



## Conversion of phosphogypsum to sodium sulfate and calcium carbonate in aqueous solution

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### Abstract

Using phosphogypsum (PG) as a raw material for the production of valuable products is interesting. In this work we present the wet chemical conversion of phosphogypsum to calcium carbonate and sodium sulfate. Calcium carbonate can be used in the fields of the industry (cement, paper...) and the environment, while sodium sulfate can be used in the glass industry, detergents... The reaction for chemical decomposition of phosphogypsum is made at room temperature in aqueous solution and studied at various concentrations and times. According to the obtained results, we concluded that the reaction is complete only after half an hour. It also presents other advantages: it is reproducible, ecological and not expensive.

**Keywords:** phosphogypsum, conversion, calcium carbonate, sodium sulfate

### 1. Introduction

Phosphogypsum is a synthetic by-product created during the commercial manufacture of phosphoric acid by the wet process. For every ton of phosphoric acid produced, about 3 tons of phosphogypsum are generated. Morocco produces every year about 15 million tons of acid phosphogypsum residues which the vast majority is discharged into the sea. Pollution problems resulting have been raised by several authors, and reuse solutions or recovery of such waste have also been proposed in other fields [1].

#### 1.1. Plaster and cement industry

The phosphogypsum can substitute natural gypsum in plaster industry, but it is necessary to remove the soluble impurities (phosphate, fluorine, organic matter...) therein. A small amount of these impurities affects the setting time and strength of plaster [2]. Several studies show the possibility of replacing natural gypsum by phosphogypsum (the dihydrate is the most appropriate form) for the manufacture of cement, provided that it undergoes a purification treatment. Phosphogypsum reduces temperature of clinkerization and set retarder in Portland cement [3-5]. The impurities contained in phosphogypsum and the abundance of natural gypsum limit the use of this by-product.

#### 1.2. Soil improvement

Baird and Kamprath [6] showed that phosphogypsum can be used as an improvement in many cultures, more effective than natural gypsum. Bejaoui I. [7] exhibit that phosphogypsum can contribute to the improvement of the permeability of the soil, the decrease of its salinity and also enriches the soil in phosphorus. However, the quantities to be used are limited by certain standards [8]. Gypsum treatments decreased saline-alkali soils pH, electrical conductivity, and chloride and sodium levels. Water infiltration and calcium levels were increased [9].

### 1.3. Thermal decomposition

Two routes, namely thermal and wet decomposition, are possible to produce commercial chemicals from phosphogypsum. Thermal decomposition of gypsum by reducing agents in inert environment such as the carbon, generate SO<sub>2</sub> gas flow which is converted to sulfates compounds. The reaction of reduction of phosphogypsum by carbon at high temperature is given as follows:



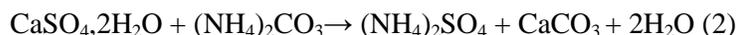
Generally, the thermal decomposition has several disadvantages (more energy, toxic and corrosive). For these reasons, aqueous conversion of phosphogypsum to calcium carbonate and some other saleable sulfate compounds was investigated.

### 1.4. Wet decomposition

Some studies using the wet decomposition of phosphogypsum are described in the following paragraphs.

#### 1.4.1. Synthesis of ammonium sulfate

The synthesis of ammonium sulfate is made by padding of carbon dioxide in a solution containing ammonia water to obtain (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, which reacts with phosphogypsum [10]. This chemical reaction is represented by the following equation:



#### 1.4.2. Synthesis of potassium sulfate

Potassium sulfate is a type of single potassium fertilizer destined mainly for the cultivation of high quality. It is especially used to replace the fertilizer KCl for the cultures sensitive to the chlorine. Several studies have been made on the production of potassium sulfate from phosphogypsum and other matter such as sylvinit, KCl and potassium carbonate K<sub>2</sub>CO<sub>3</sub>. The gypsum and the sylvinit are abundant ores. They can be used for the synthesis of K<sub>2</sub>SO<sub>4</sub> in aqueous environment. The glaserite is firstly obtained and reacts further with the sylvinit to give a 98 % pure K<sub>2</sub>SO<sub>4</sub> [11].

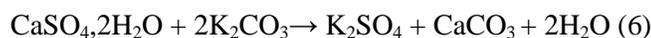


It is also possible to produce potassium sulfate by double decomposition of potassium chloride and phosphogypsum in aqueous ammonia solution at low temperatures as follows:



The conversion of KCl to K<sub>2</sub>SO<sub>4</sub> achieved 98 % after about one hour at exact stoichiometric proportions of KCl and gypsum with 40 wt % ammonia. The reaction was done at 0 °C [12].

In 1999, Abu-Eishah and al [13], prepared K<sub>2</sub>SO<sub>4</sub> at ambient temperature from a mixture containing 50 % excess phosphogypsum, 4.32 ammonia solution to phosphogypsum ratio, and aqueous solutions containing initial concentrations of 33 wt % ammonia and 7 wt % isopropanol. They found that the maximum conversion was 97.2 %. Other work realized in our laboratory, corresponds to the conversion of the phosphogypsum to K<sub>2</sub>SO<sub>4</sub> and CaCO<sub>3</sub> by wet method. The reaction of the double decomposition of phosphogypsum in aqueous solution is given below:



This reaction is reproducible and made at room temperature, the optimal concentration is equal to 0.6 mol/l with stoichiometric amounts of phosphogypsum and K<sub>2</sub>CO<sub>3</sub>, the end time of the reaction is about one hour and half [14].

#### 1.4.3. Synthesis of sodium sulfate

Balarew and al [15] studied and predicted the conversion of CaSO<sub>4</sub> in the title quaternary water-salt system. A 98 % degree of conversion of CaSO<sub>4</sub> was achieved by using calcium sulfate isolated from sea salt production

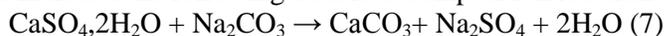
waste brines. In general, studies realized on the decomposition of phosphogypsum to calcite by using the sodium carbonate  $\text{Na}_2\text{CO}_3$  in an aqueous solution remain very few.

## 2. Experimental

Phosphogypsum sample was collected from the fertilizer plant Maroc Phosphore (dihydrate processes) settled at Jorf Lasfar near El Jadida city. The phosphogypsum was washed several times to eliminate soluble impurities and suspension materials as organic matter.

The sodium carbonate  $\text{Na}_2\text{CO}_3$  used in this research was from reagent grade chemicals, with the purity of 99 %.

Reactional mixtures were prepared from the washed phosphogypsum dissolution in the sodium carbonate solution at room temperature, as indicates the following double decomposition reaction:



The mixtures were put under stirring during different times. A white precipitate was formed ( $\text{CaCO}_3$ ), it was separated from the solution by simple filtration and dried in the oven at 100 °C. The filtrates which contain  $\text{Na}_2\text{SO}_4$  are introduced in the oven at 40 °C to recrystallize the salts. All the compounds produced in this work were identified by X-ray diffraction (X'Pert Pro MPD Panalytical) and analyzed by X-ray fluorescence (S4 PIONEER BRUKER aXS) and infrared spectra were performed on a FTIR 8400s Shimadzu spectrometer using KBr pellets. A list of operating conditions for the reactional mixtures is given in table 1.

**Table1:** Operating conditions for reactional mixtures carried in this work.

Run N°	[PG] (mol/l)	[ $\text{Na}_2\text{CO}_3$ ] (mol/l)	Time (H)	powders	filtrates
1	0.1	0.1	1.5	P1	F1
2	0.6	0.6	1.5	P2	F2
3	0.7	0.7	1.5	P3	F3
4	1	1	3	P4	F4
5	0.1	0.1	0.5	P5	F5
6	0.2	0.2	0.5	P6	F6
7	0.3	0.3	0.5	P7	F7
8	0.4	0.4	0.5	P8	F8
9	0.5	0.5	0.5	P9	F9
10	0.6	0.6	0.5	P10	F10

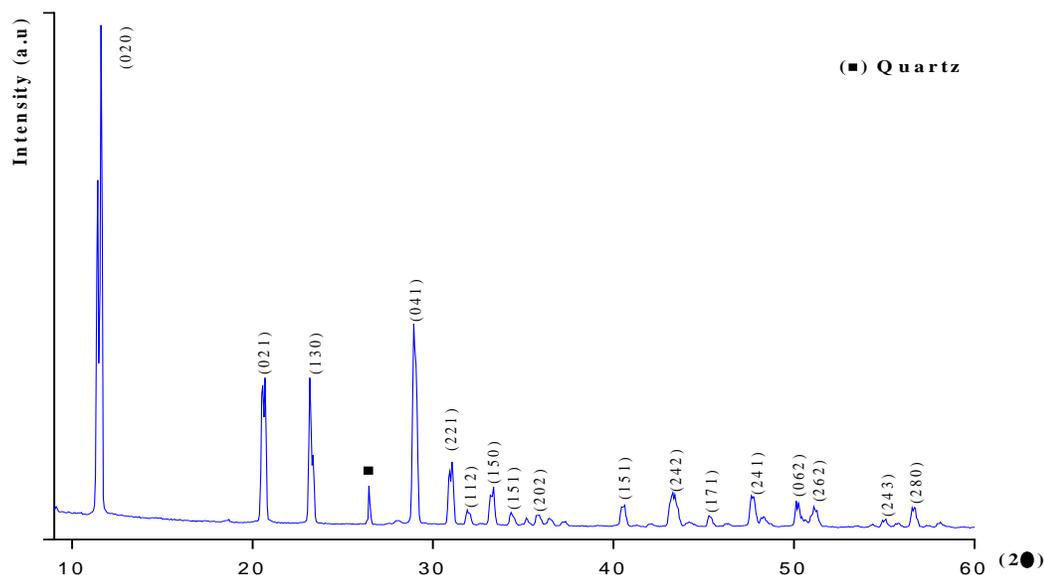
## 3. Results and discussion

### 3.1. Phosphogypsum analysis

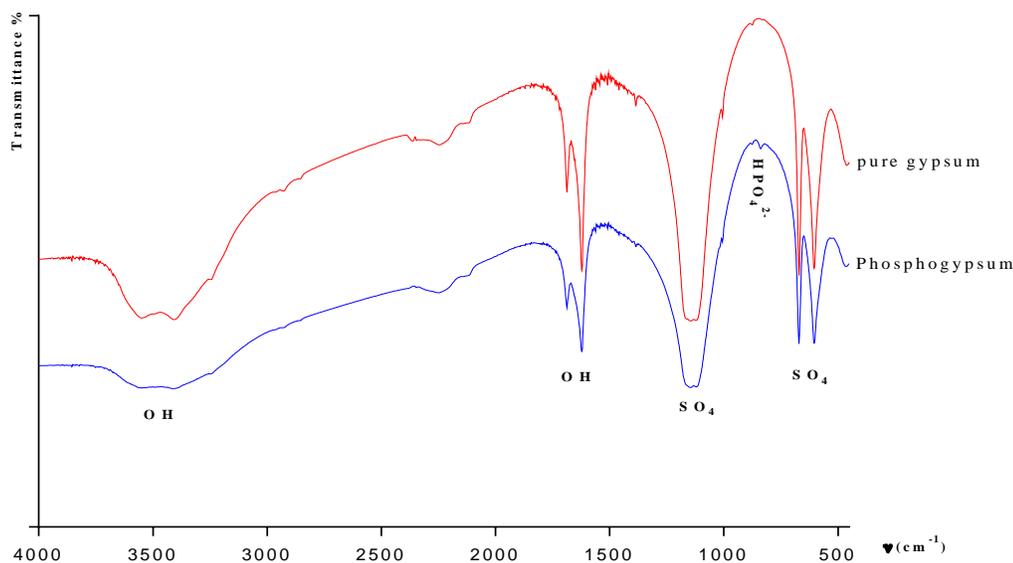
The X-ray pattern of the PG sample is presented in figure 1. The compound was identified to the calcium sulfate dihydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  which crystallizes in the monoclinic system with space group C2/c (JCPDS 33-0311), and a low quantity of quartz crystallized in hexagonal system with space group P6<sub>2</sub>22 (JCPDS 87-0703). Infrared spectrum of washed phosphogypsum and pure gypsum samples are shown in figure 2.

The superposition of the infrared spectrum of washed phosphogypsum with pure gypsum shows similar bands, except for the band at 837  $\text{cm}^{-1}$  which corresponds to  $\text{H}_2\text{PO}_4^{1-}$  and  $\text{HPO}_4^{2-}$  syncrystallized with phosphogypsum. The bands in region 3560-3250  $\text{cm}^{-1}$  and 1687-1624  $\text{cm}^{-1}$  correspond respectively to the stretching vibrational modes  $\nu$  and bending vibrational modes  $\delta$  of water. For the sulfate groups  $\text{SO}_4^{2-}$ , the bands at 1132 and 1118  $\text{cm}^{-1}$  are assigned to the asymmetric stretching vibrational modes  $\nu_3$ , while the band at 1004  $\text{cm}^{-1}$  is attributed to the symmetric stretching vibrational mode  $\nu_1$ . The two bands observed at 669 and 603  $\text{cm}^{-1}$  correspond to the bending vibrational mode  $\nu_4$  [16].

The chemical composition of washed phosphogypsum is shown in table 2. Data shows that phosphogypsum sample contains small amounts of quartz, and insoluble impurities like phosphate components, the latter being already detected by FTIR. This phosphogypsum is of sedimentary origin ( $\text{Sr}/\text{Ca} < 0.0057$ ), and it remains unexploitable in plaster industry ( $\text{P}_2\text{O}_5 = 0.687 > 0.4$ ) [16].



**Figure 1:** X-ray diffraction pattern of the Moroccan phosphogypsum.

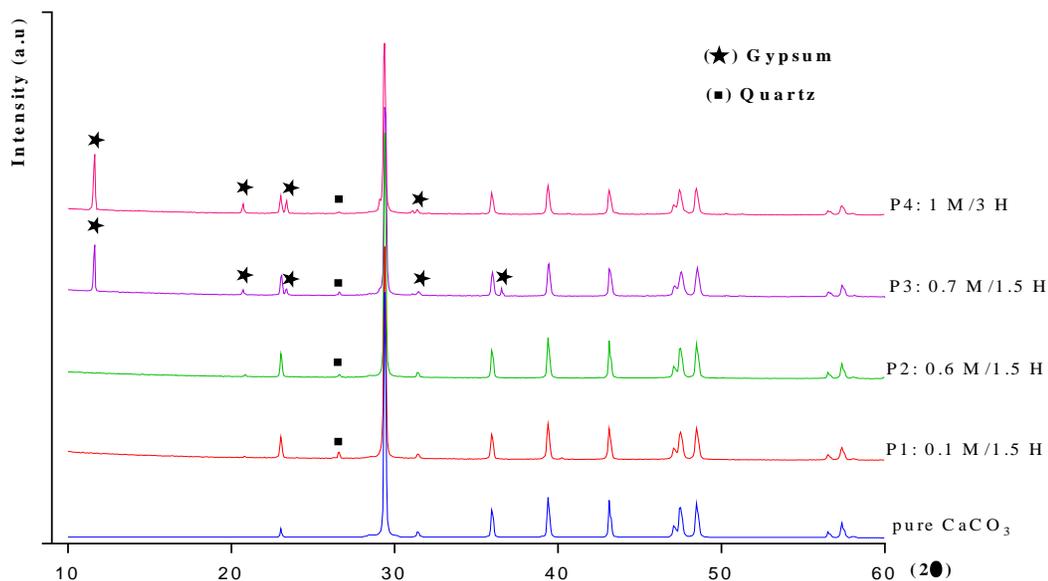


**Figure 2:** Infrared spectrum of the pure gypsum and the washed phosphogypsum.

### 3.2. Analysis of reaction products

The stoichiometric quantities of phosphogypsum and  $\text{Na}_2\text{CO}_3$  are put in aqueous solution. We increased the concentration from 0.1 to 1 mol/l, and also we selected initially the time reaction up three hours.

The X-ray powder diffraction patterns reported in Figure 3 show that the powders P1 and P2 contains only one phase isostructural with calcium carbonate  $\text{CaCO}_3$  (JCPDS N°: 05-0586). For very concentrated  $\text{Na}_2\text{CO}_3$  salt solution, the free ions activity coefficients become greater than 1. Therefore, the dissolution of phosphogypsum was difficult even if we increase the time, hence we note yet the presence of phosphogypsum in powders P3 and P4.

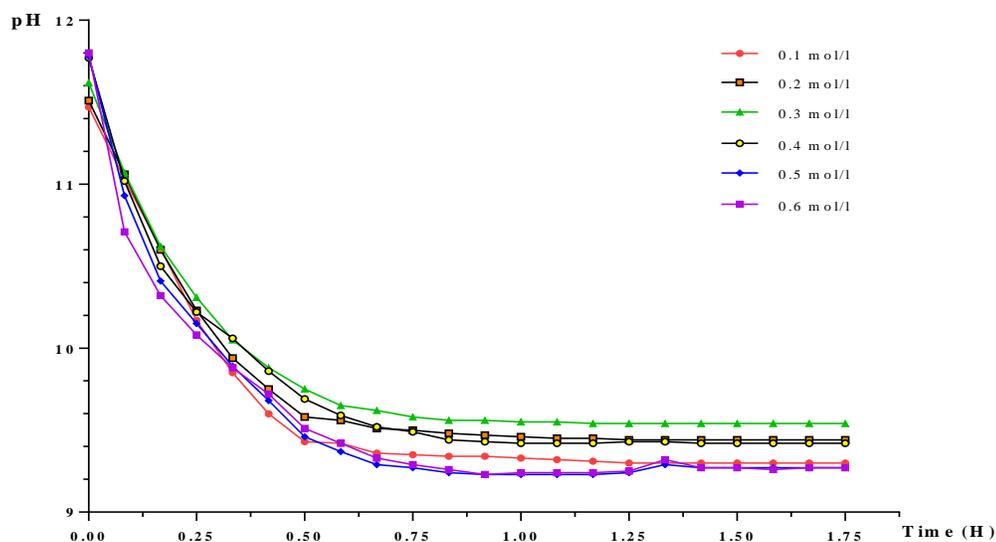


**Figure 3:** X-ray powder diffraction patterns of powders P1 to P4.

### 3.2.1. Follow-up of the reaction by pH measurements

For optimizing the time of the conversion of phosphogypsum to sodium sulfate, we have studied the variation of pH during the reactions by varying the time for different concentrations. The obtained results are schematized on the figure 4.

From pH evolution curves for the various concentrations, it is clear that the pH values decrease quickly then become constant for all concentrations (0.1 until 0.6 mol/l). The beginning of stability of the pH values observed after half an hour, giving information about the end of the reaction. We conclude that the minimum time necessary to have total decomposition of phosphogypsum into  $\text{Na}_2\text{SO}_4$  salt is half hour.

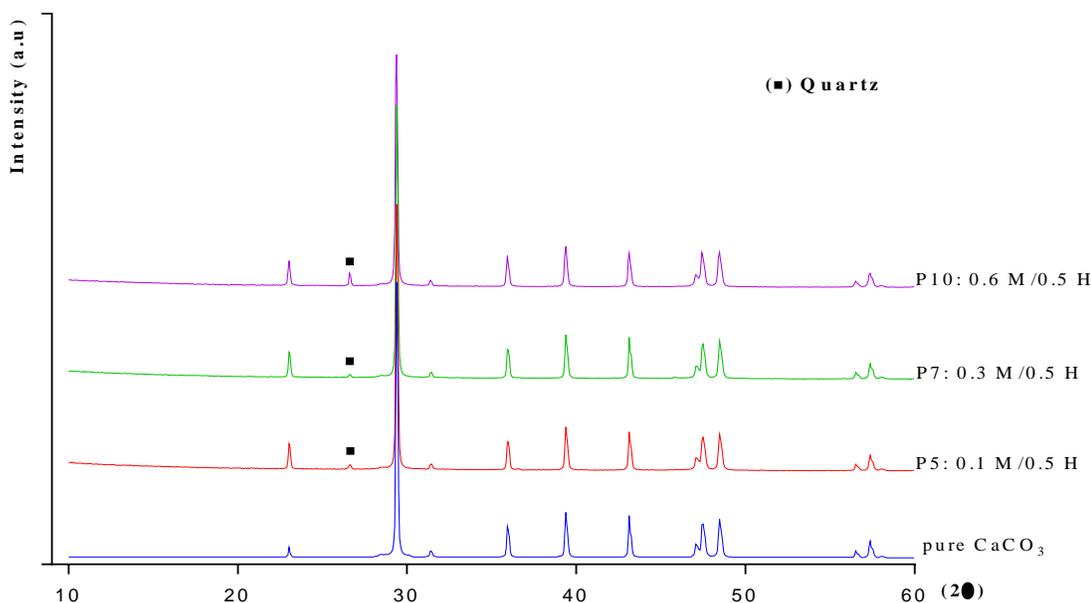


**Figure 4:** pH evolution for different concentrations.

### 3.2.2. Powders analysis

From these forecasts, we had characterized powders and filtrates obtained by the decomposition of phosphogypsum for half an hour. We limit the characterization to powders and filtrates for a diluted concentration 0.1 mol/l, intermediate 0.3 mol/l and limit concentration 0.6 mol/l.

The X-ray diffractograms of powders obtained at different stoichiometric concentrations show one phase (figure 5a). Identification of all peaks of this phase showed that the precipitate is isostructural with calcium carbonate  $\text{CaCO}_3$  (JCPDS N°: 05-0586) which exhibits a rhombohedral structure with space group R-3c. A low quantity of quartz (JCPDS N°: 87-0703) comes from impurities included in phosphogypsum remaining inert and not attacked during the reaction and appears on the X-ray diffractograms (figure 5a) as a small peak at  $26.6^\circ$ .



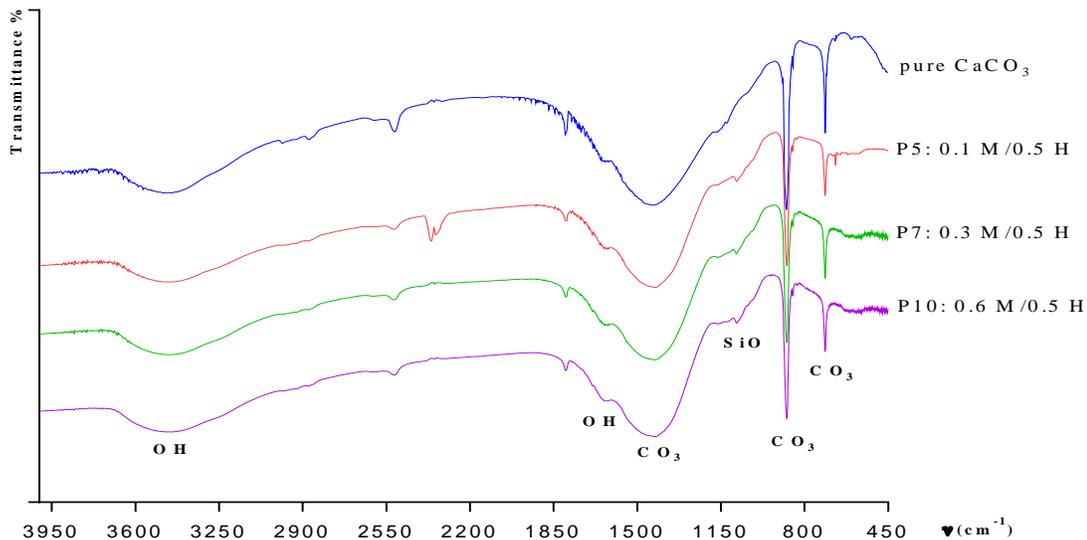
**Figure 5a:** X-ray powder diffraction patterns of powder: P5, P7 and P10.

The infrared spectra of P5, P7 and P10 powder samples are displayed in (figure 5b). The All infrared spectra are in good accordance with the spectrum of pure  $\text{CaCO}_3$ , except for a band at  $1084\text{ cm}^{-1}$  corresponding to Si-O stretching. Quartz is readily distinguished by its spectrum from other  $\text{SiO}_2$  polymorphs (glass) [17]. The bands at  $1421$ ,  $874$  and  $714\text{ cm}^{-1}$ , could be attributed to  $\nu_3$  (asymmetric CO stretching),  $\nu_2$  ( $\text{CO}_3$  out-of-plane deformation) and  $\nu_4$  (OCO bending in-plane deformation) vibration modes of calcite, respectively [18]. The broad absorption bands at  $3455\text{ cm}^{-1}$  and  $1635\text{ cm}^{-1}$  are due to stretching  $\nu$  and bending  $\delta$  vibration modes of OH groups due to adsorbed water, respectively.

### 3.2.3. Filtrates analysis

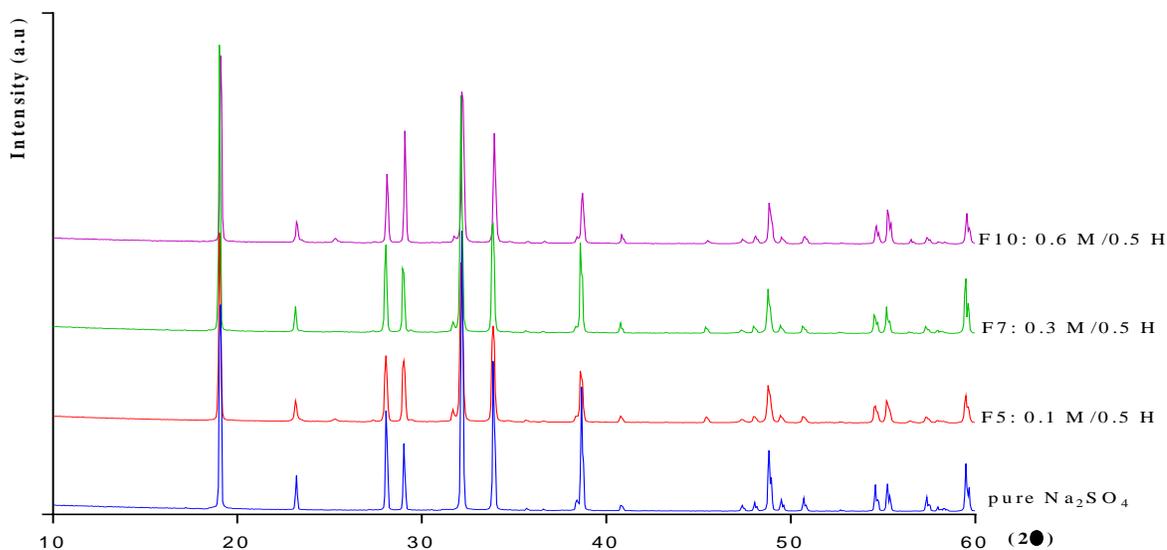
In other side, the XRD analysis of salts precipitated from filtrates, showed that salts are well crystallized and correspond to  $\text{Na}_2\text{SO}_4$  (JCPDS N°: 86-0803) which crystallizes in orthorhombic structure with space group  $F_{dd}$ . (figure 6a).

The filtrates infrared spectra are displayed in figure 6b. The main bands of  $\text{Na}_2\text{SO}_4$  can be assigned as follows: the bands appearing at  $1120\text{ cm}^{-1}$  are assigned to  $\nu_3$  asymmetric stretching vibrations whereas the bands located at  $617$ - $638\text{ cm}^{-1}$  are assigned to  $\nu_4$  asymmetric bending vibrations of  $\text{SO}_4$  groups. The bands observed at  $3443$  and  $1630\text{ cm}^{-1}$  are respectively assigned to  $\nu$  stretching and  $\delta$  bending vibrations of adsorbed OH/ $\text{H}_2\text{O}$  species [19].



**Figure 5b:** Infrared spectra of powders: P5, P7 and P10.

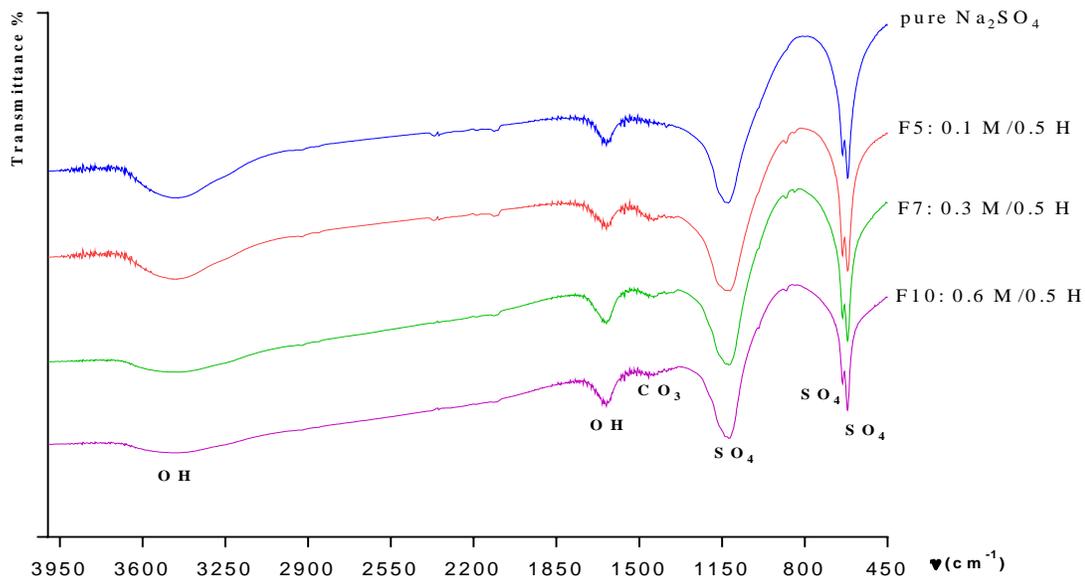
Two other bands observed with a very low intensity near  $1425$  and  $825\text{ cm}^{-1}$  corresponds respectively to the  $\nu_3$  asymmetric stretching vibration modes and  $\nu_2$  out-of-plane deformation vibration modes of carbonate groups  $\text{CO}_3$ . These bands can be due to  $\text{CaCO}_3$  passed over the filtration or to  $\text{Na}_2\text{CO}_3$  initially not very well solubilized.



**Figure 6a:** X-ray powder diffraction patterns of filtrates F5, F7 and F10.

### 3.3. Chemical elements distribution

Chemical analysis of samples gives an idea about the existing impurities and their distribution between the powders and the filtrates during the total decomposition of gypsum. The results of the chemical analysis of the powder and salt resulted by total decomposition of phosphogypsum at  $0.6\text{ mol/l}$  during about a half an hour, are collected in the table 2.



**Figure 6b:** Infrared spectra of the filtrates F5, F7 and F10.

**Table 2:** Distribution of chemical elements between the powder and the filtrate, <sup>(1)</sup> ionometric method, <sup>(2)</sup> Loss on ignition (600°C), <sup>(3)</sup> Loss on ignition (900°C).

Constituent (wt %)	CaO	SO <sub>3</sub>	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	SrO	Y <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Cl	TiO <sub>2</sub>	F <sup>(1)</sup>	H <sub>2</sub> O <sup>(2)</sup>	CO <sub>2</sub> <sup>(3)</sup>
Phosphogypsum	33.83	42.52	0.12	0.67	0.49	0.21	0.05	0.02	0.08	0.02	0.02	0.02	0.01	0.19	21.80	--
Powder P10	54.03	0.58	1.20	1.06	0.74	0.21	0.31	0.03	0.10	0.02	0.00	0.05	0.02	0.16	--	41.66
Filtrat F10	0.33	53.13	44.44	0.05	0.14	0.07	0.15	0.02	--	--	0.08	0.71	--	0.12	--	--

The results described by the previous different characterization methods are in good agreement with obtained chemical analysis. Solid impurities pass completely into the powder. Indeed, the distribution of these chemical elements is reasonable and respects the molar ratio between the phosphogypsum and the calcium carbonate ( $M_{CaSO_4 \cdot 2H_2O} / M_{CaCO_3} = 1.72$ ). That is why the contents of those elements are almost doubled when the phosphogypsum is converted into  $CaCO_3$ .

### Conclusion

Based on the results of this work, we can conclude that the decomposition of phosphogypsum by  $Na_2CO_3$  to  $CaCO_3$  and  $Na_2SO_4$  is a reproducible reaction. The optimal conditions for this reaction are listed below:

- The reaction is made with exact stoichiometric proportions of the washed phosphogypsum and the sodium carbonate.
- The operating temperature is the room temperature.
- The limit concentration is equal to 0.6 mol/l.
- The time of reaction is about a half an hour.

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