Phosphogypsum Conversion into Calcium Fluoride and Sodium Sulfate

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ABSTRACT

The phosphoric acid production in the world generates a large amount of phosphogypsum beside the emission of toxic acid fluorine gas into the atmosphere, which can cause a several environmental problems. To remedying these problems, an environmental procedure permit recycling phosphogypsum waste by NaF into valuable products, was presented in this work. According the obtained results, the proposed process is feasible and leads preparing a relatively pure CaF_2 and Na_2SO_4. This last is recommended in detergent and glass industry, while the resulting CaF_2 can be utilized in metallurgical industry. The optimum conversion conditions were achieved with the exact stoichiometric phosphogypsum and NaF at reaction duration of 90 minutes under room temperature.

1. INTRODUCTION

Phosphogypsum (PG) is an acidic by-product resulted during the production of phosphoric acid by the wet process. This latter can be expressed by the following chemical reaction [1]:

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O \rightarrow 5CaSO_4.2H_2O + 3H_3PO_4 + HF \quad (1)$$
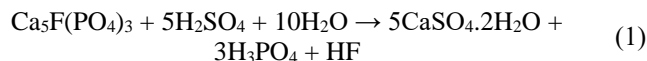
For one ton of phosphoric acid produced about 3 to 5 tons of PG are generated, with the worldwide PG generation estimated to be around 280 Mt annually. The totality of this quantity is stored in open air (28%) or dumped into water bodies (58%). Although, PG is mainly formed by calcium sulfate (effectively dihydrate) beside numerous impurities such as: phosphates, fluorides, heavy metals, and radioelements. Hence, the presence of these impurities at higher than natural levels, can cause a severe environmental problem in long term [1-3].

In addition, during the phosphoric acid process, the fluoride released as hexafluosilicic acid H_2SiF_6 (FSA) is recuperated by NaOH solution or water to obtain sodium fluoride (NaF) or anhydrous hydrofluoric acid (AHF) respectively [4, 5]. Ennaciri et al. [6, 7] have discussed and detailed very well the fluorine recovery process during the production of phosphoric acid and the phosphates fertilizers. According to these results, the estimated price of CaF_2 (fluorspar) and NaF were 260-280 \$/ton and 600-640 \$/ton respectively.

Several researches focused to reuse or to valorize the PG in different domains. The possibilities of using PG can be separated into three categories: agricultural application, building materials and raw material for chemical processes.

PG, like gypsum, can be used in the agricultural soils. It increases the acidity of these soils and improves its properties by adding the sulfate and the calcium. However, the PG use in this domain can pose certain problems such as the increase of the hazardous metals and the radioelements level in these soils [8].

At present, the major part of PG is valued in the plaster manufacture and in the cement composition. However, the use of PG in these sectors requires an adequate treatment, in order to improve the setting time, the consistency and the resistance of the plaster and the cement prepared from this residue [9].

PG can be utilized as a raw material for certain chemical production processes. The best known of these processes is the PG thermal decomposition, which permit recovering SO_2 gas necessary for the sulfuric acid (H_2SO_4) production [10].

In recent years, the wet conversion of the PG by ammonium or alkaline compounds remains more sustainable and represents an economical pathway. In addition, the products obtained by this pathway are very interesting for the agriculture, the industry, and the environment.

Several researchers indicated that the possibility to produce potassium sulfate (K_2SO_4) from the conversion of PG and potassium chloride (KCl). The basic reaction describing this process is [11]:

$$CaSO_4.2H_2O + 2KCl \rightarrow CaCl_2 + K_2SO_4 + 2H_2O \quad (2)$$
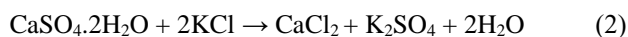
Generally, this process needs specific conditions such as: the decrease of temperature and the addition of solvents (ammonia, alcohol) to prevent the formation of undesired complex salts (syngenite $K_2Ca(SO_4)_2 \cdot H_2O$ and pentasulfate $K_2SO_4. 5CaSO_4. H_2O$).

PG can react with ammonium and alkaline carbonate to yield calcium carbonate ($CaCO_3$), ammonium and alkaline sulfate respectively. The general reaction can be expressed as following [12-15]:

$$CaSO_4.2H_2O + A_2CO_3 \rightarrow CaCO_3 + A_2SO_4 + 2H_2O \quad \text{with } A = NH_4, Na, K \text{ and Li} \quad (3)$$

Also, the reaction of PG can with alkaline hydroxide

produce calcium hydroxide (Ca (OH)$_2$) and alkaline sulfates, according to the following reaction [16, 17]:

$$CaSO_4.2H_2O + 2AOH \rightarrow Ca(OH)_2 + A_2SO_4 + 2H_2O \quad \text{with A = Li, Na and K} \quad (4)$$
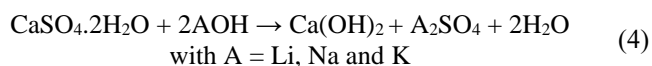
Several factors affect on these reactions (3 and 4), such as: (i) the nature of the PG used (sedimentary, igneous, sieved, purified…); (ii) the molar ratio between PG and reagents; (iii) the temperature and pressure of the mixture; and (iv) the duration of the conversion reaction [12-17].

In the recent years, certain researchers involved to convert PG by ammonium fluoride (NH$_4$F) according to the following reaction [6, 7, 18]:

$$CaSO_4.2H_2O + 2 NH_4F \rightarrow CaF_2 + (NH_4)_2SO_4 + 2H_2O \quad (5)$$
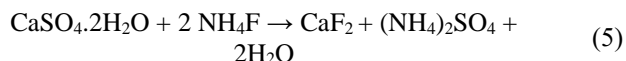
Generally, this process is more attract if effectively that the production of NH$_4$F is done by the neutralization of the recuperated hydrofluoric acid (HF) by ammonia at the plant site.

In the light of these processes (3, 4 and 5), the purity of the obtained calcium compounds (CaCO$_3$, Ca (OH)$_2$ and CaF$_2$) are about 96, 95 and 93% respectively. These rational percentages are due to the presence of the insoluble impurities, which the most of them pass into the resulting calcium precipitates [6, 7, 12-18]. For the radioactivity, the results of several works carried out on the radioactivity of PG and the resulting products show that these compounds could be considered as naturally occurring radioactive material (NORM). However, the sulfate salts recrystallized from the filtrates contain a very low amount of the toxic elements and the radionuclides [12, 19-21], which tolerate their use directly in various fields such as agriculture, cleaning products, paper industries.

In this work, we propose an environmental process which allows converting the Moroccan PG by NaF into CaF$_2$ and sodium sulfate (Na$_2$SO$_4$). The importance of this process comes from remedying of two major environmental problems, the first is related to the management of PG waste and the second concerns the reduction of the acid fluorine gases rejection into the atmosphere (greenhouse gasses emissions).

Due to its excellent physical and chemical properties, CaF$_2$ is usually employed in building material, cement modification, crystalline fluorspar, Glass industry and metallurgy [22, 23], while, Na$_2$SO$_4$ can be used in the glass industry, detergents, pulp and paper. Kostick [24] has indicated that the price of Na$_2$SO$_4$ is 130-140 \$/ton.

2. MATERIAL AND METHODS

The PG sample used in this work was taken from the fertilizer plant Maroc Phosphore (Jorf Lasfar near to El Jadida, Morocco). This PG is of dihydrate form and sedimentary origin. Sodium fluoride (min 98.5%, Sigma Aldrich) was utilized as reactant.

The experimental protocol consists firstly to wash PG to eliminate some of the soluble impurities and suspension materials [2]. After that, about 103.3 g of this PG was dissolved in 1 liter of aqueous solution contained 0.6 M/l of NaF. The reactional mixture was carried at room temperature and pressure under constant stirring (300 tr/min). After reaction duration of 90 minutes, the reactional mixture was

filtered to obtain a whitish precipitate (CaF$_2$). This latter was dried in the oven at 105°C, while the recrystallization of the recuperate filtrate yielded a transparent salt Na$_2$SO$_4$.

The different analyses carried out on the PG and the resulting compounds are realized by several techniques. The nature of mineral phases was identified by X-ray powder diffraction (Bruker D8 Advance Eco with Kα Cu radiation). Infrared spectra were performed by Fourier transform infrared spectroscopy (Thermo Scientific Nicolet iS10 FT-IR Spectrometer) using ATR technique. The Ca, Na, K and Ba concentrations were determined by flame photometer (Jenway 500-731 Model PFP7). The sulfate concentration was determined by using gravimetric method after precipitation of SO$_4^{2-}$ under barium sulfate form. The contents of P$_2$O$_5$ and F were analyzed by spectrophotometer (Rayleigh VIS-7220 G/UV-9200) and ionometric method (fluoride ion selective electrode Tacussel TR 200) respectively after necessary calibration. The concentration of the other elements (Si, Al, Mg and Fe) was determined by inductively coupled plasma mass spectrometry (ICP-MS Model HP-4500). The hydration degrees of our samples were examined by thermogravimetric analysis (TGA) (DTG-60 type SHIMADZU). The morphology of PG and the obtained CaF$_2$ was studied by scanning electron microscopy (SEM). Table 1 regrouped the listed materials and the different analyses carried out on the PG and the resulting compounds.

Table 1. List of materials and the different analyses carried out on the PG and the resulting compounds
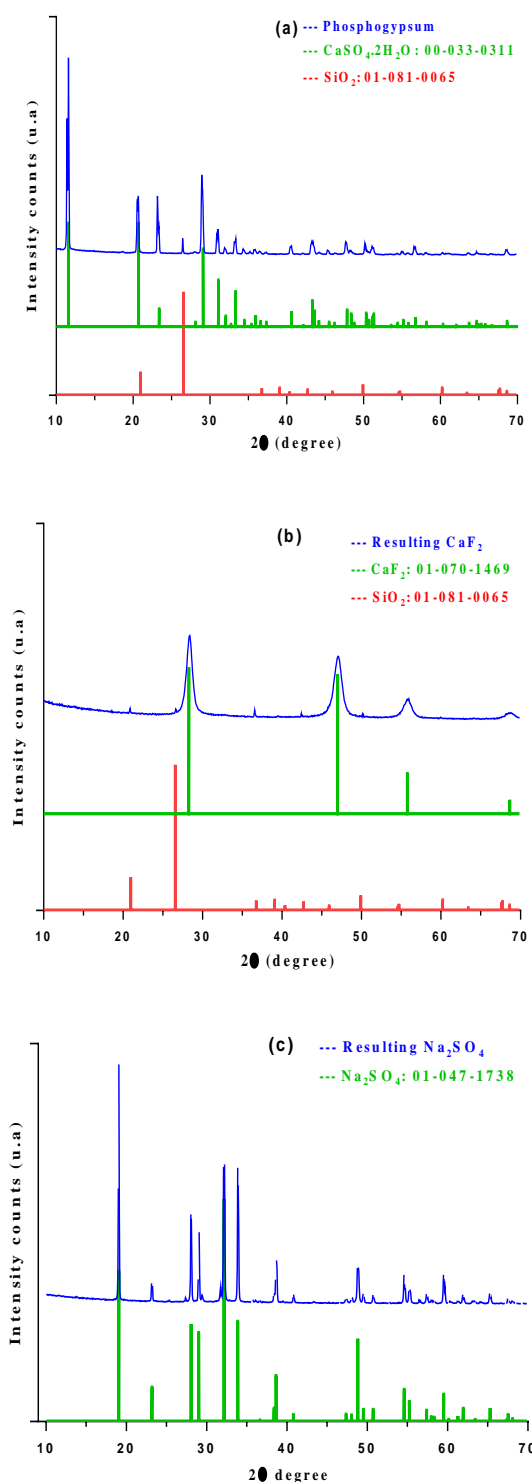
Initial reactive and operator conditions	
PG	103.3 g
NaF	25.2 g
Distilled water	1 L
Stirring	300 tr/min
Temperature	25°C
Reaction time	90 minutes
Element Analyzed and Method used	
Major Mineral phases	X-ray powder diffraction (XRD)
Minor phases	Fourier transform infrared spectroscopy (FTIR)
Morphology	Scanning electron microscopy (SEM)
Ca, Na, K and Ba	Flame photometer
SO$_4^{2-}$	Gravimetric method
P$_2$O$_5$	spectrophotometer
F	Ionometric method
Si, Al, Mg and Fe	Inductively coupled plasma mass spectrometry (ICP-MS)
H$_2$O	Thermogravimetric analysis (TGA)

3. RESULTS AND DISCUSSION

The XRD diffractogram of the PG sample is shown in Figure 1(a). It indicates well that this PG is composed principally by gypsum (CaSO$_4$.2H$_2$O, PDF N°: 00-033-0311) with a low quantity of quartz (SiO$_2$, PDF N°: 00-033-1161).
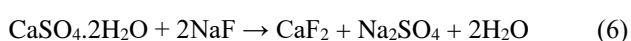
The results of the X-ray diffraction analyze carried out by Sebbahi et al. [25] and Ennaciri et al. [2] demonstrated the presence of a single phase: the dihydrate CaSO$_4$. 2H$_2$O in Moroccan PG (Jorf Lasfar) with the existence of a minority inert phase which is silica. Bourgier [26] justified the presence of two varieties of gypsum: the dihydrate and anhydrite. The presence of the latter is usually explained by the loss of water in the sample of calcium sulfate dihydrate during the

evaporation step. Laganièrs [27] has identified in addition to the gypsum, the appearance of another phase which is $CaHPO_4.2H_2O$.

Because of the large difference between the solubility of PG ($K_{ps}=3.14\times10^{-5}$ at 25°C) and CaF_2 ($K_{ps}=3.45\times10^{-11}$ at 25°C), the reaction (6) moves towards the precipitation of CaF_2 and the formation of Na_2SO_4.

Ennaciri et al. [6, 7] and Douahem et al. [28] show that the XRD diffractograms of CaF_2 prepared from the PG conversion by the different methods provided the same peaks.

Figure 1(c) shows the diffractogram of the recrystallized salt. It is clear that the diffractogram of this salt presents almost the same peaks of the sodium sulfate (Na_2SO_4, PDF N°: 01-047-1738). A comparison between the XRD diffractograms of Na_2SO_4 recovered from the PG conversion by Na_2CO_3 and NaOH showed also the similar peaks [14, 17].
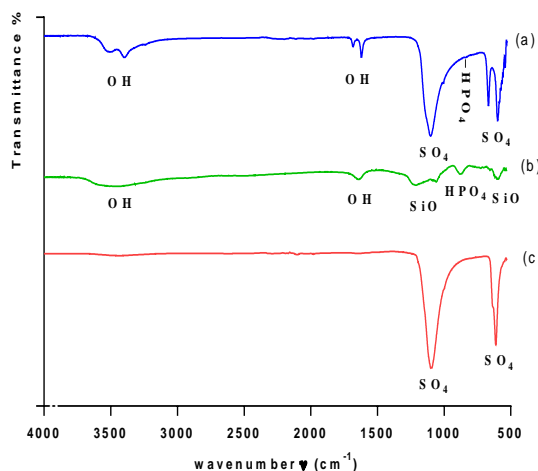
PG and obtained products were also examined by FTIR absorption. For the PG, similar bands with pure gypsum are clearly observed (Figure 2(a)) [2, 14].

The principal bands of this sample are attributed to the water and sulfate ions. The bands in region 3392-3508 and 1682;1619 cm^{-1} correspond to water νH_2O and δH_2O respectively. For the sulfate ions, the bands appeared at 1101 and 1003 cm^{-1} are assigned to the symmetric and asymmetric stretching of SO_4^{2-} respectively. The two bands observed at 666 and 598 cm^{-1} correspond to the bending of SO_4^{2-} [2, 14-17].

In other hand, the precipitate CaF_2 (Figure 2(b)) does not absorb IR radiations between 500 and 4000 cm^{-1}. The work carried out by Pandurangappa et al. [29] and Tahvildari et al. [30], indicate the same results for CaF_2 nanoparticles synthesized by both co-precipitation and hydrothermal methods. However, Seshadri et al. [31] indicated that the infrared spectrum of molecular species formed on vaporizing solid CaF_2 trapped in a solid krypton matrix at 20 K, shows the appearance of bands at 550, 520, 485, 365 and 162 cm^{-1}.

The other auxiliary bands appear at 3391-3505 and 1642 cm^{-1} are attributed to the adsorbed water νH_2O and δH_2O respectively, while the bands at 632 and 1063-1213 cm^{-1} are assigned to symmetric and antisymmetric stretching of Si-O-Si respectively [32]. The band appearing at 872 cm^{-1} corresponds to symmetric stretching of HPO_4^{2-} [26].

The infrared spectrum of the recrystallized salt (Figure 2(c)) confirms the characteristic bands of pure Na_2SO_4. The bands at 1,098 and 609 cm^{-1} are assigned to asymmetric stretching and asymmetric bending of SO_4^{2-} respectively [14]. Periasamy et al. [33] have mentioned that the characteristic bands of the pure Na_2SO_4 can be observed at 1,123 and 615 cm^{-1}.

Figure 1. XRD patterns of the PG sample (a) [6], the precipitate CaF_2 (b) and the salt Na_2SO_4 (c)

After total dissolution of PG sample in stochiometric NaF solution, the resulting precipitate (Figure 1(b)) corresponds well to calcium fluoride (CaF_2, PDF N°: 01-070-1469). Generally, the formation of CaF_2 and Na_2SO_4 during the conversion of PG can be explained by the following reaction:

$$CaSO_4.2H_2O + 2NaF \rightarrow CaF_2 + Na_2SO_4 + 2H_2O \qquad (6)$$

Figure 2. FTIR spectra of the PG sample (a), the precipitate CaF_2 (b) and the salt Na_2SO_4 (c)

Table 2 regroups the different vibration band frequencies and assignments of the PG and the obtained products.

**Table 2.** FTIR frequencies of the PG sample and the finals products

Assignment	Wave number v (cm^{-1})		
Ion /Molecule	Phospho-gypsum (a)	Precipitate CaF$_2$ (b)	Salt Na$_2$SO$_4$ (c)
H$_2$O v O-H (St)	3392-3508	3391-3505	--
δ H-O-H (D)	1682; 1619	1642	--
SO$_4^{2-}$ v_3 SO$_4^{2-}$ (ASt)	1101	--	1098
v_1 SO$_4^{2-}$ (SSt)	1003	--	--
v_4 SO$_4^{2-}$ (B)	666; 598	--	609
HPO$_4^{2-}$ v P-O(H) (SSt)	--	872	--
v P-O-H (Dhp)	835	--	--
SiO$_2$ v Si-O-Si (ASt)	1063-1213	--	--
v Si-O-Si (SSt)	--	632	--

(St): stretch region; (D): deformation; (ASt): asymmetric stretching;
(SSt): symmetric stretching; (B): bending; (Dhp): deformation hors plan.

Figure 3(a, b) shows the SEM images of PG and CaF$_2$ respectively. We observe that the morphological structure of PG is tabular with a size grading from 5 to 30 μm [2, 15]. For the obtained CaF$_2$, the morphological results reveal that the powder is formed by polycrystalline agglomerates of size less than 2 μm.

Based on the obtained results, the reaction (6) remains an efficient procedure for to preparing relatively pure CaF$_2$ from PG and NaF. In addition, Na$_2$SO$_4$ recuperated by this process is economically attractive compared with other process such as Mannheim process (reaction of NaCl with sulfuric acid at 700°C) [34].
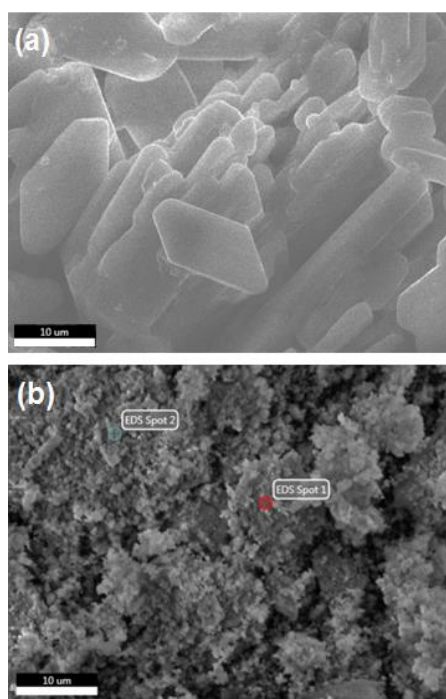
Figure 3. SEM images of the PG (a) and the obtained CaF$_2$ (b)

Table 3 represents the results of the chemical analysis of the PG sample and the obtained CaF$_2$ and Na$_2$SO$_4$. The results described previously by XRD and FTIR techniques are in agreement with the chemical analysis of the PG and the resulting compounds. Generally, the major impurities which contain PG are totally transformed into the precipitate CaF$_2$.

Table 3. Chemical composition of the PG and the finals products

Major elements (%)	Phospho-gypsum (a)	Precipitate CaF$_2$ (b)	Salt Na$_2$SO$_4$ (c)
CaO	31.28	50.41$^{(1)}$	0.42
SO$_3$	44.69	0.41	55.18
F	0.67	43.34	0.62
Na$_2$O	0.26	0.61	43.38
K$_2$O	0.02	0.04	--
P$_2$O$_5$	1.11	2.35	--
SiO$_2$	0.96	2.21	0.39
Al$_2$O$_3$	0.16	0.29	--
MgO	0.02	0.04	--
Fe$_2$O$_3$	0.02	0.03	--
H$_2$O	20.58	0.26	--
Ba (ppm)	32.95	72.30	--

(1): Expressed as % Ca.

The PG sample used in this study contains about 96.5% of CaSO$_4$.2H$_2$O. The principal impurities are P$_2$O$_5$, SiO$_2$ and Al$_2$O$_3$, MgO, Fe$_2$O$_3$, Na$_2$O and K$_2$O in lesser amounts. The presence of these impurities in PG can be attributed to the inattacked phosphate rock, the clay, the insoluble complexes (Na$_3$SiF$_6$, Na$_3$AlF$_6$, K$_3$AlF$_6$, MgSiF$_6$.6H$_2$O…) and the ions (FPO$_3^{2-}$, HPO$_4^{2-}$, Ba^{2+}…) substituting Ca^{2+} or SO$_4^2$ in CaSO$_4$.2H$_2$O [1, 2].

Generally, the chemical composition of our PG sample remains almost the same of the other sedimentary Mediterranean PGs (Tunisian, Algerian, Egyptian…). Contrary, the chemical composition of this PG sample differs to those of igneous PGs (Poland, Brazilian…), which contain higher concentration of water, fluorine... [1, 2, 21, 26].

The chemical composition of resulting precipitate represents about 93.7% of CaF$_2$ (50.41% as Ca and 43.34% as F). This degree of purity can be explained by the presence of impurities, which are nearly doubled when PG is converted into CaF$_2$. Compared with other work realized by Douahem et al. [28], the purity of CaF$_2$ obtained from the conversion of the Tunisian PG by NaF is about 98%. This can be explained by the purity of the Tunisian PG and NaF used in this work. Ennaciri et al. [6, 7] have showed that the purity of CaF$_2$ obtained from the conversion of Moroccan PG by mixture of NH$_3$/HF and NaF/HF are 93.4 and 93.0% respectively.

The important impurities in the precipitate CaF$_2$ are P$_2$O$_5$ (2.35%) and SiO$_2$ (2.21%). These insoluble impurities rest inert or in attacked during the PG conversion and remains in the precipitate [6, 7, 13, 14]. The existence of sulfur in the precipitate is due to Na$_2$SO$_4$ traces, which are adsorbed in the surface of CaF$_2$ particle through the filtration. The precipitate contained also a low amount of Al, Mg and Fe, which come from clays. Generally, the content of these impurities is similar to that reported in other CaF$_2$ obtained from the PG conversion [6, 7].

Regarding the trace elements and the radioelements, the pervious researches focused on PG conversion, mentioned that these elements are found with resulting calcium precipitates, while the filtrate of the dissolution process rest uncontaminated from these elements [6, 7, 12, 19, 21].

Fluorspar is used in steel manufacture and other metallurgical operations principally to ensure the desired fluidity in the slag and to assist in refining the bath of molten metal but without changing the basicity or acidity of the slag. Also, the addition of this matter permits removing simultaneously the main impurities (S, P, N, O, H…) out of metals in the highest level. Generally, the majority of the researches related to the use of fluorspar in metallurgy insists that this fluorspar should contain not less than 85% CaF_2. Certain researchers added other norms such as content of Si, S and Ba (see Table 4). Also, even when conforming to or excelling these chemical standards, must be available in quantity and preferably in adequate physical form [22, 23, 35-39].

Table 4. Chemical composition of the obtained CaF_2 compared with the chemical standards for used in metallurgy

Content (%)		CaF_2	SiO_2	SO_3	Ba
	This work	93.7	2.21	0.41	0.00
CaF_2 obtained from the PG conversion	[6]	93.4	2.13	0.26	0.00
	[7]	93.0	2.01	0.46	0.00
	[28]	98	--	--	--
	[35]	85 <	--	--	--
Standard to use fluorspar in metallurgy	[36]	85 <	< 5	--	--
	[22]	85 <	< 5	< 0.75	--
	[23]	85 <	10-15	< 2 as $BaSO_4$	

Based on these requirements and the results of chemical analyses of the precipitate, we conclude that the resulting CaF_2 can be utilized directly in this metallurgical industry. Also, the use of the obtained CaF_2 as synthetic fluorspar can contribute to conserve the naturel reserves of fluorite.

The recrystallized salt is characterized by high amount of sodium (43.38% as Na_2O) and sulfur (55.18% as SO_3). The existence of major impurities (Ca, Si and F) in this salt are originally reported to the presence of these elements in NaF reagent or to the fine particle of CaF_2, which passed into salt during the filtration. Generally, the obtained salt Na_2SO_4 is a relatively pure product, which could be used directly in the industry of detergent, glass, pulp and paper [17].

4. CONCLUSION

In this work, we have elaborated a feasible process which allows converting PG waste by using the sodium fluoride. This process is realized in aqueous solution and leads to zero-waste with recovery of interesting products CaF_2 and Na_2SO_4.

The total conversion of PG is achieved at room temperature for an exact stoichiometric proportion of PG and NaF during a time reaction of 90 minutes.

The environmental interest of this process is reducing the quantity of PG rejected and minimizing the emission of fluorine gas. For a numerical approach, about 15 Mt of PG (the annual quantities of PG generated by the fertilizer industry of Morocco) can be treated by 7.325 Mt of NaF to obtain 6.809 Mt of CaF_2 and 12.383 Mt of Na_2SO_4.

The purity of Na_2SO_4 salt tolerates it to be commercialized or used in detergent industry. Since the resulting CaF_2 obtained is considered as a material which can be applied directly in the metallurgical industry.

In the economical approach, the PG conversion by NaF_2 does not require any difficult operation (simple filtration, room temperature) for recuperating CaF_2 and Na_2SO_4, but the cost analysis of this process rest generally not good. The cost effectiveness is realizable only in case of the environment protection (subsidy from the environment protection fund).

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NOMENCLATURE

PG	phosphogypsum
FSA	hexafluosilicic acid H_2SiF_6
AHF	anhydrous hydrofluoric acid HF