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A preliminary study of phosphogypsum transformation into calcium fluoride

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Abstract: Phosphogypsum is a waste by-product of the phosphate fertilizer industry, which is usually disposed in the environment because of its restricted use in industrial applications. The aim of this study is to reduce this environmental risk by producing calcium fluoride and sodium sulphate from phosphogypsum and sodium fluoride. To optimize this reaction, many factors have been considered such as temperature, reaction time, NaF/phosphogypsum molar ratio, stirring speed, reagents adding mode and phosphogypsum mass. The obtained results have shown that the NaF/phosphogypsum molar ratio, the reaction time and the phosphogypsum mass were the most influential parameters. Optimal conversion conditions were obtained with the NaF/phosphogypsum ratio between 1.5 and 2, at an average reaction time between 30 minutes and 120 minutes and at room temperature. In these conditions, the results are very satisfactory, in terms of quantity and quality of the obtained CaF_2 and $Na_2 SO_4$, the conversion rate has exceeded 95%.

Keywords: phosphogypsum, calcium fluoride, conversion, conditions

INTRODUCTION

Phosphogypsum is an industrial waste which is generated from phosphoric acid industry [1].The manufacturing of one ton of phosphoric acid produces 4-5 tons of phosphogypsum [2]. World phosphogypsum production is estimated to be around 280000 tons per year [3]. This large amount of waste has created severe environmental problems [4-5] because, aside $CaSO_4,2H_2O$, phosphogypsum contains many heavy metals that can contaminate soils and water [6]. Several studies have been focused on reducing this environmental risk. Manjit et al. tried to use phosphogypsum for cement and plaster manufacture [7]. Yang et al. used calcined phosphogypsum to activate the fly ash-lime systems [8]. Dedgrimenci et al. applied phosphogypsum in soil stabilization [9]. This waste was employed by Papastefanou et al. in agriculture [10]. Abu Eishah et al. have tried to convert phosphogypsum into K_2SO_4 in the presence of ammonia and isopropanol. Conversion would reach 97.2% but this process proved to be very complicated as it used many reagents [11]. Aagli et al. [12] have studied the effect of temperature on the solubility of $CaSO_4$ in concentrated aqueous solutions of KCl, HCl and in mixtures of both of them and at various temperatures and concentrations. The maximum conversion rate of phosphogypsum into K_2SO_4 is about 87%, a low average compared with other works. [7-12]

In our work, we have used NaF to convert phosphogypsum to CaF_2 and a saturated Na_2SO_4 solution according to reaction (1).

$$CaSO_4.2H_2O + 2NaF \rightarrow CaF_2 + Na_2SO_4 + 2H_2O \quad (1)$$

We have chosen to produce CaF_2 (s = 0.016g/L) since it exhibits lower solubility compared to $CaSO_4$ (s = 2.41g/L). The formed CaF_2 is of great importance in the field of manufacture of gamma sensors [13], as well as radiation in the field of dental care [14], in the area of treatment of optical fiber and the widest use in the fluor industry. The produced CaF_2 can adsorb heavy metals [15] and the application of this method in an industrial scale can decrease significantly the imported amounts of this product. Moreover, the by-product Na_2SO_4 has many important application fields namely in the Kraft process (paper and pulp) [16] and in the detergent industries [17]. Sodium sulfate is utilized

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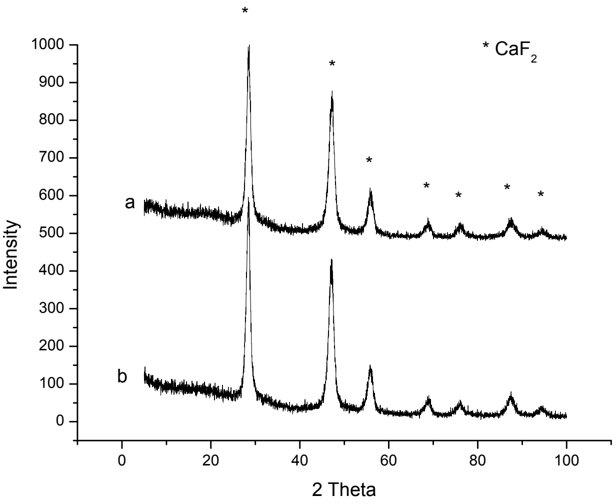

Figure 1. diffractogramms of prepared solids:
a) Adding phosphogypsum to a NaF solution
b) Adding water to a mixed phosphogypsum and NaF

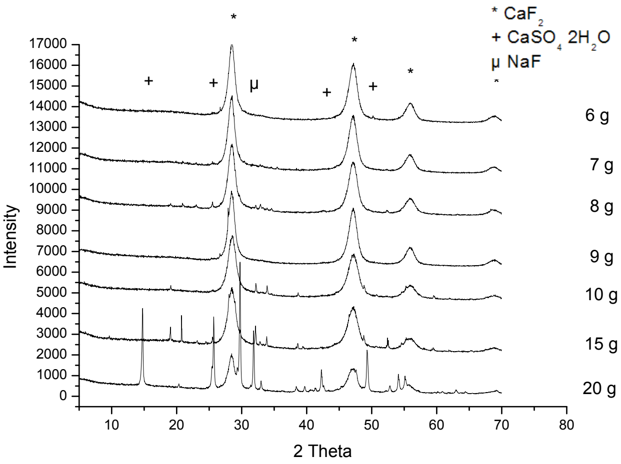

Figure 3. Diffractogramms of precipitated solid at different phosphogypsum masses

in glass manufacturing for clarification [18], in the textile industry since it facilitates the penetration of dyes [19] and in chemical industries [20].

In order to optimize this conversion according to reaction (1), we have studied the influence of several parameters; the stirrer speed, the reagents adding mode, the mass of phosphogypsum, the reaction time, the temperature and the NaF/ phosphogypsum ratio.

MATERIALS AND METHODS

1. Conversion reaction protocol

A predetermined mass of NaF solution was added to each sample of phosphogypsum mass. This resulting mixture was carried out at a defined constant temperature for a specified period of time. The experimental protocol used is as follows:

1. Weight the fixed mass of phosphogypsyum
2. Add the necessary mass of NaF (depending on the mode adopted as it mentioned in section 3.2.)
3. Inject the jacketed glass reactor (250 mL) in a batch process in order to maintain a constant temperature by water circulation.
4. Magnetic stirring was maintained throughout the reaction.
5. Solid and liquid samples were separated by centrifugation method during 12 minutes.

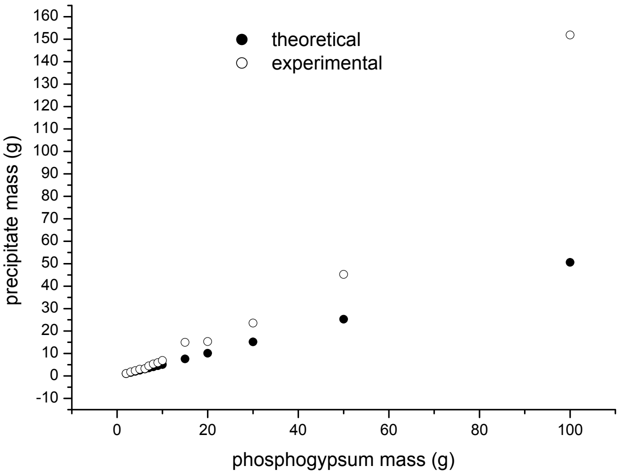

Figure 2. Variation of precipitate masses versus phosphogypsum mass

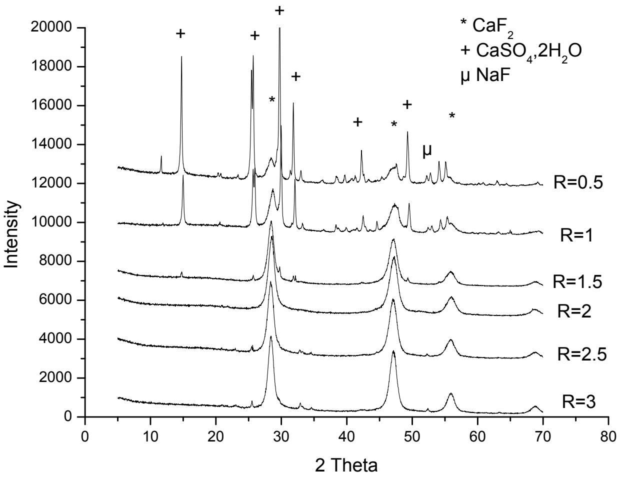

Figure 4. Diffractogramms of precipitated solids at different molar ratios

Table I. Percentages of removed and remaining ions at different molar ratio

NaF/phosphogypsum ratio	0.5	1	1.5	2	2.5	3
% Ca^{2+} removed	97.59	97.32	96.78	99.36	99.10	98.01
% F^- removed	99.34	99.75	99.87	98.87	96.81	97.95
% Na^+ remaining	90.06	90.34	80.53	96.27	67.56	69.07
% SO_4^{2-} remaining	45.92	65.76	72.3	79.72	81.80	86.90

Table II. Percentages of removed and remaining ions at different reaction time

Reaction time(min)	20	30	60	90	120	180	240
% Ca^{2+} removed	90.15	98.76	98.29	98.19	98.56	97.57	88.16
% F^- removed	94.13	97.56	98.17	97.79	96.49	92.49	87.34
% Na^+ remaining	89.79	97.67	98.23	96.71	90.83	78.59	74.16
% SO_4^{2-} remaining	60.31	80.31	91.11	90.43	87.32	65.43	50.14
Experimental mass(g)	7.14	5.88	5.17	5.42	6.77	9.59	11.23
Theoretical mass(g)				5.06			

2. Solid and liquid samples analysis

Na^+ ions concentrations were analyzed by a flame photometer BWB Technologies, while Ca^{2+} ion concentration was determined by flame atomic absorption spectrometer (AAS Vario 6). SO_4^{2-} ion concentration was determined by the gravimetric method. The ion meter (781-pH/ionMeter. Metrohm), equipped with a crystalline membrane electrode, was used to determine fluoride ion concentration. Solid phases were characterized by XRD using a Philips PW 3040 generator, PW 3050/60 ϴ /2 ϴ goniometer and PW 3373/00 copper cathode.

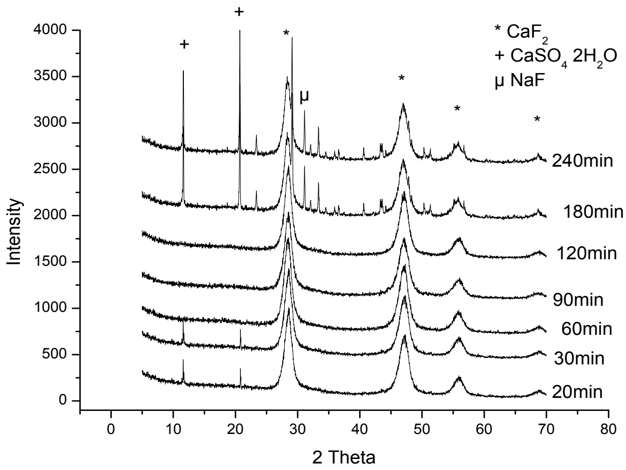

Figure 5. Diffractogramms of precipitated solids at different reaction times

RESULTS AND DISCUSSION

In order to carry out this reaction, several preliminary experiments were conducted to determine the influential variables and to specify the optimum.

1. Stirrer speed

The minimum speed required to give a uniform suspension in the reactor is above 400 rpm. A speed of 600 rpm was chosen for all further experiments in order to ensure the homogeneity of formed precipitate.

2. Reagents adding mode

Reagents were added according to two different modes:

- Preparing NaF aqueous solution, then adding gypsum solid.
- Mixing phosphogypsum and NaF in the solid state by milling followed by adding water.

The results obtained through these methods were rather similar. The X-ray diffraction analysis of precipitated solids presented in Figure 1 confirmed that the way of adding reagent is not effective.

The X-ray diffractogramms of the two solids prepared by these different methods provided the same peaks. For this reason, we have chosen to adopt the first method of adding reagents since it is the simplest.

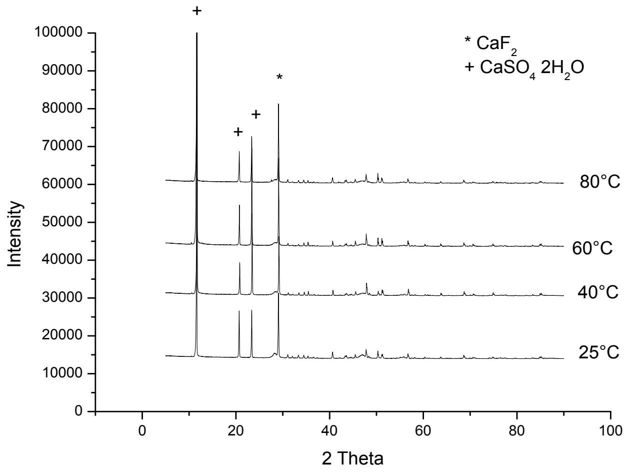

Figure 6-a. Diffractogramms of formed solids at different temperatures (R=0.5)

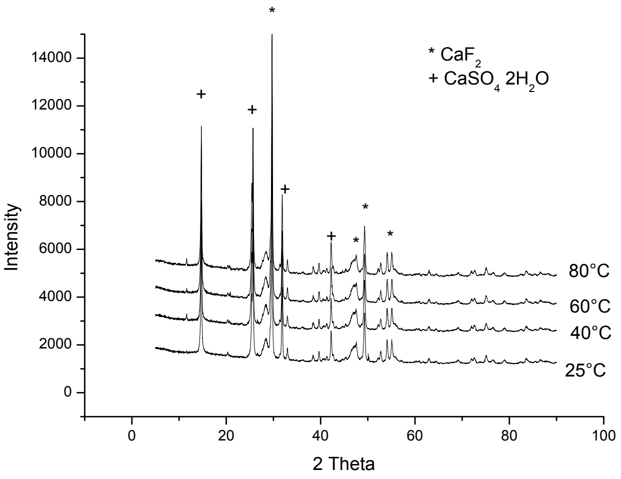

Figure 6-b. Diffractogramms of formed solids at different temperatures (R=1.5)

3. Variation of phosphogypsum to solvent ratio

In order to determine the variation of phosphogypsum to solvent ratio to find the optimum mass of phosphogypsum required to form CaF_2, we varied phosphogypsum mass from 2 to 100 g in fixed solution volume equal to 100 mL. In these different experiences we respect the stoechiometry of reaction (1) (the NaF / phosphogypsum molar ratio is equal to 2) and the reaction time is fixed at 60 minutes.

The following curve (Figure 2) shows the variation of theoretical and experimental masses of precipitates depending on phosphogypsum mass.

Figure 2 showed a similarity between the two curves until reaching limit mass of phosphogypsum equal to 10 g. It should be noted that there is a discrepancy between the masses of the two precipitated solids beyond this value.

In order to confirm this result, the obtained precipitates were analyzed by XRD. The diffractograms (Figure 3) showed that, for a phosphogypsum mass lower than 10 g; the precipitate formed is purely CaF_2. Beyond this mass, the formed solid is composed of CaF_2 and unreacted phosphogypsum.

In order to respect the stoechiometric molar ratio of reaction (1) and to ensure the saturation of the NaF solution, the phosphogypsum mass required is set to equal 6.14 g.

According to these results, we can limit the range of phosphogypsum mass between 6.14 g and 10 g for volume of solution equal to 100 mL.

4. NaF/phosphogypsummolar ratio

The molar ratio (R = NaF / phosphogypsum) was varied from 0.5 to 3. The reaction was carried out at room temperature during 1 hour and for added mass of phosphogypsum equal to 10 g.

For R<1.5 (phosphogypsum is in excess relative to NaF), results are listed in Table I. It showed that the percentages of both Ca and F remaining in solution are very low; this result can be explained by two possibilities: either the precipitate formed is totally CaF_2 or the reaction is not achieved and the phosphogypsum remains insoluble. To confirm any of these hypotheses, we have appealed to the XRD analysis (Figure 4). It confirmed the second prediction since the analysis of the precipitate showed that it is composed of a mixture of CaF_2 and $CaSO_4.2H_2O$. For $R \geq 1.5$, the analysis of Table 1 shows that the percentage of reacted Ca and F exceeds 98% and the percentage of Na and SO_4 remaining in solution exceeds 80%.

We can, therefore, deduce that the filtrate is mainly the solution of Na_2SO_4 and the precipitate is only the CaF_2.

Figure 4 confirmed that the improvement of the precipitate purity starts from R = 1.5.

5. Reaction time

To determine the optimum reaction time, at R = 2 (stoechiometric condition), with added mass of phosphogypsum equal to 10 g and V=100 mL, we have varied the reaction time between 20 minutes and 4 hours.

Table II showed that the percentages of Na and SO_4 ions present in solution remained constant until 120 min. Beyond this value, these percentages decreased which was probably due to the reverse reaction and the reappearance of phosphogypsum.

For t = 20 min, we found that the percentages of removing ions in filtrate (% Ca= 90.15and % F= 94.13) are low, which leads us to deduce that the reaction is not yet complete.

These results were confirmed by XRD analysis. Figure 5 showed that the precipitate is found to be pure CaF_2 when t <120 min and beyond this value, the precipitate is a mixture of CaF_2 and $CaSO_4.2H_2O$. The precipitate formed at t = 20 min is not the pure CaF_2.

A comparison between the mass of the recovered precipitate and the theoretical mass of CaF_2 (Table II) showed that these values are closer between 30 min and 120 min.

Thus, the purity of the precipitate formed was improved from t = 30 min, and, beyond 2h, there was a recurrence of $CaSO_4.2H_2O$. Thus, we can limit the range of the reaction time between 30 min and 2 h.

6. Variation of reaction temperature

In order to move forward with the results of reactions carried out with molar ratio less than 2, the reaction temperature was varied (25, 40, 60 and 80° C) to improve the quality and increase the quantity of the formed CaF_2.

Figures 6-a and 6-b showed two diffractograms of the respectively formed solids at molar ratios 0.5 and 1.5 with a reaction time equal to two hours. It is clear that temperature variation does not improve the purity of the formed product. The diffractograms presented almost the same peaks, therefore, we choose to work at room temperature.

CONCLUSION

The conversion of phosphogypsum to calcium fluoride (solid phase) and sodium sulfate (liquid phase) was carried out using a small scale batch reactor. The variation of different parameters were studied to optimize this reaction: the stirrer speed, reagents adding mode, mass of phosphogypsum, reaction time, reaction temperature and the NaF / phosphogypsum molar ratio.

Using a phosphogypsum mass varying between 6.14 and 10 g in 100 mL aqueous solution of NaF while respecting a NaF /phosphogypsum molar ratio from 1.5 to 2 with a reaction time between 30 min and 120 min at room temperature, the conversion can be achieved with a percentage exceeding 96%.

This work enables to determine the optimal domains of each factor and the modeling and the optimization of this conversion will be the aim of the next research work. Furthermore, this significant result offers a solution for the treatment of the phosphogypsum waste.

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