

Optimization of conditions to convert phosphogypsum into Ca(OH)_2 and Na_2SO_4

H. El Alaoui-Belghiti ^{(a,*), M. Bettach} ^{(a), I. Zdah} ^{(a), Y. Ennaciri} ^{(a), J. Assaoui} ^{(b) And A. Zegzouti} ^(c)

^(a) LPCM, Laboratory of Physical Chemistry of Materials, Faculty of Science, Chouaib Doukkali University, El Jadida, Morocco.

^(b) Department of chemistry, Faculty of Science, Chouaib Doukkali University, El Jadida. Morocco.

^(c) Laboratory of Science of inorganic materials and their Applications, Faculty of Science - Semlalia, Cadi Ayyad University, Marrakech. Morocco.

Abstract

With a view to finding solutions to the problems of Moroccan phosphogypsum (PG) in the long term, a research theme has been developed in our laboratory on the valorization of this residue by its conversion into marketable products by soft chemistry way less expensive. Thus, we investigated the optimal experimental conditions allowing a good efficiency of PG conversion by using NaOH to synthesize marketable products such as Ca(OH)_2 and Na_2SO_4 of high purity. We varied the reagent concentrations and the attack durations to optimize these conditions. The quality of the products obtained is checked by XRD, IR and ICP to determine the distribution of PG impurities between obtained products. The morphology and size distribution were also established by SEM and laser granulometry.

* Corresponding author:
belghitihanan@gmail.com

Received 29/01/2020,

Revised 10/06/2020,

Accepted 16/06/2020

Keywords: Phosphogypsum valorization, Portlandite, Sodium sulfate, CO_2 sequestration treatment.

1. Introduction

The industrial activity of fertilizer plant Maroc Phosphore is constantly increasing year after year. The wellbeing of millions of people around the world depends on it but it also generates a number of environmental problems. One of these problems is the emission of carbon dioxide which is at the top of the greenhouse gases. It has lifetime exceeding 120 years and contribute to about 55 % of global warming [1]. Phosphogypsum (PG) is a byproduct of the production of phosphoric acid used in the manufacturing of fertilizers which is also causing pollution problems when it is stored or discharged into the Atlantic Ocean. Pollution problems resulting from PG have been brought forward several scientists [2–4]. The originality of this work is to find a solution to both these problems by PG decomposing using soft chemistry. The process is very interesting because it is cheaper and allows having marketable products which finds their applications in several industrial domains. In this subject, several works have been carried out in our laboratory which allowed synthesizing alkali sulfates from phosphogypsum and alkali carbonates [5–7]. In this work, we use Moroccan phosphogypsum as a raw material to search the optimal conditions to produce calcium hydroxide Ca(OH)_2 and sodium sulfate Na_2SO_4 . Ca(OH)_2 can be used as material for the storage of thermal energy, in cement industry or as adsorbent for wastewater, including radioactive elements [8,9]. In addition, Ca(OH)_2 obtained by conversion of PG can be used in-situ to sequester CO_2 thus avoiding transport costs. Na_2SO_4 is widely used in the detergents, glasses, water treatment industry and paper. Direct synthesis of Na_2SO_4 is generally prepared by the Mannheim process. The reaction is carried out in muffle furnaces between 500 and 600 °C [10]. It is therefore clear that the method proposed in this work, which does not require heating, remains very advantageous economically and environmentally. We varied the duration of the attack and the concentration of NaOH in order to find the optimal conditions to carry out this conversion. Characterization by XRD and IR show that the PG conversion is possible and total. ATG-ATD analysis explained the influence of impurities on the thermal behavior of the reaction products. Finally, the chemical analysis was carried out by various methods.

2. Materials and methods

To carry out this study, we used a considerable amount of PG, which we procured from the Maroc Phosphore fertilizer factory. We washed it several times to remove acid traces, soluble impurities and organic matter contained in the supernatant. We then dried the washed PG in an oven at 60 °C. The sodium hydroxide NaOH used in this research was from reagent grade chemicals, with the purity of 99 %. Reactional mixtures of washed phosphogypsum and sodium hydroxide solution were prepared at ambient temperature and were put under stirring (500 tr/min) during different times (Table 1). A white precipitate Ca(OH)_2 was formed, it was separated from the solution by simple filtration and dried in the oven at 60 °C. The filtrates which contain Na_2SO_4 are introduced in the oven at 60 °C to recrystallize the salts. Precipitates obtained by different reaction mixtures at different concentrations, thus corresponding salts are analyzed by X-ray diffraction using a Bruker diffractometer (D8 Advance with Cu-K α radiation $\lambda = 1.5418 \text{ \AA}$). The XRD patterns were scanned from $2\theta = 10$ to 60° . Infrared spectra were performed by Fourier transform infrared spectroscopy (Nicolet iS10 Thermo Fisher spectrometer using FTIR iTR. Concentrations of trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS Model HP-4500) after acid digestion. The quality control method included the use of a reagent blank, standard reference materials and replicates. The sulfate ions content in different samples were measured by gravimetric method. Grain size distribution using the dry sieving method NF P94-056. Particle size analysis was determined by laser granulometry in wet suspensions MASTERSIZER 2000 MALVERN. Moreover, morphology and microstructures were performed by scanning electron Microscopy, SEM (EDAX AMETEK) at 10 kV. Experimental conditions for preparing the various samples are illustrated with their corresponding names in Table 1.

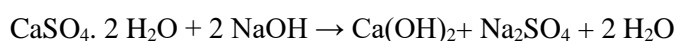
Table 1. Operating conditions for the mixtures carried in this work.

Run N°	Time (h)	[PG] (mol/l)	[NaOH] (mol/l)	Precipitate name	Filtrate name
1	2	0.1	0.2	P 0.1M stoichiometric 2h	F 0.1M stoichiometric 2h
2	2	0.1	0.2+40%	P 0.1M+40% NaOH 2h	F 0.1M+40% NaOH 2h
3	2	0.1	0.2+50%	P 0.1M+50% NaOH 2h	F 0.1M+50% NaOH 2h
4	2	0.1	0.2+55%	P 0.1M+55% NaOH 2h	F 0.1M+55% NaOH 2h
5	2	0.1	0.2+60%	P 0.1M+60% NaOH 2h	F 0.1M+60% NaOH 2h
6	0.5	0.1	0.2+55%	P 0.1M+55% NaOH 0.5h	F 0.1M+55% NaOH 0.5h
7	1	0.1	0.2+55%	P 0.1M+55% NaOH 1h	F 0.1M+55% NaOH 1h
8	3	0.1	0.2+55%	P 0.1M+55% NaOH 2h	F 0.1M+55% NaOH 2h
9	4	0.1	0.2+55%	P 0.1M+55% NaOH 4h	F 0.1M+55% NaOH 4h
10	2	0.3	0.6	P 0.6M stoichiometric 2h	F 0.6M stoichiometric 2h
11	2	0.3	0.6+10%	P 0.6M+10% NaOH 2h	F 0.6M+10% NaOH 2h
12	2	0.3	0.6+15%	P 0.6M+15% NaOH 2h	F 0.6M+15% NaOH 2h
13	2	0.3	0.6+20%	P 0.6M+20% NaOH 2h	F 0.6M+20% NaOH 2h
14	0.5	0.3	0.6+15%	P 0.6M+15% NaOH 0.5h	F 0.6M+15% NaOH 0.5h
15	1	0.3	0.6+15%	P 0.6M+15% NaOH 1h	F 0.6M+15% NaOH 1h
16	3	0.3	0.6+15%	P 0.6M+15% NaOH 3h	F 0.6M+15% NaOH 3h
17	4	0.3	0.6+15%	P 0.6M+15% NaOH 4h	F 0.6M+15% NaOH 4h
18	0.5	1.5	3	P 1.5 M stoichiometric 0.5 h	F 1.5 M stoichiometric 0.5 h
19	1	1.5	3	P 1.5 M stoichiometric 1h	F 1.5 M stoichiometric 1h
20	2	1.5	3	P 1.5 M stoichiometric 2h	F 1.5 M stoichiometric 2h
21	3	1.5	3	P 1.5 M stoichiometric 3h	F 1.5 M stoichiometric 3h
22	4	1.5	3	P 1.5 M stoichiometric 4h	F 1.5 M stoichiometric 4h

3. Results and Discussion

3.1. Optimization of conversion conditions

Series of experiments were performed to follow the reactivity of Moroccan phophogypsum with NaOH. Our goal is to find the optimum conditions such as concentration and reaction durations. To realize this study, we have chosen concentrations of PG ranging from 0.1 M to 2 M of PG. We have started with stoichiometric reagents (0 % excess of NaOH) as indicates the following decomposition reaction:



RX diffractograms mixtures of 0.1 M PG with a stoichiometric proportion of NaOH (a) and with various NaOH excess (b, c, d) are shown in Figure 1. For the stoichiometric mixture (a), obtained precipitate contains a small amount of Ca(OH)_2 but the majority phase still remains $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ indicating that PG is not completely decomposed. Tests with NaOH excess are tested. The results show that it is necessary to reach 55 % NaOH excess (c) to have a total decomposition of PG. We also studied the effect of the reaction duration. The results are presented in Figure 2. We varied stirring duration from 0.5 h (a) to 4 h (d). The total decomposition of PG requires 2 h for this concentration (0.1 M PG). Diffractogram of obtained whitish precipitate corresponds mostly to portlandite Ca(OH)_2 (JCPDS N°: 01-076-0571) which exhibits an hexagonal structure with space group P-3m. A small amount of calcite (CaCO_3) (JCPDS N°: 00-003-0596) was produced as a result of carbonation during the sample preparation process. A low quantity of quartz (JCPDS N°: 00-033-1161) is also detected. It comes from impurities included in PG remaining inert and not attacked during the reaction and appears on the X-ray diffractograms. To verify the influence of the initial reagent concentrations, we conducted reactions in concentration 0.3 M PG (). The stoichiometric mixture shows that the decomposition of the PG is not complete, indeed, the diffractogram (a) shows that the obtained precipitate contains portlandite Ca(OH)_2 and PG ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). 15% excess of NaOH (c) makes this conversion possible and PG completely disappears. We then sought the optimal duration of this conversion (Figure 4) by fixing 0.3 M PG with 15 % NaOH excess. Diffractograms show the disappearance of the PG after only 1h (b). Similar results are obtained when more concentrated PG (0.6, 0.7 and 0.8 M) reaction mixtures are prepared. DRX analysis shows that an excess of 5 % NaOH and duration of 30 minutes are necessary for a total PG decomposition. When we increase PG concentration to 1 M, the reaction becomes stoichiometric without NaOH excess. In order to obtain highly concentrated salt Na_2SO_4 and therefore easy to recrystallize, we have increased the concentration of PG to 1.5 M. We chose to stop the PG concentration at 1.5 M to obtained thernadite concentration less than its maximum solubility at 20 °C which is 220 g/L (1.55 M). So we avoid the precipitation of Na_2SO_4 with the precipitate. Diffractograms in Figure 5 show that the minimum time for this conversion is 30 min for the case of the 1.5 M PG concentration. After all these tests, we have determined the optimal conditions of PG conversion which are 1.5 M PG, 3 M NaOH, at ambient temperature during 30 min. In these conditions, PG conversion became total and stoichiometric.

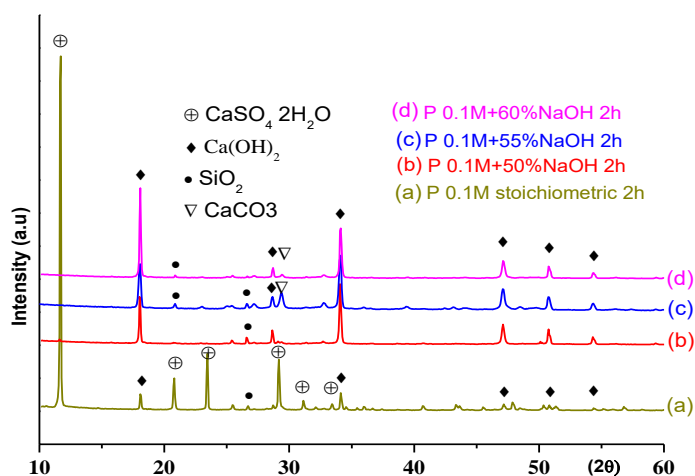


Figure 1. Diffractograms of precipitates obtained for the mixture of 0.1 M PG and different excess of NaOH during 2 hours

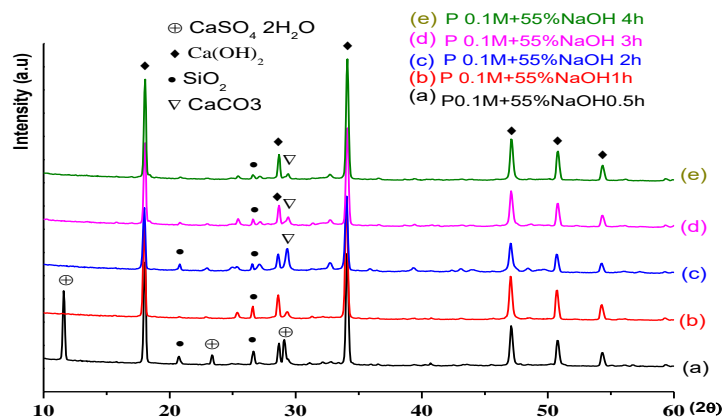


Figure 2. Diffractograms of precipitates obtained for the mixture 0.1 M PG and 55% excess of NaOH at various durations

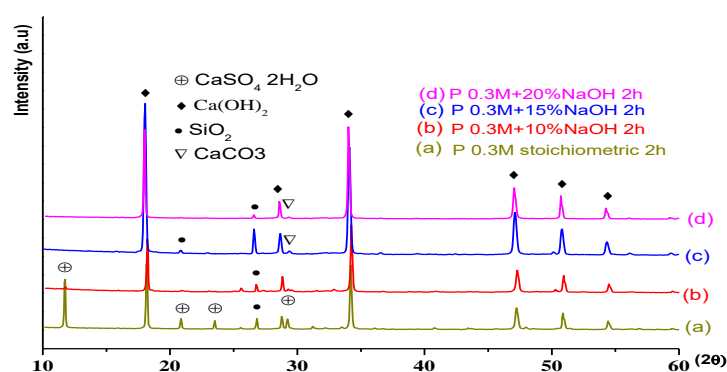


Figure 3. Diffractograms of precipitates obtained for the mixture of 0.3 M PG and different excess of NaOH during 2 hours

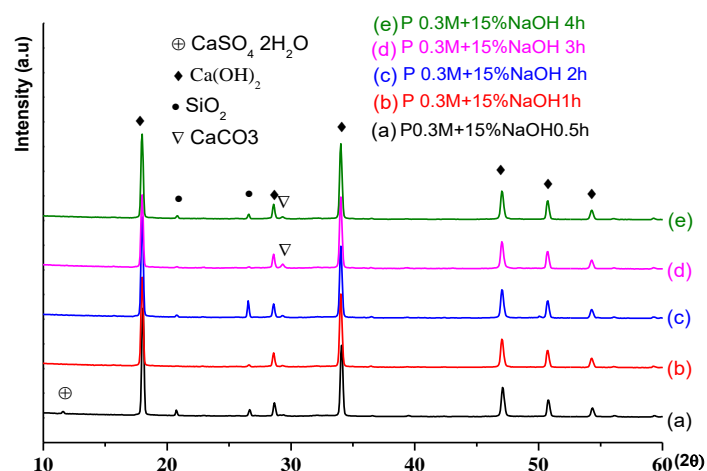


Figure 4. Diffractograms of precipitates obtained for the mixture 0.3 M PG and 15% excess of NaOH at various durations

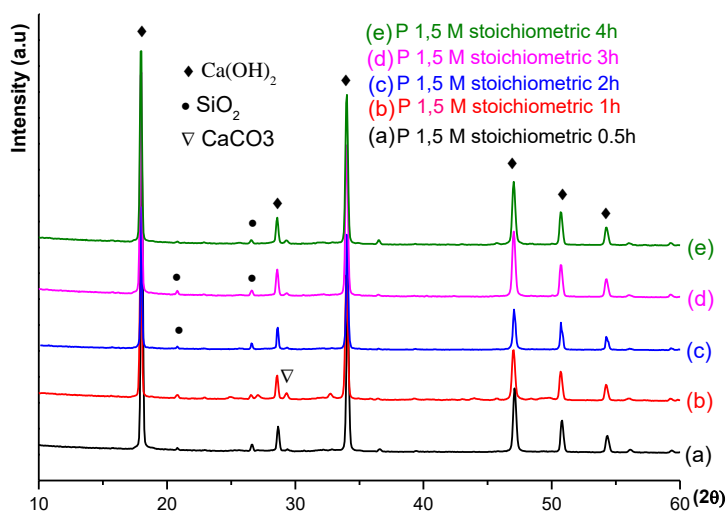


Figure 5. Diffractograms of precipitates obtained for stoichiometric mixture 1.5 M PG and NaOH at various durations.

Salts recovered from filtrates for the stoichiometric mixture 1.5 M are also analyzed by XRD. Figure 6 shows that salts are well crystallized and correspond to thernadite Na_2SO_4 (JCPDS No: 00-005-0631) of orthorhombic structure with the F_{dd} space group.

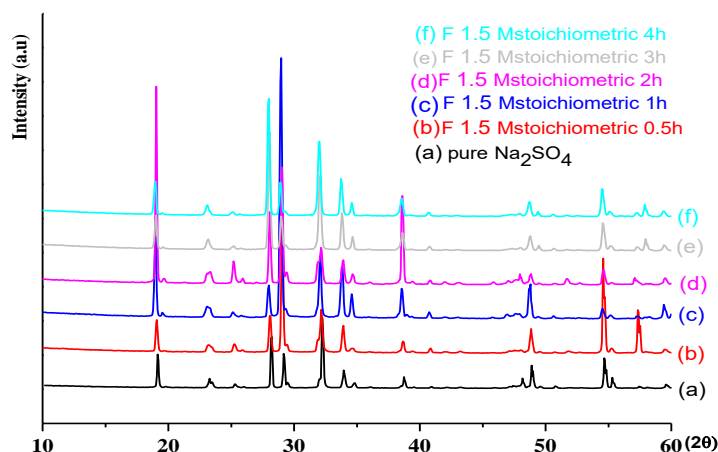


Figure 6. Diffractograms of salts obtained for stoichiometric mixture 1.5 M PG and NaOH at various durations.

We followed the evolution of pH for each concentration, precisely mixtures which gave a total conversion of PG (Figure 7). This study shows a quick decrease in pH at the beginning of the reaction due to the precipitation of OH^- ions during the $\text{Ca}(\text{OH})_2$ formation. The end of the reaction is manifested by fixed values of pH. This behavior allows determining, exactly, duration of each of the reactions. Therefore, mixtures of 0.1 M, 0.3 M and 0.6 M of PG require reaction times of 2 h, 1 h 24 and 30 min respectively. We note that more concentrated mediums are favorable for the fast $\text{Ca}(\text{OH})_2$ precipitation. These results are in agreement with those obtained by DRX study

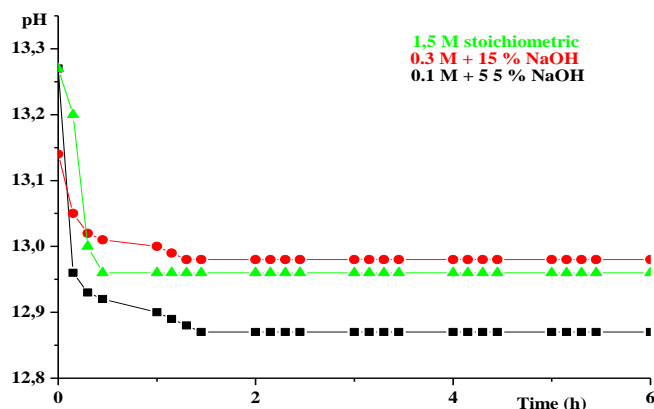
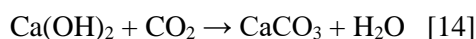


Figure 7. pH evolution for mixtures giving a total conversion of PG.

3.2. IR analysis

Infrared spectra of obtained precipitates and corresponding salts obtained by reactions leading to total PG conversion are presented in Figure 8 and Figure 9 respectively. For the precipitates (Figure 8), a narrow absorption band at 3639 cm^{-1} due to the O–H stretching band in the crystal structure of portlandite $\text{Ca}(\text{OH})_2$ is observed. The band at around $537\text{--}607\text{ cm}^{-1}$ is assigned to Ca–O stretching vibration in $\text{Ca}(\text{OH})_2$ [11,12]. In addition, absorption bands at 1433 and 874 cm^{-1} are assigned to different vibration modes C–O of carbonate groups CO_3^{2-} [12,13]. The presence of calcium carbonate could be explained by partial carbonation of $\text{Ca}(\text{OH})_2$ by atmospheric CO_2 during their preparation, forming as following reaction.



The band observed at 1100 cm^{-1} is assigned to Si–O stretching mode of SiO_2 [5,7]. These results are in agreement with those obtained by X-ray diffraction and confirm that the conversion of PG becomes total. For the filtrates (Figure 9), infrared spectra show the main bands of Na_2SO_4 can be detected. The band appearing at 1096 cm^{-1} is assigned to ν_3 asymmetric stretching vibrations whereas the bands located at $611\text{--}636\text{ cm}^{-1}$ are assigned to ν_4 asymmetric bending vibrations of SO_4 groups. Two other bands observed at 1433 and 876 cm^{-1} correspond respectively to the ν_3 asymmetric stretching vibration modes and ν_2 out-of-plane deformation vibration modes of carbonate groups CO_3 . These bands can be due to the presence of CaCO_3 which pass in filtrate [15]

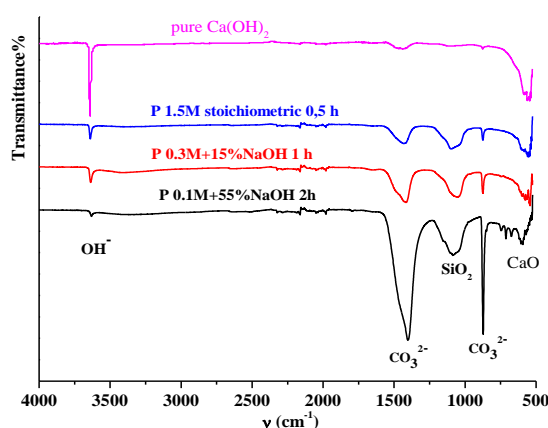


Figure 8. FTIR Spectra of precipitates obtained by reactions leading to total PG conversion.

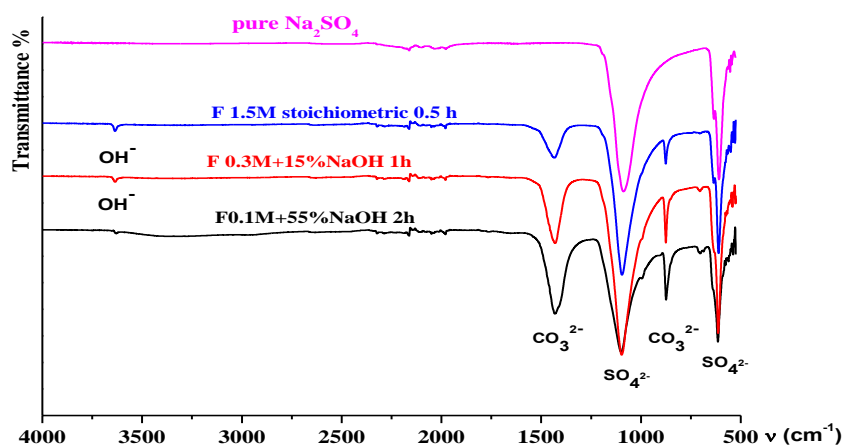


Figure 9. FTIR Spectra of salts obtained by reactions leading to total PG conversion.

3.3. Thermogravimetric Analysis

TGA-TDA curves of precipitate (P 1.5 M stoichiometric 0.5 h) and salt (F 1.5 M stoichiometric 0.5 h) are represented in Figure 10 and Figure 11 respectively. We chose for this study, only products obtained by the optimal conditions. TGA curve of precipitate exhibits two weight losses indicating that there is elimination of water and carbon dioxide. Decomposition of Ca(OH)_2 occurs at around 450 °C ($\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$) whereas CaCO_3 decomposes over a temperature range 500 °C to 750 °C ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) accompanied by endothermic peaks in TDA Curves. TGA results confirm that an amount of calcium carbonate (CaCO_3) was produced as a result of the carbonation of Ca(OH)_2 during the sample preparation process (Figure 10). Similar range of decomposition temperatures were found by Kim and Olek [16].

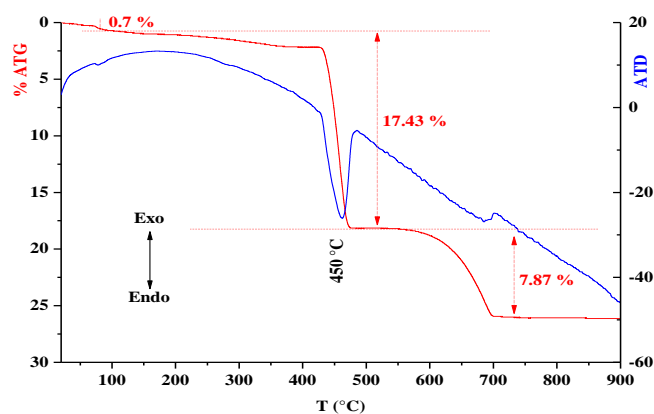


Figure 10. TGA-TGA curves of precipitate obtained at optimal conditions (P 1.5 M Stoichiometric 0.5 h).

TGA curve of the salt is presented in Figure 11. A low weight loss between the temperatures 100 and 900 °C is observed. This loss is due to the removal of adsorbed water and traces of carbonate. Weight loss is negligible; consequently we can conclude that obtained salt is anhydrous. An endothermic peak at 258 °C is observed on the DTA curve, which corresponds to Na_2SO_4 phase transition from orthorhombic (III) form to the hexagonal (I) form. This transition is observed at 265 °C by Rao et al for pure Na_2SO_4 [17]. The other endothermic peak at 869 °C is due to melting temperature of the obtained Thernadite. Melting temperature for pure Na_2SO_4 is 884 °C

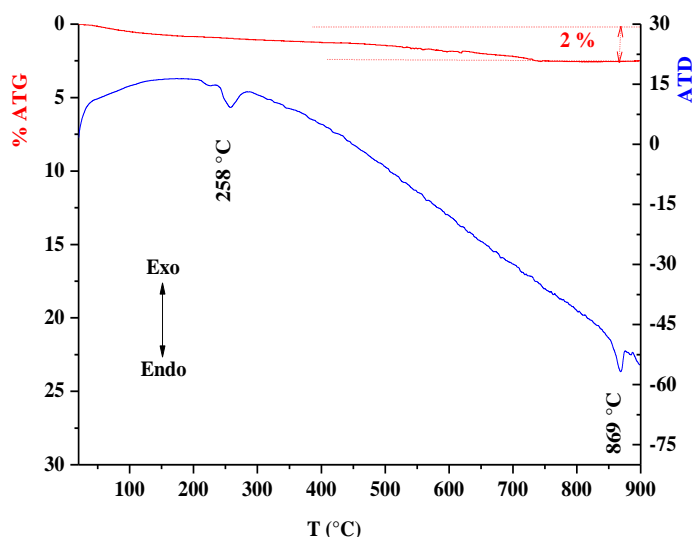
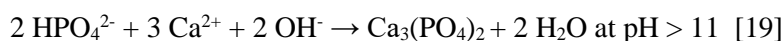


Figure 11. TDA-TGA curves of Filtrate obtained at optimal conditions (P 1.5 M Stoichiometric 0.5 h).

3.4. Chemical analysis

We performed chemical analyzes of the starting PG and products that have been synthesized in optimal conditions.

Table 2 summarizes the concentration (% by mass) of different species and impurities in PG and in obtained products. It is difficult to make a complete assessment of all kinds of impurities in the PG. Nevertheless, we can name some of them and follow their distribution. Major impurities of PG are originated from phases that have low solubility like minerals without transformation during the phosphoric attack as fluorine (CaF_2) and quartz (SiO_2) or from co-crystallized compounds as MgF_2 or K_2SiF_6 and inert phases as Na_3AlF_6 . Chemical analysis shows that F and Si are mainly transferred to the precipitate which explain the presence of Mg, K and Al, in the produced portlandite. P_2O_5 content in the precipitate reaches a significant value of 1.52 %. This content can be attributed to secondary reactions during PG conversion which lead to CaHPO_4 and / or $\text{Ca}_3(\text{PO}_4)_2$ formation depending on the pH of the medium as shown in the following reactions :



Traces elements in PG (Table 3) can be attributed in plus of phosphate rock, to an additional source associated with the sulfuric acid used for the production of phosphoric acid [20,21]. The majority of these trace elements are also transferred to the precipitate. So, the crystallized Salt is mainly composed by Na_2O and SO_3 (36.73 wt.% and 56.86 wt.%, respectively). CaO content (3 wt%) is probably deriving from the non-separated rests of portlandite or calcite contained in the precipitate. The presence of portlandite and calcite is also detected by IR analysis in the salt. Mn, V, Cu, Zr, Cd and Li elements are not detected in salt but the other impurities exist in very low levels. According to the chemical analysis, we perceive that most of the impurities contained in the PG waste pass into the precipitate which provides a more pure salt Na_2SO_4 [22].

Table 2. Major elements in PG, portlandite (P 1.5 M stoichiometric 0.5 h) and thernadite (F 1.5 M stoichiometric 0.5 h) obtained in optimal conditions.

% elements	CaO	SO ₃	Na ₂ O	F ⁻	P ₂ O ₅	Fe ₂ O ₃	K ₂ O	SiO ₂	MgO	Al ₂ O ₃	L. O. I
PG [22]	31.71	43.40	0.27	1.10	1.20	0.07	0.05	0.74	0.05	0.09	20.80
Precipitate	69.56	3.00	2.07	0.10	1.52	0.02	0.033	3.38	0.063	0.115	26
Filtrat	3.01	56.86	37.63	0.06	0.20	0.01	0.03	---	0.025	0.025	2

Table 3. Trace elements in PG, portlandite (P 1.5 M stoichiometric 0.5 h) and thernadite (F 1.5 M stoichiometric 0.5 h) obtained in optimal conditions.

Trace elements (ppm)	Ba	Mn	V	Cu	Zr	Cd	Li	Pb	Cr	Y
PG [22]	30.08	0.04	7	55	19	1.34	<1	1.9	7.5	135
Precipitate	59.5	2	9	10.5	13	2	<1	4	11	284.02
Filtrat	6.5	<1	<1	<1	<1	<1	<1	3.00	5.5	1.375

3.5. Morphologic study

The morphology of Portlandite (P 1.5 M stoichiometric 0.5 h) was observed by SEM. In

Figure 12 (a, b, c and d) we can notice, mainly, the existence of two types of grains, those of small size around 1 μm with spheric form and others of larger size which have an elongated thin plates form. there are also aggregates in size of around 25 to 30 μm . By examining carefully the shapes of certain grains, we can observe crystals in small quantities which develop characteristic faces of the orthorhombic shape corresponding to Calcite CaCO_3 . The particle size distribution of the resulting Portlandite is studied by laser granulometry in wet suspension (Figure 13). It reveals the existence of two populations, the first (3.13%) has a diameter size around 0.7 μm while the second, which is major (70.76%), has a diameter size of about 37 μm . these results are in good agreement with those obtained by SEM which confirm the existence of smaller particles and aggregates of larger sizes.

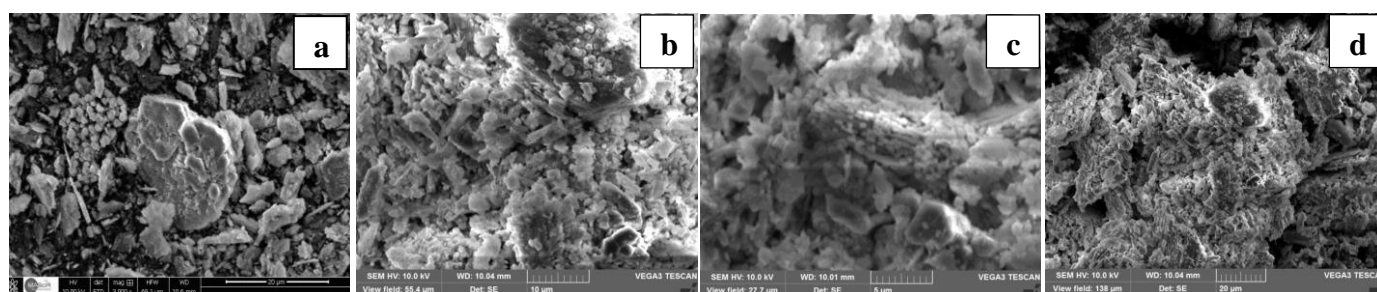


Figure 12. SEM images of precipitate (P 1.5 M stoichiometric 0.5 h)

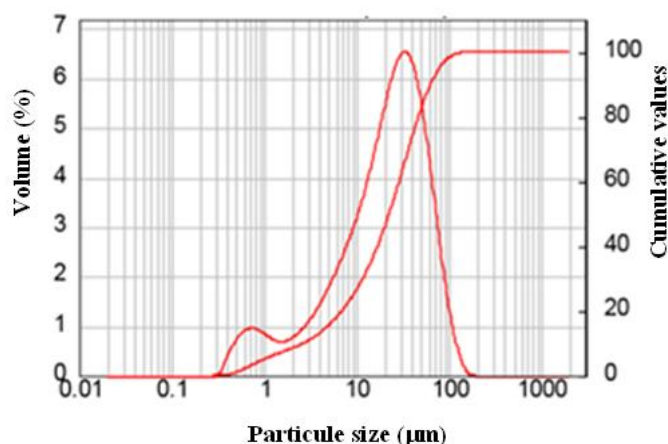


Figure 13. Particule size distribution of precipitate (P 1.5 M stoichiometric 0.5 h)

Conclusion

The phosphoric acid production process generates several tones of phosphogypsum. After filtration, the phosphogypsum appears as fine wet sand. The solubility of toxic elements of phosphogypsum in seawater and its acidity increase pollution risk. The process proposed in this article falls within the framework of environmental protection and contributes to the valorization of this industrial waste by its total conversion using NaOH into marketable products. The process used is simple to apply. The reaction conditions are optimized at 1.5 M of phosphogypsum mixed with stoichiometric proportion of NaOH 3M at 20 °C under stirring (500 tr/min) during 30 minutes. The XRD shows that the conversion of the PG is total. $\text{Ca}(\text{OH})_2$ and Na_2SO_4 are successfully obtained. The IR confirms the formation of these products. The ICP shows that most of impurities remain in the precipitate $\text{Ca}(\text{OH})_2$ and Na_2SO_4 salt is more pure, with concentrations of certain elements below the detection limits. The use of PG in industrial production to replace natural gypsum is the best solution to the environmental problems caused by PG.

References

- [1] V.P. Khanduri, C.M. Sharma, S.P. Singh, *Environmentalist*. 28 (2008) 143–147.
- [2] C.S.K. Mishra, S. Nayak, B.C. Guru, M. Rath, *J. Ind. Pollut. Control*. 26 (2010) 57–60.
- [3] J.A. Ortega-García, F.A. López-Hernández, A. Cárcelos-Álvarez, J.L. Fuster-Soler, D.I. Sotomayor, R. Ramis, *Environ. Res.* 156 (2017) 63–73..
- [4] R. Tirado, M. Allsopp, *Greenpeace Res. Lab. Tech. Rep.* (2012) 3–30.
- [5] Y. Ennaciri, M. Bettach, A. Cherrat, A. Zegzouti, *J. Mater. Environ. Sci.* 7 (2016) 1925–1933.
- [6] Y. Ennaciri, H. El Alaoui-Belghiti, M. Bettach, *J. Mater. Res. Technol.* 8 (2019) 2586–2596.
- [7] Y. Ennaciri, M. Bettach, *Mater. Manuf. Process.* 33 (2018) 1727–1733.
- [8] M. Schmidt, *Institute of Energy Storage - University of Stuttgart* (2017).
- [9] M. Wuerth, M. Becker, P. Ostermeier, S. Gleis, H. Spliethoff, *J. Energy Resour. Technol. Trans. ASME*. 141 (2019) 1–6.
- [10] S. Austin, A. Glowacki, *Hydrogen, Ullmann's Encycl. Ind. Chem.* (2000) 394–427.
- [11] M. Khachani, A. El Hamidi, M. Halim, S. Arsalane, *J. Mater. Environ. Sci.* (2014) 615–624.
- [12] M.J. Blesa, J.L. Miranda, R. Moliner, *Vib. Spectrosc.* 33 (2003) 31–35.
- [13] T. Liu, Y. Zhu, X. Zhang, T. Zhang, T. Zhang, X. Li, *Mater. Lett.* 64 (2010) 2575–2577.

- [14] A.H.T. Kandil, M.F. Cheira, H.S. Gado, M.H. Soliman, H.M. Akl, J. Radiat. Res. Appl. Sci. 10 (2017) 24–33.
- [15] A. Periasamy, S. Muruganand, M. Palaniswamy, Rasayan J. Chem. 2 (2009) 981–989.
- [16] T. Kim, J. Olek, Transp. Res. Rec. (2012) 10–18.
- [17] K.J. Rao, C.N.R. Rao, J. Mater. Sci. 1 (1966) 238–248.
- [18] F. Burriel Marti, F. Lucena Conde, S. Arribas Jimeno, J. Hernández Méndez, Química analítica cualitativa, Editorial Thomson (1985). Cooling, D.J., Hay, P.S., Guilfoyle, L., 2002. Carbonation of bauxite residue, in: 6th International 468 Alumina Quality Workshop. (2002) 185–190.
- [19] P.M. Rutherford, M.J. Dudas, J.M. Arocena, Sci. Total Environ. 180 (1996) 201–209.
- [20] M. Rentería-Villalobos, I. Vioque, J. Mantero, G. Manjón, J. Hazard. Mater. 181 (2010) 193–203.
- [21] R. Pérez-López, J.M. Nieto, I. López-Coto, J.L. Aguado, J.P. Bolívar, M. Santisteban, Appl. Geochemistry. 25 (2010) 705–715.
- [22] Y. Ennaciri, I. Zdah, H. El Alaoui-Belghiti, M. Bettach, Chem. Eng. Commun. 207 (2020) 382–392.