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CO_2 Mineral Sequestration by Using Phosphogypsum as Adsorbent

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ABSTRACT

The production of phosphoric acid from natural phosphate rock by the wet process gives rise to phosphogypsum, a major industrial by-product with about 5 tons produced for each ton of phosphoric acid, and world widely phosphogypsum generation is estimated to be around 100-280 m per year. Phosphogypsum is mostly disposed of without any treatment, usually by dumping in large stockpiles and/or water supplies. In the framework of the fight against global climate change and the effort to reduce carbon dioxide emissions. A simple method for CO_2 mineral sequestration is presented in this work, using phosphogypsum waste as a calcium source. This present study proposes the carbonation technology, based on aqueous alkaline industrial waste, as a contribution to reduce global CO_2 emissions. X-ray diffraction patterns and thermogravimetric analysis demonstrate the high efficiency of portlandite precipitation by phosphogypsum dissolution using sodium hydroxide solution. Mineral carbonation experiments, performed at ambient pressure and temperature, resulted in total conversion of the portlandite into carbonate.

Keywords: Phosphogypsum, Mineral sequestration, Carbon dioxide, Adsorption, Carbonation

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INTRODUCTION

The wet chemical phosphoric acid treatment process is the widely used to produce phosphoric acid. This process produces phosphogypsum "PG" (mainly calcium sulphate $CaSO_4.2H_2O$) as a by-product which accounts for around 90% [1]. In fact, in this process, the raw phosphate is treated by sulfuric acid and, besides the main product H_3PO_4, PG is obtained together with hydrofluoric acid as depicted in Equation 1. Accordingly, about five tons of phosphogypsum is produced for every ton of phosphoric acid manufactured [2,3]. PG´s characteristics are strongly influenced those of the phosphate ore. The composition of PG is mainly made of:

- Gypsum,
- Impurities, including al, p, f, si, fe and mg, and trace elements [4],
- Soluble impurities: salts or acids which are not removed by the washing process (P_2O_5 and Fluor primarily soluble). These acids give the phosphogypsum a low pH (usually between 2 and 4),
- Insoluble impurities: silica, no attacked ore, carbon organic…,
- Syncristallized P_2O_5 and trace elements, mainly heavy metals.

Four methods are being used by the phosphate industry to dispose of surplus PG, namely: (i) Discharging to water bodies; (ii) Backfilling in mine pits; (iii) Dry stacking; and (iv) Wet stacking [5]. Of the 110 million tons PG produced worldwide, only 15% is used mainly as fertilizers and conditioner for soils, particularly in acid soils with high levels of Al and calcareous ones [6], as a feed additive for livestock and food safety [7], in mine to reduce ammonia volatilization from urea fertilizer [8], and in the recovery of Sulphur [5].

Despite these applications, the problem of this by-product remains far being solved and always environmentally threatening. The current research focused effectively on the application of PG as CO_2 sequester adsorbent, which leads immediately in decreasing the CO_2 emissions. Three possibilities for sequestration of CO_2 are currently being studied: aqueous carbon sequestration, geological carbon sequestration and mineralogical carbon sequestration [9]. Mineral sequestration being a natural process leading to the formation of carbonates as result of the binding of carbon dioxide to a mineral [10]. It allows the removal of CO_2 from industrial and transport activities [11-14]. Potentially suitable feedstock's for mineral carbonation include Ca and Mg silicate ores [15,16], such as wollastonite ($CaSiO_3$) [17,18], serpentine and olivine (Mg_2SiO_4) [10], lime (CaO) [19], and industrial residues, such as steel [20] and solid waste from the incinerators [21]. Bottom ash also offers early opportunities for mineral carbonation [22,23].

During the process, gaseous CO_2 is primarily dissolved into the solution forming carbonic acid. Equation (2-6) illustrates chemically the steps leading to the carbonatation.

In this work, we have considered the calcium rich waste of phosphoric acid production plants as a new material for CO_2 sequestration. The experimental conditions to obtain the maximum carbonation efficiency are researched. The carbonation process is carried out under atmospheric conditions. The reaction by-product obtained is calcium carbonate that is easy to handle and could be disposed of or even commercialized.

CO_2 reacts with water to form carbonic acid (H_2CO_3) according to Equation 2-4:

$CO_2 + H_2O \rightarrow H_2CO_3$ (2)

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ (3) CO_2 dissolution

$HCO_3^- \rightarrow H^+ + CO_3^{2-}$ (4)

CaO can also react with water to produce calcium cations according to Equation (5-6):

$CaO + H_2O \rightarrow Ca^{2+} + 2OH^-$ $Ca(OH)_2$ Extraction of Ca^{2+} (5)

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ Precipitation of calcium carbonate (6)

MATERIAL AND METHOD

The samples, collected from the rotary separation filter of PG from the phosphoric acid, they were first dried at 60ºC. The operating procedure is executed in the following order: the phosphogypsum is dissolved in a sodium hydroxide (NaOH). 20 g of PG was dispersed, at ambient temperature and pressure, in 80 ml of distilled water. Then, 9.3 g of NaOH was added and the mixture kept for 3 hrs under constant stirring, after dissolving phosphogypsum we recovered two phases: solid phase composed of calcium hydroxide $Ca(OH)_2$, and after evaporation of the liquid phase we recovered white salts of sodium sulfate Na_2SO_4.$Ca(OH)_2$ will undergo a simple carbonation: 2 g of this precipitate was dispersed in 40 ml of distilled water with magnetic stirring and a CO_2 stream (1 bar, 1.2 $L.s^{-1}$) was bubbled through the solution for 15 min at room conditions, the mixture remained overnight in the CO_2-rich water. The resulting solid is filtered under vacuum and dried at 60°C in an oven. Figure 1 summarizes the method and experimental set-up is shown in Figure 2.

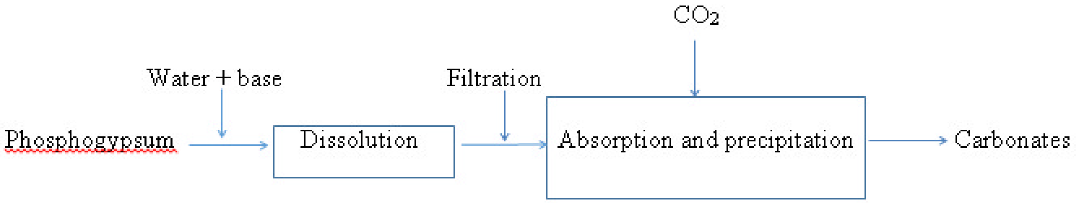

Figure 1: Scheme of experimental methodology

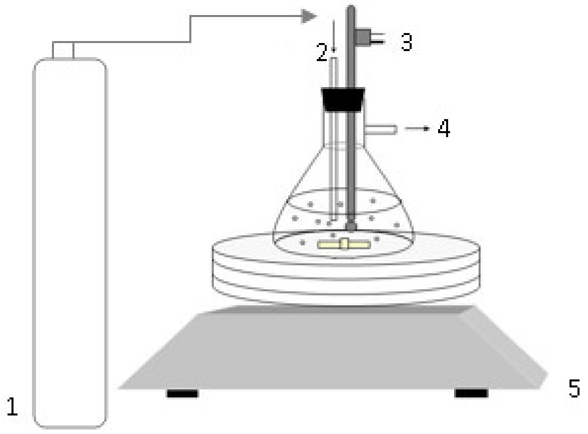

Figure 2: Overview of equipment for mineral carbonation: 1: CO_2 bottle of gas, 2: is the input gaz 1.2 L s-1, 2: the pH meter, 3: the outlet gaz, 5: the magnetic stirrer

PG and the other products of dissolution and carbonation were characterized by the Energy Dispersive spectroscopy X (EDX) and chemical analysis for major elements. They were identified by X-ray Diffraction (XRD) with a diffractometerX'Pert PRO PANALATYCAL, equipped with a scintillation detector with X'Celerator Ultrafast radiation beam Kα (λ=0.154060 nm), operating at the voltage 40 kV and current 30 mA with a copper target. Data were collected in 2θ-range 10º to 80º and by X-ray Fluorescence (XRF; OXFORDMDX1000), the efficiency of the carbonation was determined by (XRD). Fourier Transform Infrared (FTR Bruker VERTEX 70) with a resolution of 4 cm^{-1} where the band ranges varies from 400 to 7500 cm^{-1}(IR) and quantified by thermogravimetric analysis (TGA-60H Shimadzu). The phosphogypsum and the synthesized solid productsin the form of pellets prepared by using pelletizer (SPECAC EUROLABO) were observed on a Scanning Electron Microscope (SEM) (FEI QUANTA 200) equipped to probe EDX surface microanalysis.

RESULTS AND DISCUSSION

Mineral composition

Analysis of XRD spectrum of PG (Figure 3) indicates that it is made up mainly of $CaSO_4.2H_2O$ [24]. The dissolution of PG by a soda solution produced two phases solid and liquid. After having analysed the two phases by XRD the solid phase is composed mainly of calcium hydroxide ($Ca(OH)_2$) (Figure 4). After evaporation of supernatant liquid, the resulting transparent salt indicates that is mostly composed of thenardite of $NaSO_4$ as shown in Figure 5. These results confirm the total transformation of phosphogysum into $Ca(OH)_2$ which will produce $CaCO_3$ as in Equation (6 and 7).

$CaSO_4, 2H_2O + 2NaOH \rightarrow Ca(OH)_2 + Na_2SO_4 + 2H_2O$ (7)

$Ca\ (OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ Precipitation of calcium carbonate (6)

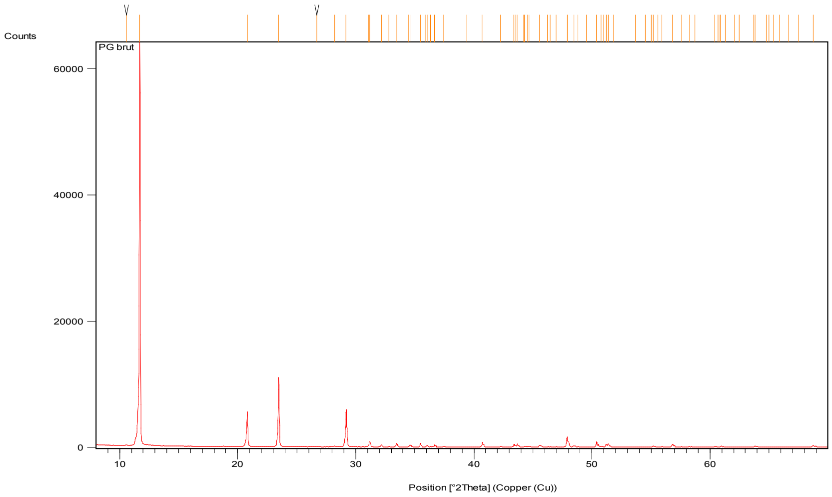

Figure 3: Diffractogram of the raw phosphogypsum

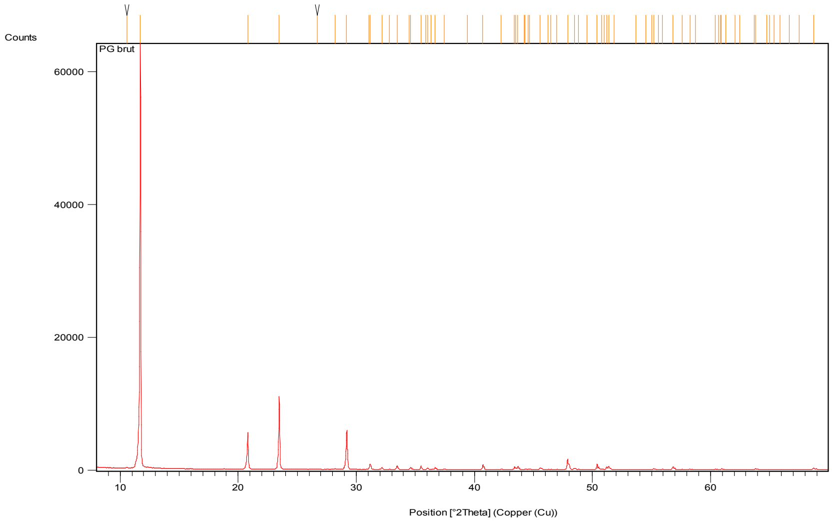

Figure 4: Diffractogram of the portlandite ($Ca(OH)_2$)

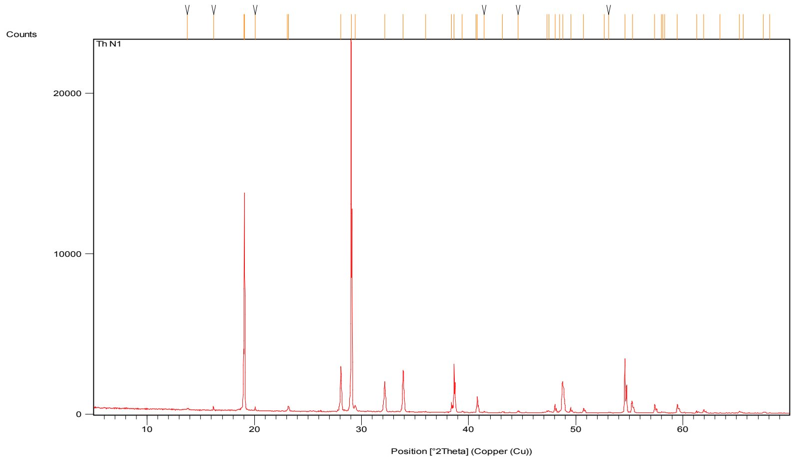

Figure 5: Diffractogram of thenardite Na_2SO_4

Figure 6 represent the IR spectrum of phosphogypsum: tow absorption bands at 3393.00 and 1691.41 cm^{-1} corresponding to the vibration of H-O-H and water content were observed; also the spectrum exhibited an absorption band at 2237.35 cm^{-1} due to the vibration of SO_4^{2-}, where the absorption at 1618.78 cm^{-1} related to gypsum and the hemihydrate species. The spectrum of the phosphogypsum sample showed that phosphogypsum had the same absorption as that observed for pure and natural gypsum. After carbonation, Figure 7, show absorption band of carbonate: 1077.49 cm^{-1}, 871.70 cm^{-1}, 1396.56 cm^{-1} and 712.31 cm^{-1} [25].

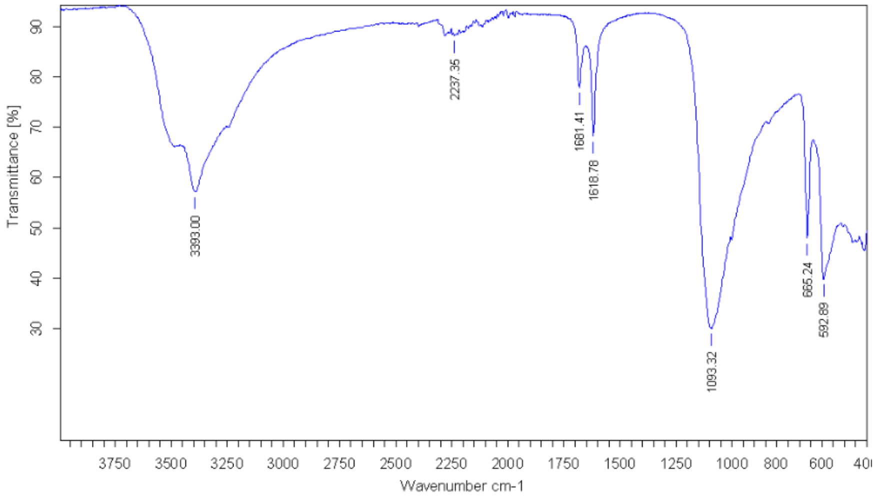

Figure 6: IR spectrum of phosphogypsum

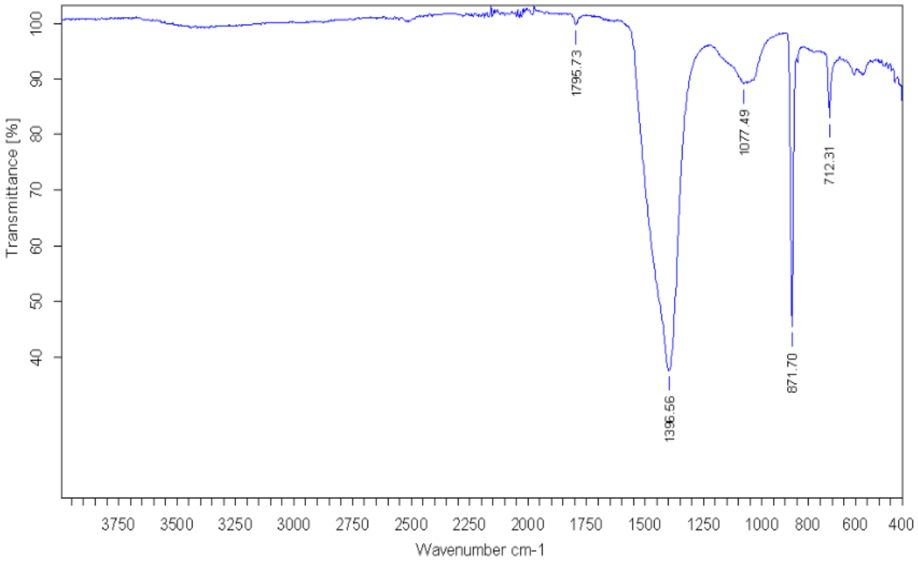

Figure 7: IR spectrum of calcium carbonate

Morphologic characterisation

Moroccan phosphogypsum shows a percentage of fines of about 22%. The SEM analysis indicates that it is composed of tabular crystals [26] and length between 1 and 100 µm as shown in Figures 8 and 9. Image of $CaCO_3$ (Figure 10) indicates that the particles present spherical form [27] which is characteristic of calcite. EDX analysis (Figure 11) shows that phosphogypsum is made up mainly of Ca and S which were in agreement with natural gypsum and with results obtained previously by XRF (Table 1).

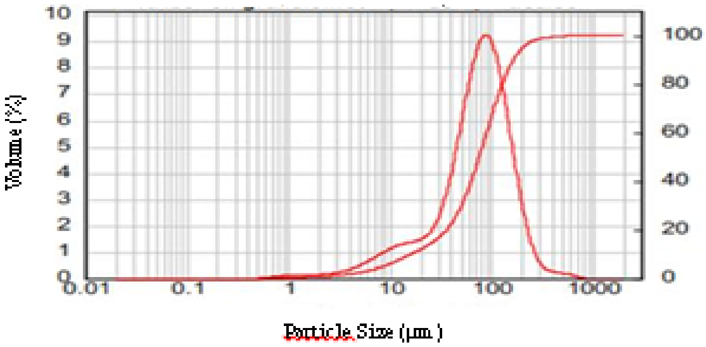

Figure 8: Particle size distribution of phosphogypsum all of the phosphogypsum crystals have a size between 1 and 100 microns

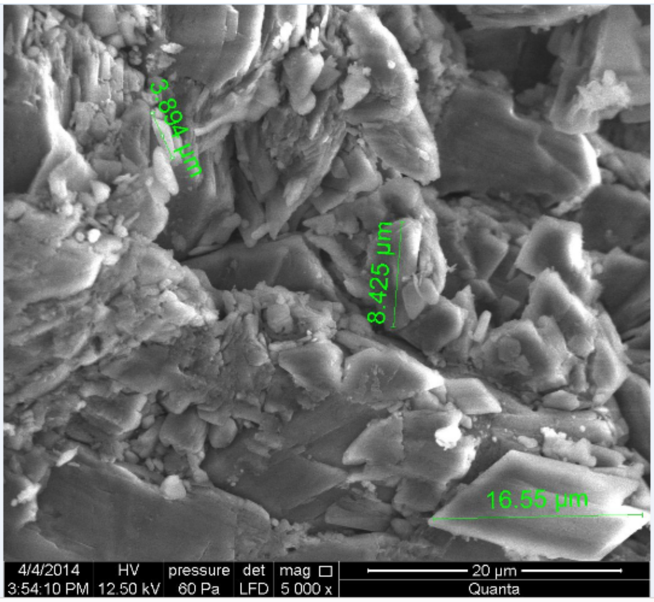

Figure 9: SEM image of phosphogypsum

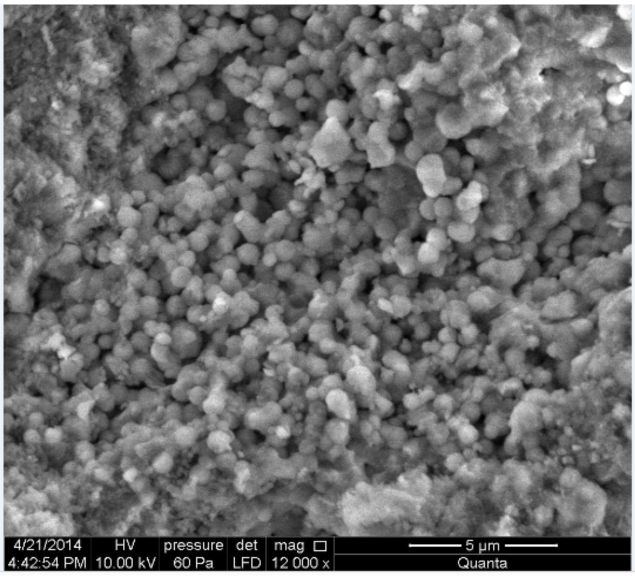

Figure 10: SEM image of calcium carbonate

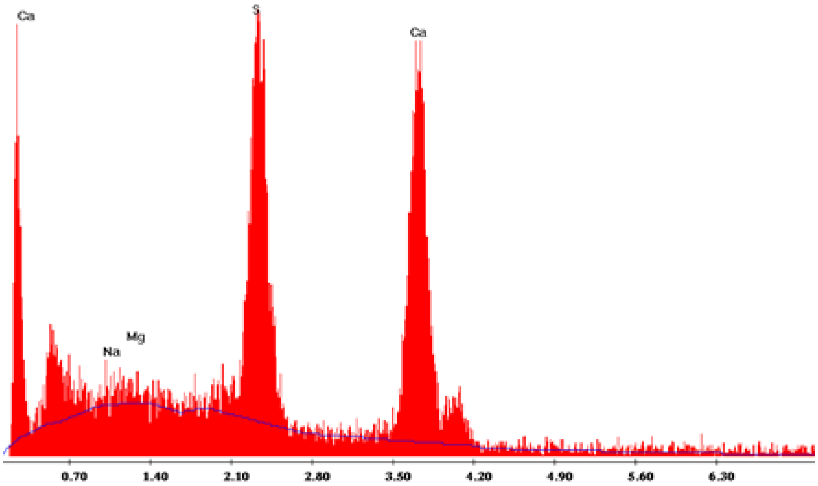

Figure 11: EDX spectrum of the crude phosphogypsum

Table 1: Major element concentration of the samples analyzed by X-ray fluorescence

Major elements (%)	Phosphogypsum	Portlandite	Thenardite	Calcite
SiO_2	0.90	2.53	0.13	1.64
Al_2O_3	0.00	0.05	0.006	0.00
Fe_2O_3	0.28	0.25	0.002	0.20
CaO	30.17	65.31	0.18	51.19
MgO	0.00	0.00	0.00	0.00
SO_3	43.97	3.59	55.3	2.14
K_2O	0.04	0.10	0.002	0.05
Na_2O	0.00	0.65	21.1	0.12
LOI	24.64	27.52	23.28	44.66
LOI: loss of ignition				

Major and trace elements

We have used XRF to determine the major element concentrations of the different solid phases from PG dissolution, results are in agreement with the mineralogical composition estimated by XRD (Table 1). Raw PG is composed in majority by SO_3 "S" (43.97 wt%) and CaO "Ca" (30.17 wt%) [25]. Portlandite is mainly composed of Ca (65.31 wt% as CaO). The solid obtained from evaporation is composed of S (55.3 wt%) and Na_2O "Na" (21.1 wt%). Si, Al, Fe and K are the other major impurities in PG. The main trace elements in PG, analyzed by Activation neutronic, are Cr, U, Ni, V, Se and Zn are also shown in Table 2.

Table 2: Contents of trace elements measured by analysis with neutron activation

Trace elements (mg kg^{-1})	Phosphogypsum	Thenardite	Portlandite	Calcite
Cr	5.69	<1.50	5.90	1.50
As	ND	ND	ND	ND
U	3.76	<0.40	9.76	4.97
Ni	3.21	6.39	10.37	7.07
V	4.22	ND	8.34	7.84
Se	0.28	<0.20	3.25	0.76
Cd	ND	ND	ND	ND
Pb	0.92	<0.60	8.54	3.73
Zn	12.75	<0.50	12.61	14.91
Th	ND	ND	ND	ND

CO_2 capture efficiency

The CO_2 capture efficiency was determined by powder XRD. Figure 12 depicts the diffractogram of the carbonated portlandite resulted from the aqueous carbonation procedure. This result shows a total conversion of the original portlandite to calcite according to Equation 6.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ Precipitation of calcium carbonate (6)

TGA of the calcite was carried out to determine the output of carbonation, results are shown on Figure 13, there is a single thermal event at 756°C, with a weight loss of 36.77%, which corresponds to the loss of a molecule of CO_2 from the calcium carbonate

(Equation 8), in agreement with the literature [28].

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (8)$$

The ratio between the amount of carbonate formed in the carbonation process (X_{exp}) and the theoretical amount of carbonate (X_{theo}) is the carbonation efficiency (C_E):

$$C_E = \frac{X_{exp}}{X_{th}} \qquad (9)$$

It is about 90 % in our case (Table 3).

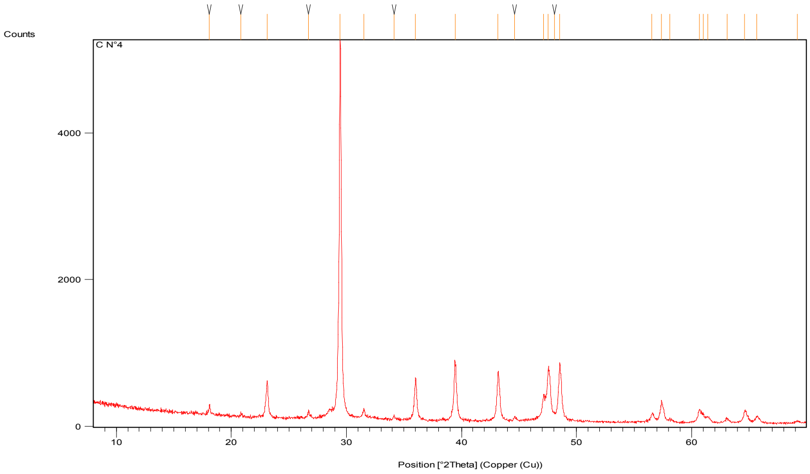

Figure 12: Diffractogram of calcium carbonate

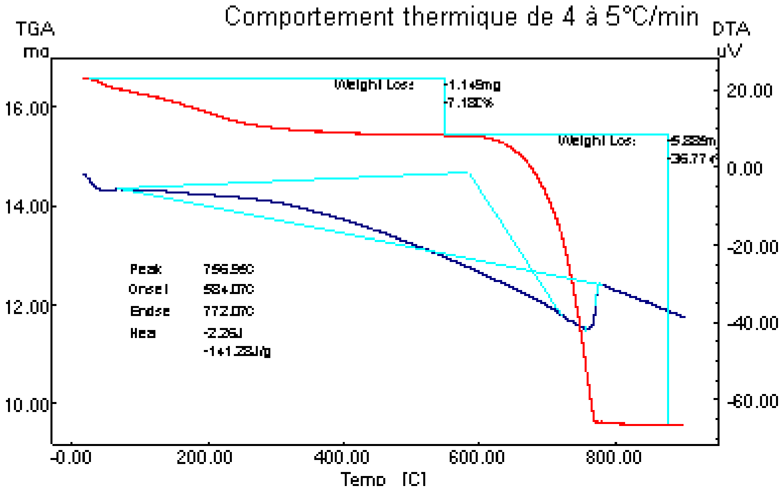

Figure 13: TG and DTG of calcium carbonate product

Table 3: The carbonation efficiency

	CaO (%)	CO_2 (%)	C_E(%)
Phosphogypsum	30.17	-	-
Calcite	51.19	37	90

CONCLUSIONS

Total conversion of phosphogypsum (PG), an industrial stable and very abundant by-product of the phosphoric acid industry, into portlandite (calcium hydroxide) and sodium sulphate was confirmed. The high carbon dioxide capture efficiency of the resulting portlandite was demonstrated. Portlandite was produced by dissolution of PG and reaction with sodium hydroxide. The total and rapid conversion of portlandite into calcite makes the proposed methodology an attractive and ecological solution for the tow environmental problems.

AKNOWLEDGMENTS

Some experiments, material characterizations and interpretation of results of this study were performed by Dr. Khadija Morsli (Recherche and Développement, Groupe OCP, El Jadida, Morocco), thanks for her.

CONFLICTS OF INTEREST

As corresponding author and on behalf of all co-authors, I declare the manuscript entitled ''CO_2 mineral sequestration by using phosphogypsum by-products as adsorbent" agrees with all the rules of your journal, especially those concerning the "Disclosure of potential conflicts of interest''.

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