Original Research Article

Comparative Study of the Transformation of Phosphogypsum and Pure Gypsum into Valuables Products

Yassine Ennaciri * ⓘ **, Mohammed Bettach** ⓘ

Department of Chemistry, Laboratory of Physical Chemistry of Materials (LPCM), Faculty of Sciences, Chouaib Doukkali University, El Jadida, Morocco

A R T I C L E   I N F O

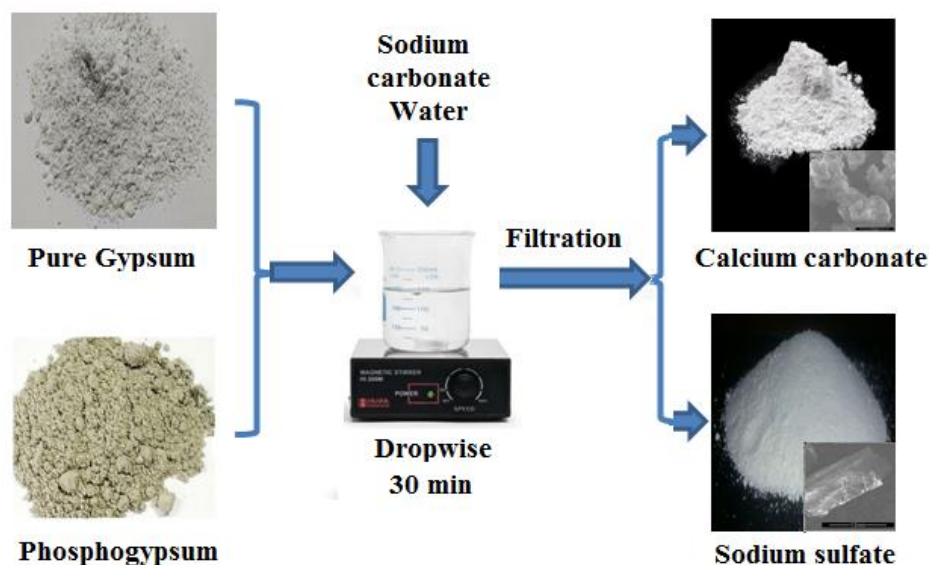**A B S T R A C T**

The production of phosphoric acid in the world generates an enormous amount of a by-product named phosphogypsum (PG). A large quantity of this PG is stockpiled or dumped into environment, causing several environmental problems. This research study proposes an attractive process for transforming the PG into calcite ($CaCO_3$) and thenardite (Na_2SO_4). A parallel study of the conversion of pure gypsum (GRH) was also realized to compare their reactivity with that of PG. The following of the PG and GRH conversion reaction was evaluated using by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). While, the quality of the products obtained under the optimum condition were proved by scanning electron microscopy (SEM), flame photometer (FP), inductively coupled plasma mass spectrometry (ICP-MS) and thermogravimetric analysis (TGA-DTA). A result revealed that, PG rest more reactive than GRH and yields the desired results at short reaction time under room temperature.

G R A P H I C A L   A B S T R A C T

* Corresponding author: Ennaciri, Yassine

✉ E-mail: yassinemaster@gmail.com

Introduction

Phosphogypsum (PG) is the principal by-product generated by the phosphoric acid (H_3PO_4) production sites. At these sites, one ton of phosphate rock leads to the production of 1.7 tons of PG. Also, the production of one tonne of phosphoric acid generates the equivalent of 3 to 5 tonnes of PG. In Morocco, the current phosphoric acid production capacity is around 4.4 million tonnes of P_2O_5, which gives more than 15 million tonnes of PG yearly [1-3].

After filtration, the PG is in the form of very fine wet sand and their characteristics are varying according to the ore origin and the attack process. These factors determine the crystalline morphology of the PG and effect on the presence of soluble or insoluble impurities (phosphate, fluorine, heavy metals, and organic matter) in its structure [2-4].

At present, the management of PG in the world remain a difficult environmental problem to solve due to the enormous quantity produced annually (around 100-150 million tonnes wet PG/year). In recent years, the problems of the storage and the valorization of PG become one of the major preoccupations of the researchers and the industrialists [2].

Generally, the PG generated around the world is stored in the open air in special landfills. This pathway was adapted in Florida (USA) and Huelva (Spain). Also, PG can be dumped into the waters of the sea or the estuaries. This route was adapted in Tunisia (Sfax) and Morocco (Jorf Lasfar). At the present, the various phosphoric acid production sites continue to reject over 86 % of the PG into environment, which caused several problems [2, 4]. The negative environmental impacts of PG dumps can be caused essentially by the leaching or the erosion of hazardous elements (Ra, Cd, Pb, Cr, Hg and As) from PG and thus manifested in the contamination of surface water and groundwater, soil and atmosphere [4, 5].

In the order to use or to valorize the PG, several tests were carried out in this area. PG can be reused in agriculture, cement and plaster manufacturing and also as raw material for chemical processes.

(i): Agriculture: In the context of the PG application in the agricultural field, certain studies have been carried out by several researchers. PG addition to the saline soils increases their pH and ameliorates its characteristics by supplement S and Ca. However, the added amounts most be limited by certain standards [5].

(ii): Plaster manufacturing: the PG utilization in the plaster manufacturing does not require grinding as with natural gypsum, but it is necessary to remove the impurities such as phosphorus, fluorine, organic matter.... A small amount of these impurities affects setting time and strength of this plaster. The remove of these impurities from PG can be done by modification of the phosphoric acid manufacturing process, or by adequate purification processes, which permit in particular to neutralize the residual acidity [3, 6].

(iii): Cement sector: gypsum is used in the cement industry as an addition (about 5 %) to regulate their hydraulic setting. The addition of PG can effect the resistance, the consistency and the setting time of the cement processed by this by-product [3, 7].

(iv): PG may be employed as a resource for some chemical processes. The PG thermal decomposition is the most known of these processes. It permits recuperating sulfur dioxide gas essential for the sulfuric acid generation [8].

In recent decade, the PG conversion by ammonium or alkaline compounds ($(NH_4)_2CO_3$, K_2CO_3, NaOH...) rests very attractive and economical processes. Thus, the products recovered through this route ($(NH_4)_2SO_4$, K_2SO_4, Na_2SO_4...) are very interesting for the industry, the agriculture and the environment [8-21].

Several researchers have realized the transformation of PG by Na_2CO_3. Mulopo and Ikhu-Omoregbe [16] and have transformed PG (igneous origin) by Na_2CO_3 under room temperature. The results show that the PG transformation is total after 105 min with an excess of Na_2CO_3. Trendafelov *et al.* [18] predicted the transformation of gypsum (isolated from sea salt production waste brines). The reaction is total for exact proportion between gypsum and Na_2CO_3 through a reaction time of 4 h. Chapman *et al.* [8] and Abdel Wahab *et al.* [19] have studied this transformation under 40 and 60 °C respectively. The PG transformation is achieved for an excess of Na_2CO_3 during 10 min and 20 min, respectively. Other works realized by Vlasjan *et al.* [20] and Masmoudi-Soussi *et al.* [21], mentioned that the total PG transformation can be reached also for an excess of Na_2CO_3 under 60 and 80 °C during 1 and 2 h, respectively.

According to these results, the majority of PG transformations are restraining by the effect of Na_2CO_3 excess and the temperature increase. In addition, these studies are not focused on the properties of the resulted products.

In this context, we present a simple procedure allow producing $CaCO_3$ and Na_2SO_4 through the transformation of two kinds of gypsum (PG and pure gypsum (GRH)) by Na_2CO_3. The objective to use these gypsums (PG and GRH) is to realize a comparative study between theirs reactivity. The strengths points of this process are: (i) the PG transformation is carried out with exact stoichiometric between PG and Na_2CO_3; (ii) under room temperature, and (iii) during short reaction time of 30 min. Also, the obtained products ($CaCO_3$ and Na_2SO_4) have accomplished several analyses in the order to improve their quality.

Experimental

In this work, the PG sample was collected from the phosphoric acid plant situated nearly El Jadida. The origin of this PG is sedimentary. The used pure gypsum (GRH) is an analytical reagent grade (Riedel de Haën, 100 %).

The experimental protocol involves initially washing PG to eliminate the majority of the soluble impurities [3]. Next, different quantities (per g) of the washed PG and GRH were dispersed in one liter of Na_2CO_3 solution for different concentration, under constant stirring (300 rpm) at room temperature and pressure during reaction time of 30 min. This reaction time was selected as ideal reaction time for achieved a total PG conversion [10, 17]. Finally, the reactional mixtures were filtered to obtain a precipitate ($CaCO_3$), which is dried in the oven at 106 °C. While, the recuperate filtrates recrystallization generate a clear salts (Na_2SO_4).

The PG sample and the obtained products are characterized by numerous analyses techniques. The mineralogical phases were determined by X-ray diffraction (D8 Advance, Bruker diffractometer, Kα Cu radiation). Infrared spectrums were recorded by FTIR Spectrometer (Nicolet iS10, Thermo Fisher Scientific) using potassium bromide (KBr) pellets technique. Morphological characterization was performed using scanning electron microscopy (ESEM, FEI Quanta 200).

The contents (%) of the elements (Ca, Na and K) were deduced by flame photometer (500731 PFP7, Jenway). The other chemical elements such as Si, Fe, Mg and Al were analyzed by inductively coupled plasma with mass spectrometry (4500 ICP/MS, Hewlett-Packard). The concentration of sulfate was deduced by the gravimetric method (precipitation of SO_4^{2-} ($BaSO_4$) by using $BaCl_2$ solution. The P_2O_5 and F contents were determined by spectrophotometer (VIS-7220G UV-9100/9200, Rayleigh) and ionometric method (Fluoride ISE TR 200, Tacussel) respectively after essential standardization. The hydration degrees of our samples were deduced

by simultaneous thermogravimetric and differential thermal analyzer (DTG/60, Shimadzu).
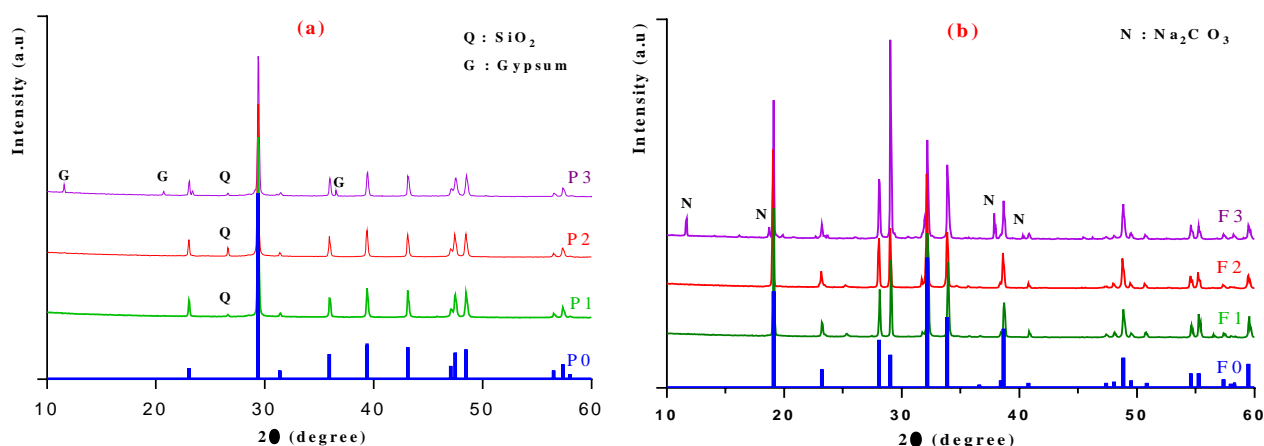
Results and Discussion

The chemical compositions of the PG sample indicate that it is formed mostly of 96 % of $CaSO_4.2H_2O$ (Table 2). The major impurities are P_2O_5, SiO_2 besides Al_2O_3, Fe_2O_3, MgO, Na_2O and K_2O with lower quantity. In previous researchers, we have discussed and detailed very well the physico-chemicals properties of this PG. Generally, the properties of this PG are approximately similar to the other Moroccan PGs [1, 2, 15].

The effects of initial concentration of Na_2CO_3 on the transformation of PG and GRH into Na_2SO_4 through reaction time of 30 min at room temperature were realized by changing its concentration from 0.4 to 0.7 mol/L. The mixtures of Na_2CO_3 with PG and GRH are stoichiometric.

The results acquired by XRD analysis expose that for stoichiometric PG and Na_2CO_3 concentration of 0.5 and 0.6 mol/l, the precipitates P1 and P2 (Figure 1a) and the salts obtained after the crystallized of the filtrates F1 and F2 (Figure 1b) show a single phase agreeing to the calcite P0 ($CaCO_3$, JCPDS N°: 05-0586) and the thenardite F0 (Na_2SO_4, JCPDS N°: 86-0803) respectively.

The XRD diffractograms of the precipitates obtained by GRH transformation to Na_2SO_4 are also represented in Figure 2a. For Na_2CO_3 concentrations equal to 0.4 and 0.5 mol/L, the precipitates P4, P5 and filtrates F4, F5 are formed principally by calcite and thenardite respectively. When we increase Na_2CO_3 concentration to 0.6 mol/L, we note yet the presence of gypsum in precipitate P6.

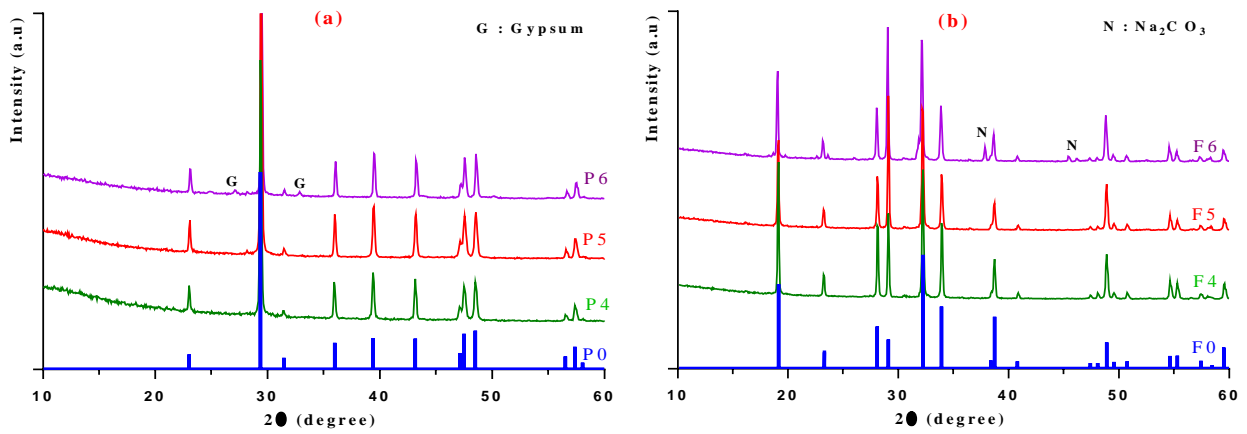**Figure 1.** XRD diffractograms of the precipitates (a) and the filtrates (b) recovered from PG transformation for different stoichiometric Na_2CO_3 concentration at room temperature during reaction time of 30 min.
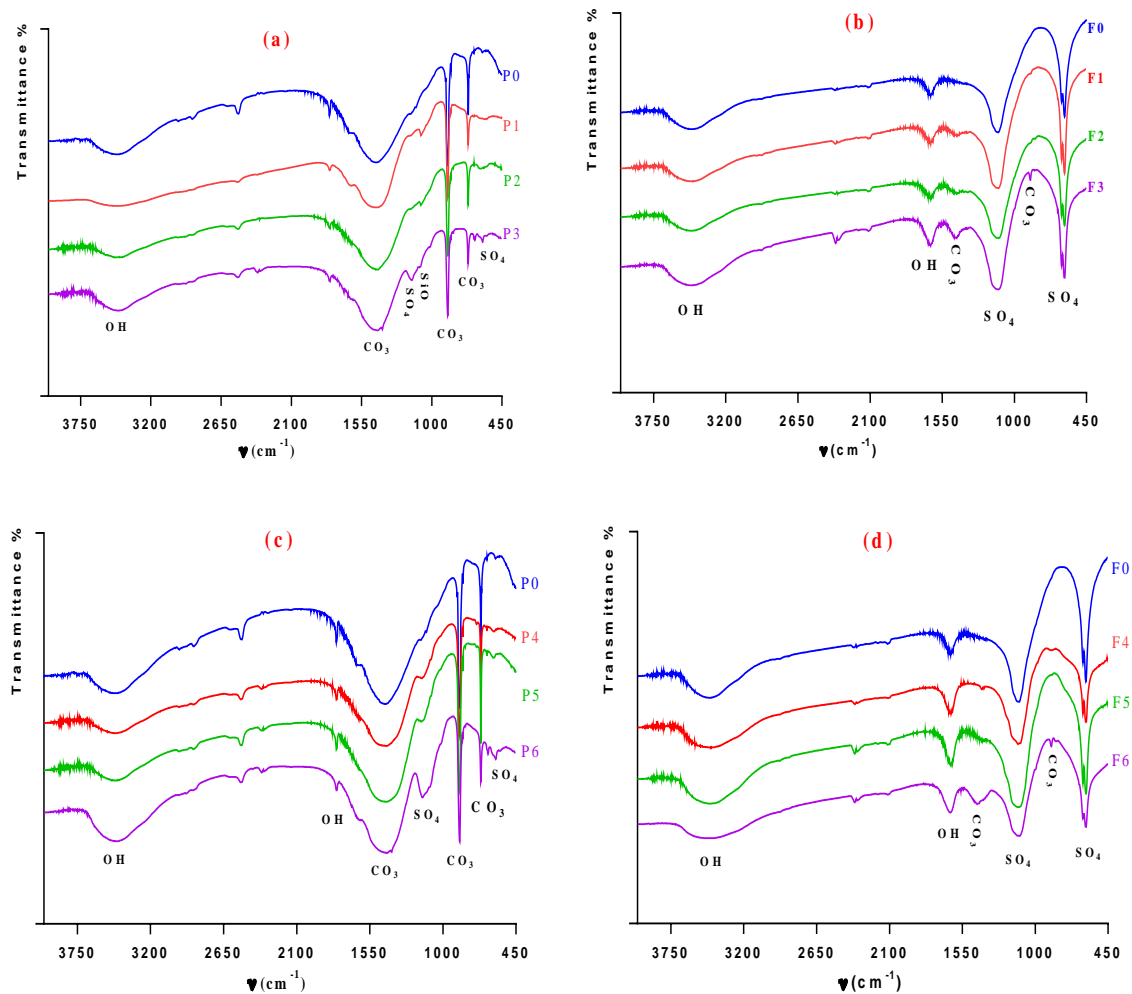
We conclude that from stoichiometric mixture of PG and Na_2CO_3 with concentrations of 0.7 mol/L, the reaction is incomplete because the PG remains in the precipitate. On the other hand, in the case of a GRH/Na_2CO_3 mixture, the reaction is not complete from the concentration 0.6 mol/L. Therefore PG is more reactive then GRH and the effect of salinity are predominant in the case of GRH.

The existence of gypsum in the precipitate P6 recovered through GRH conversion engenders the presence of Na_2CO_3 beside Na_2SO_4 in the filtrate F6 (Figure 2b).

Figure 2. XRD diffractograms of the precipitates (a) and the filtrates (b) recovered from GRH transformation for different stoichiometric Na_2CO_3 concentration at room temperature during reaction time of 30 min.

Figure 3. FTIR spectrums of the precipitates (a and c) and the filtrates (b and d) recovered from PG and GRH transformation respectively, for different stoichiometric Na_2CO_3 concentration at room temperature during reaction time of 30 min.

The temperature effect on the PG transformation was also studied by Kolokolnikov and Shatov [17]. These authors indicated that the increase of temperature (40 to 90 °C) has a very little influence on the reaction time and the yield of the PG conversion.

The recovered products were also examined by FTIR technique. The FTIR spectrums of the precipitates P1, P2 (Figure 3a) and the filtrates F1, F2 (Figure 3b) obtained via the PG conversion by Na_2CO_3 for concentration 0.5 to 0.6 mol/L, show similar bands with pure $CaCO_3$ (P0) and Na_2SO_4 (F0) respectively. We have observed also the same results for the precipitates P4, P5 (Figure 3c) and the filtrates F4, F5 (Figure 3d) resulted from the conversion of GRH by Na_2CO_3

for the concentration 0.4 and 0.5 mol/L respectively.

The presence of bands at 600 and 1155 cm^{-1} of SO_4^{2-} (gypsum) in the precipitates P3 and P6 recuperated during PG and GRH conversion respectively (Figure 3a and 3c), justifies the existence of bands at 870 and 1425 cm^{-1} of CO_3^{2-} (Na_2CO_3) in the filtrates F3 and F6 (Figure 2b and 2d).

The results obtained from the characterization of the resulted products by XRD and FTIR are adequate.

Table 1 represents the vibration band frequencies and assignments of the precipitates and the filtrates.

Table 1. FTIR frequencies of the obtained products.

Assignment		Wave number ν (cm^{-1})	
Ion /Molecule	Vibration mode	Precipitates	Filtrates
H_2O	ν (stretch region)	3300-3600	3300-3600
	δ (deformation)	–	1634
	ν_3 (asymmetric stretching)	1438-	1440
CO_3^{2-}	ν_2 (out-of-plane deformation)	870	874
	ν_4 (bending in-plane deformation)	711	–
SO_4^{2-}	ν_3 (asymmetric stretching)	1150	1120
SO_4^{2-}	δ_4 (bending)	600	638; 617
SiO_2	ν (asymmetric stretching)	1080	–

According to XRD and FTIR results, it was found that the GRH was less reactive than PG. This is due to the difference of the purity, the granulometry and the impurities nature, which favor the PG dissolution.

In the next paragraph, the precipitate P2 and the filtrate F2 recuperated from a total PG transformation to Na_2SO_4 at room temperature was selected for all further analyses in order to define the physico-chemicals properties and the quality of these final products.

Table 2 regrouped the chemical analysis results accomplished on the precipitate P2 and salt F2.

In the light of these results, $CaCO_3$ represents around 96 % of the chemical composition of this

precipitate. Generally, the insoluble impurities presented in PG are transferred completely into calcite. The concentration of Na in the precipitate is higher compared to that in PG. This can be explained by the existence of the adsorbed Na_2SO_4 at the calcite surface through the filtration. Certain chemical elements like Si stay inert through the PG conversion. The presence of P in the precipitate is due to inattacked phosphate rock or to the insoluble phosphate compounds ($CaHPO_4$, $Ca_3(PO_4)_2$, $CaHPO_4.2H_2O$). We note also the detection of Fe, Mg and Al in the precipitate, which indicated the existence of clays. For the fluorine in soluble form (effectively H_2SiF_6 and HF) moves into the filtrate, while the

insoluble complexes such as ($CaFPO_3.2H_2O$, $MgSiF_6$, K_3AlF_6, Na_3AlF_6, Na_2SiF_6 and K_2SiF_6) remain in the precipitate.

For the recrystallized salt F2, the chemical analysis proves that this salt is constituted by 99 % of Na_2SO_4. The presence of Ca, Si and P in this salt may be due to the very $CaCO_3$ fine particles, which pass into the filtrate. In addition, the presence of K can be explained to K existing in initial reagent Na_2CO_3.

According to these results, the recovered salt Na_2SO_4 rest generally a pure product, which can be utilized directly in the detergent industry, pulp, paper and glass.

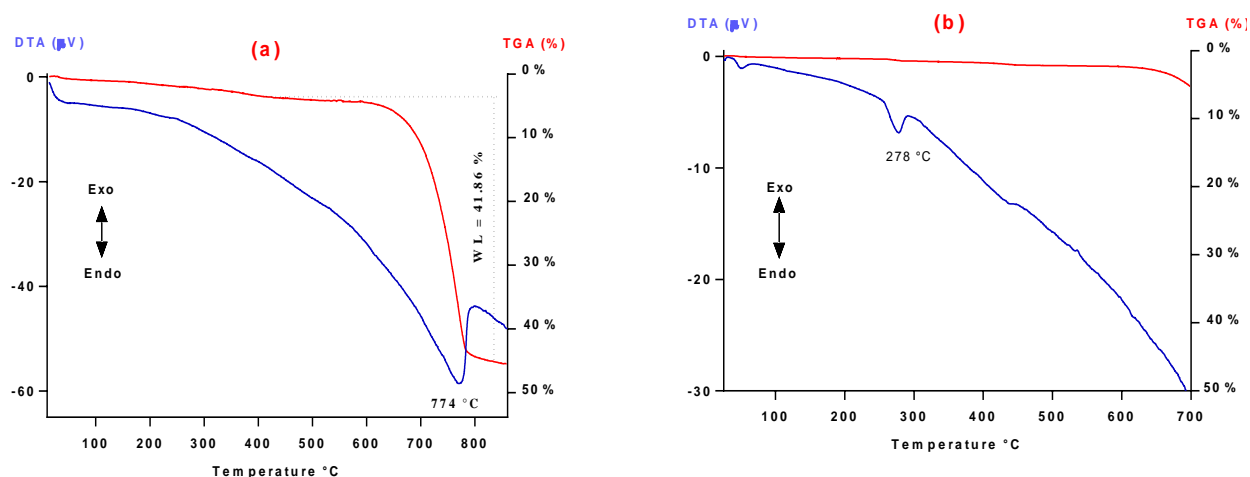**Table 2.** Chemical compositions of the precipitate P2 and the salt F2.

Major elements (%)	PG [1,15]	Precipitate P2	Salt F2
CaO	31.28	54.18	0.29
SO_3	44.69	0.22	55.74
H_2O	20.58	0.18	0.28
CO_3	–	41.86	–
F	0.67	0.59	0.14
Na_2O	0.26	0.49	43.36
K_2O	0.02	0.00	0.06
P_2O_5	1.11	1.20	0.04
SiO_2	0.96	1.02	0.09
Al_2O_3	0.16	0.18	0.00
MgO	0.06	0.04	0.00
Fe_2O_3	0.06	0.03	0.00

The thermal analysis TGA-DTA of the obtained products was represented in Figure 4. This analysis was conducted in order to evaluate the purity of these samples and to determine its amount of H_2O and CO_2. Concerned the precipitate P2 (Figure 4a), a slight weight loss was observed below 450 °C. This is due the removal of the water (adsorbed and crystallized) of certain impurities ($CaHPO_4.2H_2O$, $CaFPO_3.2H_2O$...). Around 774 °C, an endothermic peak was detected, which is owing to the calcite decarbonation ($CaCO_3$ (s) → CaO (s) + CO_2 (g)) accompanied with a weight loss of 41.86 % (the weight loss of pure calcite is 44 % for the temperature 900 °C). According to these results, the thermal study of the resulted calcite demonstrates good energy efficiency [13].
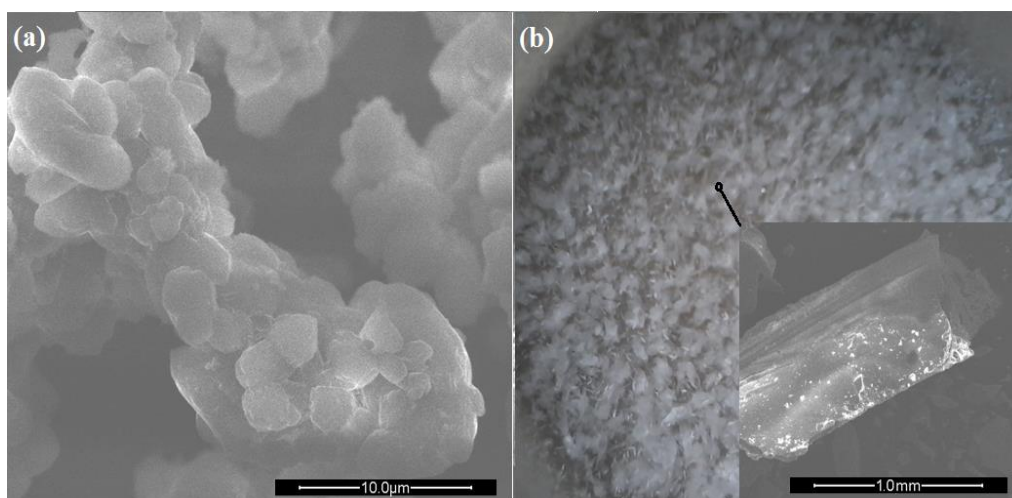
For the salt F2, TGA and DTA curves (Figure 4b) indicate a very low weight loss remarked in the range 100-300 °C, which shows that this salt is anhydrous. At temperature 278 °C, an endothermic peak was observed, which corresponds to Na_2SO_4 phase transition from orthorhombic (III) form to the hexagonal (I) form. Rao *et al*. have showed this transition at 265 °C for pure Na_2SO_4 [22]. The difference between this temperature transitions is due to the impurities presence in the obtained salt.

Figure 4. TGA-DTA curves of the precipitate P2 and the salt F2

The morphology of the precipitate P2 and the salt F2 are visualized by SEM. We observe that the calcite crystals form is in agglomerates of superimposed fine scales with a medium surface area. The regular diameter of these scales is 2 µm with thickness of 1 µm (Figure 5a).

Concerned the salt, the photograph (Figure 5b) shows the presence of macro-crystals in the rods form with length between 2-4 mm. This permits to recover Na_2SO_4 simply after recrystallization.

Figure 5. SEM images of the precipitate P2 and the salt F2.

The results acquired by the both of the morphological and thermal analysis of the obtained calcite favored its usage in the environment fields (cycle $CaCO_3/CaO$).

In the economical approximate, the transformation of PG by Na_2CO_3 necessitate generally simple operation (availability, use PG without any specific pretreatment, room temperature and easy filtration) for recovering $CaCO_3$ and Na_2SO_4. In environmental approach, this process permits reducing the quantity of PG rejected and benefit about 89.82 $ for each tonne PG converted (Table 3). This cost is attractive compared to that estimated by Chapman *et al*. (83.06 $) [8].

Table 3. Comparison between some recent reports in electrochemical determination of AC and CP

		Quantity	Cost*	Total ($)*
Raw Material:	$CaSO_4.2H_2O$	1.000 t	available	–
Chemical Reagent:	Na_2CO_3	0.615 t	150 $/t [23]	92.25
Utility Cost:	Water	9.68 m³	0.8 $/m³ [24]	7.74
	Power	100 KW	0.16 $/KWh [24]	16
	Transport, TVA, Maintenance...			Max 5
Finals Products:	$CaCO_3$	0.581 t	123 $/t [25]	71.46
	Na_2SO_4	0.825 t	154 $/t [26]	127.05
	$2H_2O$	0.209 m³	–	–
Benefit:	–	–	–	89.82

* These costs are estimated for Morocco during the period 2014-2020.

Conclusion

From this study, it is clear that the conversion of PG by Na_2CO_3 into $CaCO_3$ and Na_2SO_4 remains a simple, economic and environmental process. The PG conversion: (i) takes short reaction time (30 min) to complete, (ii) needs no costly or specific conditions (stœchiometric proportions, room pressure and temperature) and (iii) yields very pure products (the purity of $CaCO_3$ and Na_2SO_4 is 96 and 99 % respectively).

Compared to GRH gypsum, PG was totally converted to $CaCO_3$ and Na_2SO_4 for maximum concentration of 0.6 mol/L, while the conversion of GRH by Na_2CO_3 requires a lower concentration of 0.5 mol/L.

Additionally, the physico-chemical properties of the produced $CaCO_3$ approve to use it in the environment and the industry domains, whereas the recovered Na_2SO_4 can be used as detergent.

The technical and the economic feasibility of the PG conversion to $CaCO_3$ and Na_2SO_4, show that this approach rest preferred and more attractive.

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Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Yassine Ennaciri : 0000-0002-2442-7397
Mohammed Bettach : 0000-0003-1795-1796

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