

Procedure to use phosphogypsum industrial waste for mineral CO₂ sequestration

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Abstract

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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 CO₂ 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

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The wet-acid process for manufacture of phosphoric acid (i.e. H₃PO₄) for fertilizers involves the chemical attack of phosphate rock ore (mainly apatite, Ca₅(PO₄)₃OH) with sulphuric acid (H₂SO₄), generating a gypsum by-product known as phosphogypsum (CaSO₄·nH₂O). The phosphogypsum waste is

1 usually slurried with water and then pumped out of the fertilizer industrial plant
2 to nearby settling/disposal area, using a system of pipes. Recycling of
3 phosphogypsum is limited by the high content of metallic impurities and
4 radionuclides [1].
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10 In Spain, the phosphoric acid production began in 1968 in an industrial
11 complex located at the estuary formed by the union of the Tinto and Odiel river
12 mouths (Huelva, SW Spain). The phosphogypsum has been stockpiled over an
13 area of 1200 ha containing about 120 million tonnes on the salt marshes
14 associated with the right margin of the Tinto river, less than 1 km away from the
15 city centre. In fact, the area covered by the phosphogypsum stack is roughly
16 similar to the surface area covered by the city of Huelva itself, with a population
17 of 149.000. The proximity of the waste to the city has also aroused considerable
18 controversy for its alleged implications for the health of the local population;
19 however, most studies have concluded that populations living close to stacks
20 are not exposed to any significant health risk (see for example [2]). Moreover,
21 salt marshes on the Tinto-Odiel estuarine system hold an important part of
22 Europe's ornithological biodiversity and they were declared UNESCO Biosphere
23 Reserve in 1983 and RAMSAR-NATURA wetlands sites in 1989. Sudden
24 changes in land-use and direct dumping of phosphogypsum on these salt
25 marshes dramatically altered the visual landscape and degraded the marshland
26 occupied by the stack. The high content of metals and U-Th series
27 radionuclides in phosphogypsum and the impact of these wastes on the quality
28 of sediments and waters of surrounding environmental receptors have been
29 widely described [3-6].
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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 km² 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 CO₂ 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 CO₂ emissions directly from localised sources, mobile sources (e.g. transport), and even past CO₂ emissions. The mineral sequestration process involves a reaction where aqueous ions (mainly Ca and Mg from silicates [9] or hydroxides) react with CO₂ to form stable carbonate minerals and it has controlled the CO₂ content on the atmosphere for millennia. The costs associated with industrial scale mineral sequestration are a major

1 drawback of this technology, but they could be significantly reduced by using
2 industrial alkaline wastes as aqueous Ca and Mg sources ([10-14]).
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5 In light of the above, the aim of the present study is to evaluate the use of
6 phosphogypsum waste as a Ca source for carbon dioxide mineral
7 sequestration. We believe that this new methodology is especially attractive and
8 ecologically clean, since it has the potential to reduce two environmental
9 problems simultaneously: 1) management of hazardous industrial waste; and 2)
10 greenhouse gasses emissions.
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25 **2. Experimental procedure**

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27 Several samples (approx. 2 kg) were collected from the phosphogypsum
28 stack in November of 2009 at different depths from bore-holes carried out using
29 a soil sampling auger. In the laboratory, samples were oven-dried (40 °C) until
30 complete dryness, ground and homogenised. The data relative to one
31 representative sample of phosphogypsum are discussed in this paper.
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40 The proposed methodology starts by the dissolution of the raw sample in an
41 alkaline solution. The dissolution experiments were conducted in 20 mL of high-
42 purity water where 5 g of phosphogypsum were dispersed by magnetic stirring
43 at room pressure and temperature. Immediately after, 2.34 g of NaOH were
44 added to reach a OH^-/Ca molar ratio of 2. The mixture was kept at room
45 temperature for 3 h under constant stirring. The phosphogypsum dissolution
46 resulted in the precipitation of a whitish solid phase and a supernatant liquid.
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1 yielded transparent salts, which were later characterized as a second solid
2 phase.
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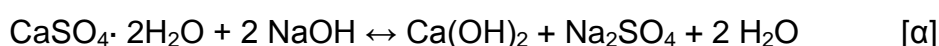
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5 The carbonation capacity and efficiency of the solid phase precipitated in
6 the dissolution experiments were assessed by a simple carbonation
7 experimental set-up: 2 g of this precipitate were dispersed in 40 ml of high-
8 purity water under magnetic stirring into a reactor, and a CO₂ flux (1 bar, 20
9 cm³/s) was bubbled through the suspension for 15 min at room pressure and
10 temperature. Afterwards, the sample was left to rest overnight into the CO₂-rich
11 water. The resulting solid phase was separated by centrifugation and dried in air
12 at 80°C, and the supernatant discarded. In figure 1, the entire experimental
13 procedure is sketched.
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27 Chemical characterization of the raw phosphogypsum and the solid
28 products from dissolution and carbonation experiments was performed by X-ray
29 fluorescence (XRF; AXIOS Panalytical instrument) for major elements and
30 pseudo-total acid-digestion followed by analysis with inductively coupled plasma
31 mass-spectrometry (ICP-MS; HP-4500 instrument) for trace elements.
32 Crystalline phases of the samples were identified by X-ray diffraction (XRD) in a
33 diffractometer (Philips X'Pert) with Cu-K α radiation, from 5.00° to 70.00° with a
34 step of 0.05° and counting time of 80 s. The carbonation degree of the samples
35 was studied by thermogravimetric analyses (TGA; STD Q600) carried out under
36 a nitrogen flux of 100.0 ml/min, starting from ambient temperature and
37 increasing by 10 °C/min up to 1000 °C.
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57 **3. Results and discussion**

58 59 *3.1 Analysis of the samples prior to CO₂ sequestration* 60 61 62 63 64 65

1 The XRD of the raw phosphogypsum sample is shown in figure 2. The
2 diffraction pattern indicates that the sample is composed mainly of gypsum
3 (CaSO₄· 2H₂O, PDF number: 99-101-0394), as expected [15]. After the
4 dispersion of this sample in water and the addition of NaOH, the resulting
5 whitish precipitate correspond mostly to portlandite (Calcium hydroxide,
6 Ca(OH)₂, PDF number: 99-100-0115), as shown in the diffractogram of the
7 figure 2 and as expected by reaction [α]:
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17 and considering the large difference between gypsum and portlandite's
18 solubility constants, being the solubility constant of gypsum $K=3.14 \cdot 10^{-5}$ and
19 that of the portlandite $K=5.02 \cdot 10^{-6}$ [16]. Finally, the diffractogram of the
20 transparent salts precipitated by evaporation of the supernatant liquid (figure 2)
21 indicates that is mostly composed of thenardite (Na₂SO₄, PDF number: 99-100-
22 4889), again as expected regarding reaction [α]. These results confirm the
23 efficiency of the reaction [α] as a procedure to deal the raw phosphogypsum
24 waste and obtain a roughly pure portlandite.
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39 Major element concentrations determined by XRF of the different solid
40 phases from phosphogypsum dissolution were in agreement with the
41 mineralogical composition estimated by XRD (Table 1). Raw phosphogypsum
42 composition is clearly dominated by S (50.2 wt% as SO₃) and Ca (44.7 wt% as
43 CaO). However, the calcium content of the gypsum was slightly higher than
44 expected stoichiometrically, revealing the existence of other different calcium
45 compounds poorly crystallized, not easily observable by XRD (Figure 2).
46 Portlandite is mainly composed of Ca (89 wt% as CaO); again, calcium content
47 remains slightly higher than expected, so minor calcium compounds are carried
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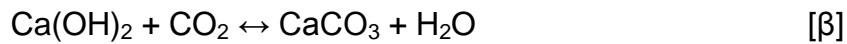
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in this portlandite phase as impurities, possibly calcium phosphate from original rock. Finally, the solid obtained from the supernatant evaporation is characterized by high contents of S (55.8 wt% as SO₃) and Na (42.7 wt% as Na₂O). Other major impurities 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 (CaCO₃, PDF number: 99-101-2108) was achieved. The carbonation reaction is as follow:



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 CO₂ at 700°C (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

1 and incorporated into the structure of the calcite by co-precipitation [18]. Albeit,
2 adsorption on the calcite surface could be also a significant mechanism for
3 retention of metals as long as their concentrations in solution are lower than the
4 limit of 10^{-5} M established by Zachara et al. [19], as is the case in our
5 experiments of portlandite dissolution and carbonation. Nevertheless, whatever
6 the scavenging process, calcite precipitation is a successful mechanism for
7 reducing metal mobility in natural aqueous systems [20].
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17 A sustainable and environmental-oriented procedure to manage of these
18 wastes is inferred from these results. In a realistic and numerical approximation
19 to quantities of phosphogypsum that are generated annually by the fertilizer
20 industry of Huelva, the reagents to develop the proposed methodology are
21 summarized as follows: to treat 2 Mt of phosphogypsum, 0.92 Mt of NaOH will
22 be needed, and 0.4 Mt of H₂O from phosphogypsum, 1.64 Mt of Na₂SO₄ and
23 0.84 Mt of Ca(OH)₂ will be produced. This amount of Ca(OH)₂ could be used to
24 subsequently capture 0.50 Mt of CO₂, yielding 1.16 Mt of CaCO₃. Based on
25 these results, an estimation of the carbon capture capacity of the entire
26 stockpiled phosphogypsum waste was made. 55.2 Mt of NaOH will be needed
27 to treat 120 Mt of phosphogypsum, enabling capture 30 Mt of CO₂.
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46 **4. Conclusions**

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49 In this work, total conversion of phosphogypsum industrial waste into
50 portlandite (calcium hydroxide) and sodium sulphate was confirmed, and the
51 high carbon dioxide capture efficiency of the resulting portlandite was
52 demonstrated. Portlandite was produced by dissolution of dihydrated calcium
53 sulphate from the phosphogypsum and reaction with sodium hydroxide. The
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main impurities contained in the phosphogypsum were transferred to the portlandite and, subsequently, to the final calcite after bubbling CO₂, 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 CO₂ emissions generated by the same industry.

Furthermore, mineral CO₂ 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. .

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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

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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 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) from Huelva (Spain), of the solid filtered where portlandite ($\text{Ca}(\text{OH})_2$) 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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3 **Tables**
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	PHOSPHOGYPSUM	PORTLANDITE	Na ₂ SO 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 ₂ O	1.16	2.12	42.7
Cl	0.72	0.04	0.23
P ₂ O ₅	0.67	1.21	n.d.
SiO ₂	0.43	0.64	0.16
Al ₂ O ₃	0.24	0.27	n.d.
MgO	0.14	0.13	n.d.
Fe ₂ O ₃	0.07	0.20	n.d.
SrO	0.07	0.06	0.02
Y ₂ O ₃	0.02	0.04	n.d.
LOI ^(b)	21.2	14.3	27.9

Table 21
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	PHOSPHOGYPSUM	Na₂SO₄	PORTLANDITE	CALCITE
	<i>Trace elements (mg kg⁻¹)</i>			
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

	PHOSPHOGYPSUM	Na ₂ SO ₄	PORTLANDITE
Major elements (%)			
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MgO	0.14	n.d.	0.13
Fe ₂ O ₃	0.07	n.d.	0.20
SrO	0.07	0.02	0.06
Y ₂ O 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.

	PHOSPHOGYPSUM	Na ₂ SO ₄	PORTLANDITE	CALCITE
<i>Trace elements (mg kg⁻¹)</i>				
Cr	3.70	<l.d.	7.59	8.17
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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.

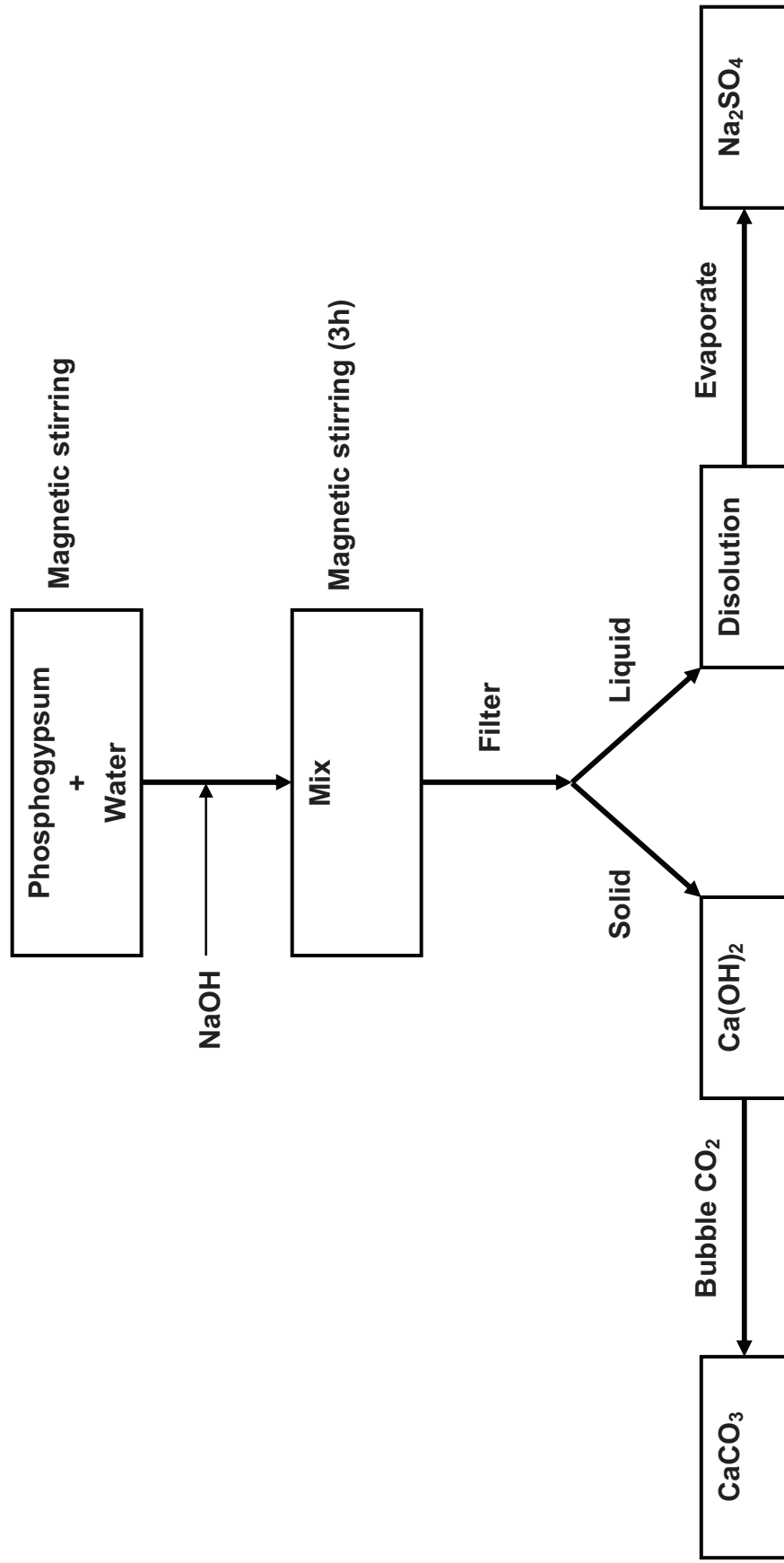


Figure 1. Flowchart of the experimental methodology.

Figure(s)

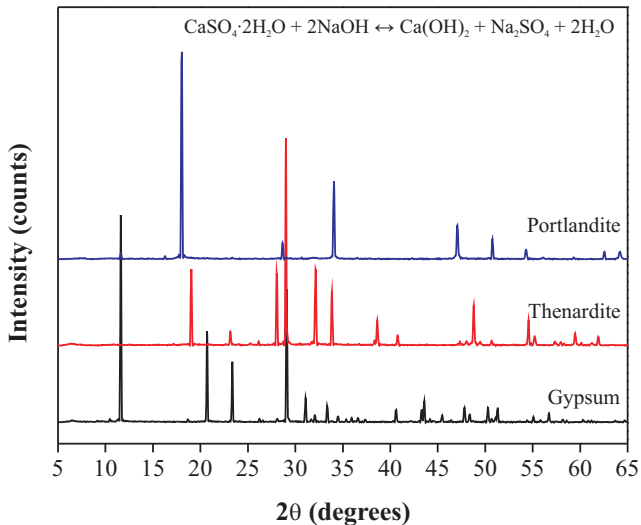


Figure 2.- Diffractograms of the raw phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) from Huelva, of the solid filtered where portlandite ($\text{Ca}(\text{OH})_2$) can be clearly observed, of and the solid phase obtained from supernatant evaporation where the diffraction pattern of thenardite (Na_2SO_4) is clearly matched. Diffractograms were shifted for clarity.

Figure 3

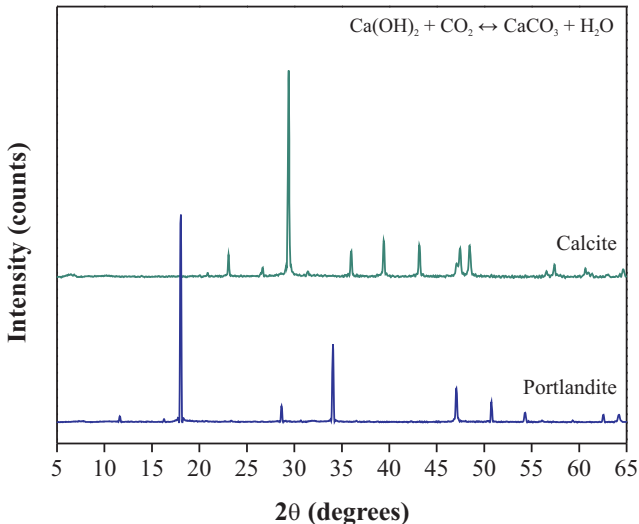


Figure 3.- Diffractogram of the carbonated portlandite. No other phase than calcium carbonate is observed. Portlandite diffractogram has been repeated for comparison purposes only. Diffractograms were shifted for clarity.