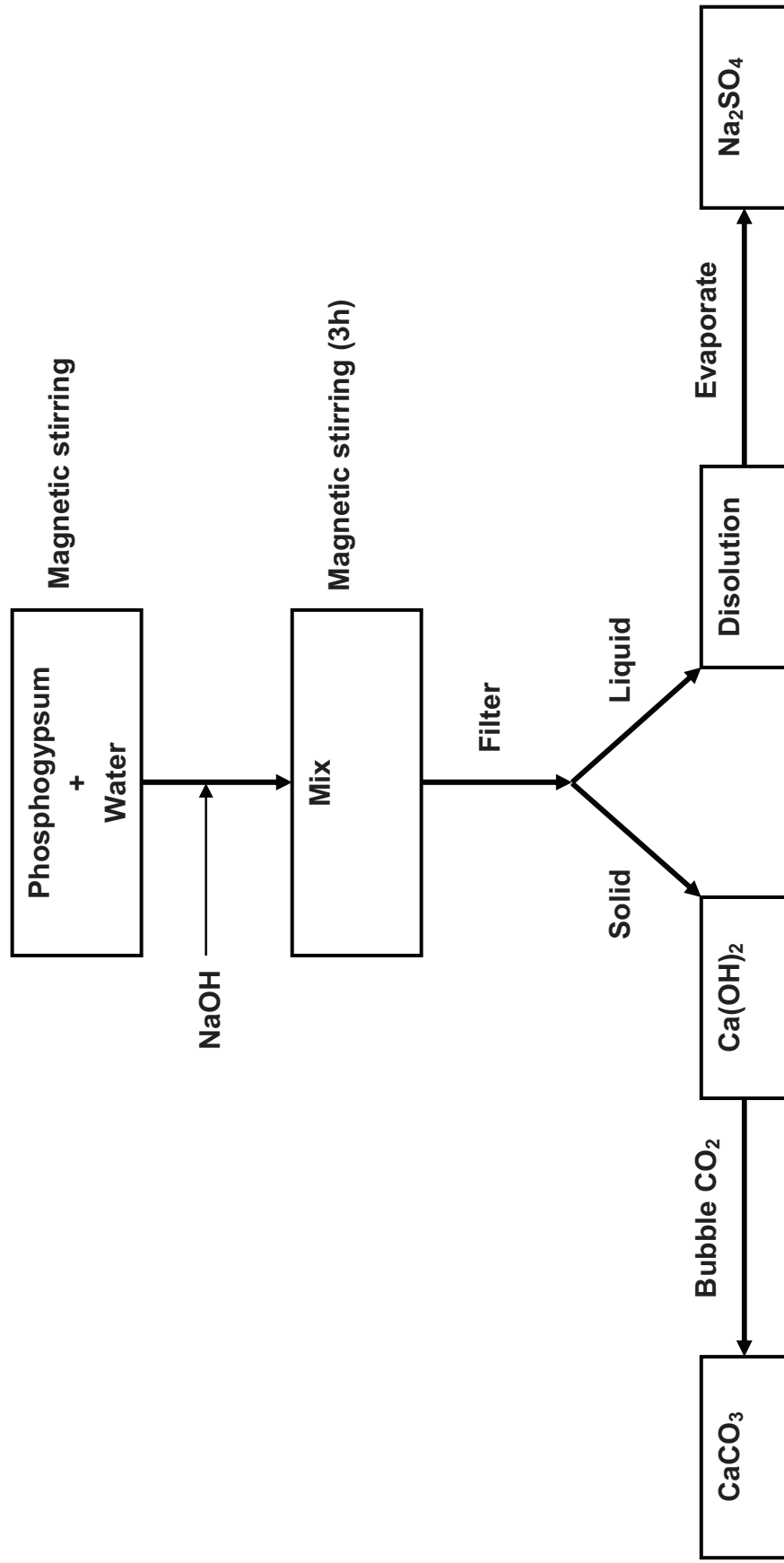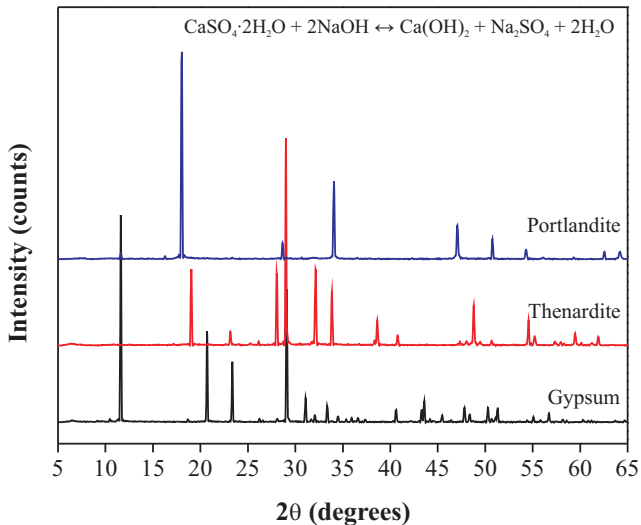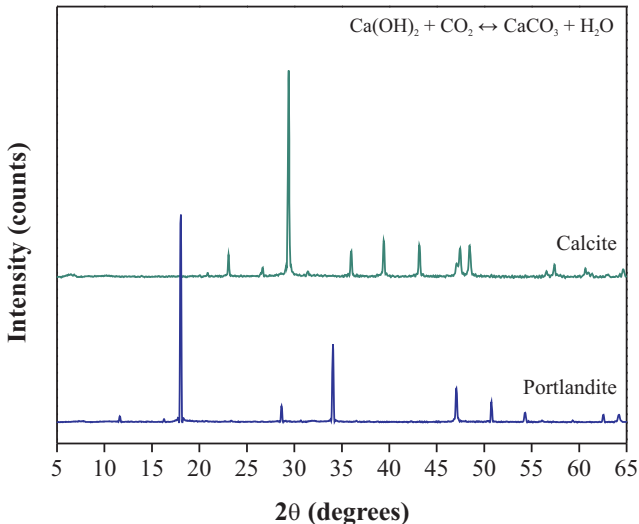
Figure(s)

Figure 1. Flowchart of the experimental methodology.

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Figure 3

Figure 3.- Diffractogram of the carbonated porlandite. No other phase than calcium carbonate is observed. Portlandite diffractogram has been repeated for comparison purposes only. Diffractograms were shifted for clarity.