

Sustainable Approach for Recovery of Sulfur from Phosphogypsum

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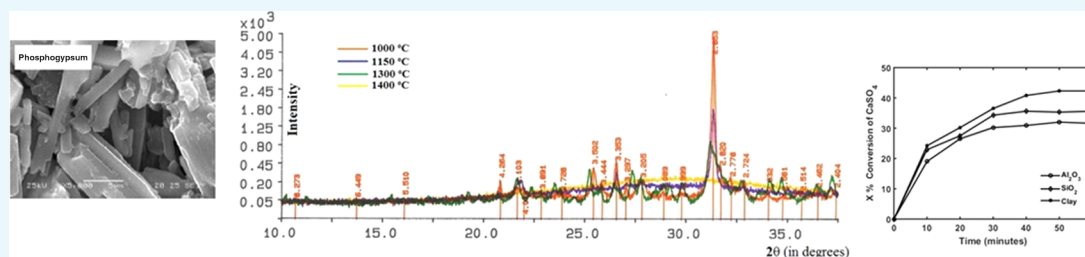
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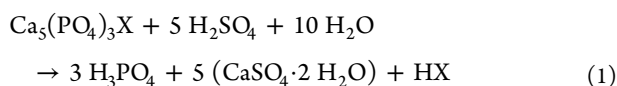


ABSTRACT: Phosphogypsum releases have a detrimental effect on flora and fauna and also cause economic loss due to the loss of sulfur. This study contributes to solving this problem using a process that consists of the valorization of this byproduct. A new sustainable method that consists of using sulfuric acid is proposed to process the Algerian phosphogypsum to recover the sulfur, which is imported in huge quantities until today. The experiments carried out in this investigation have enabled us to recover sulfur in the form of SO₂ using appropriate additives such as silica, alumina, clay, and charcoal as reducing agents. These additives accelerate the desulfurization process and decrease the decomposition temperature of calcium sulfate. As a result, these additives allow the reduction of energy used and simultaneously increase the concentration of SO₂. X-ray diffraction shows that thermochemical decomposition is not complete and that the sulfur present in the residue exists in the form of CaSO₄ and CaS at 1150 °C. After calcination of phosphogypsum, the analysis of the residues obtained shows that they have a chemical composition almost identical in terms of quality to that of clinker, which can further be used in the cement production.

1. INTRODUCTION

For decades, the world has made considerable efforts to increase the agricultural production to meet ever-increasing food needs. One of the practices is the use of phosphate fertilizers, which are obtained from phosphoric acid and phosphate. Countries like Algeria have large deposits of phosphate but need large quantities of sulfuric acid to produce phosphoric acid and fertilizers. A continuous increase in the price of sulfur leads to an increase in the cost associated with the production of phosphoric acid and phosphate. In addition to the increased price of sulfur, the manufacture of phosphoric acid leads to another serious problem that affects the environment, which is the co-production of phosphogypsum (PG). Phosphogypsum is a discarded byproduct from the processing of phosphate rock in plants producing phosphoric acid and phosphate fertilizers, such as superphosphate. The wet chemical phosphoric acid treatment process, or “wet process,” in which the phosphate ore is digested with sulfuric acid, is widely used to produce phosphoric acid and calcium sulfate, mainly in dihydrate form (CaSO₄·2H₂O)

The daily production of phosphogypsum in the town of Annaba (Algeria) amounts to 2600 tons for 500 tons of phosphoric acid.¹ Currently, this phosphogypsum is released into the sea after use. Phosphogypsum releases are detrimental on two fronts. They constitute an important pollution factor, particularly when it comes to discharges into the sea or into rivers, and they cause the loss of large quantities of sulfur. The problem of contaminated phosphogypsum (CaSO₄·2H₂O) has already become a global ecological problem that needs serious attention. For this reason, the management and secondary use of the huge amount of industrial phosphogypsum (PG) is essential.^{2–4} For example, a huge amount of phosphogypsum has accumulated in Florida (more than 1 billion tons); in Europe (where the contaminated phosphogypsum is discharged into the River Rhine close to the North Sea); and in Canada, Morocco, Togo, India, China, Korea, Israel, Jordan, Syria, Russia, and other parts of the world.⁵ The only countries using significant amounts of phosphogypsum are Japan and

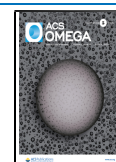


where X may include OH, F, Cl, or Br.

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West Germany. As it becomes more difficult to obtain permission to dump synthetic gypsum, more of it may be used in building materials. Currently, synthetic gypsum does not have any economic advantage over natural gypsum, mainly because of the impurities it contains. Research into potential uses of waste/byproduct materials in road construction materials is currently being undertaken in South Africa and other countries. Large stockpiles of phosphogypsum are located at the now nonoperative Chloorkop plant of AECI (2 million tonnes) as well as at the Potchefstroom plant (5 million tons increasing by 240 000 tons per annum). Both of these sources are within economic haul distance for road projects in Gauteng Province as well as other areas in North West Province and Mpumalanga.^{6,7} A huge amount of phosphogypsum is generated in the United States with significant production in Texas, Florida, and Louisiana. Major research studies have been carried out in all of these States, and in all cases, PG was found to be a potentially useful substitute for traditional road construction materials. Numerous experimental sections have, however, been constructed in Texas and monitored over extended periods with very good results.⁸ Phosphogypsum is used as raw material for manufacturing non-fired load-bearing wall bricks.⁹ Recently, scientists in North Africa are trying to use phosphogypsum in the manufacture of bricks to satisfy the high demand of housing.^{10,11} Phosphogypsum is finding an increasingly widespread use as a physical conditioner of both dryland and irrigated soils and as a chemical amendment for alleviating, by leaching the effects of subsoil acidity on root development in crops. As a solid waste, it is now increasingly used as a calcium supplement in agriculture.^{12–14}

2. RESULTS AND DISCUSSION

For use in the gypsum–sulfuric acid process, the humidity must be reduced as much low as possible. The kinetics of dehydration of phosphogypsum at various temperatures (between 105 and 220 °C) is studied. The results are shown in Figure 1, which shows the weight loss of phosphogypsum as

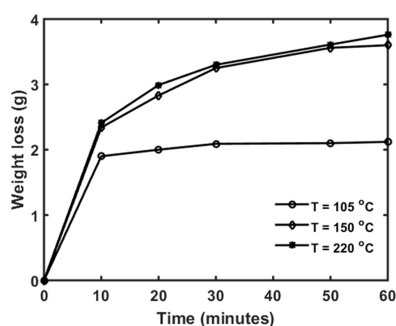


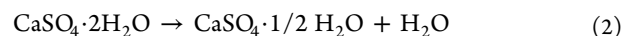
Figure 1. Weight loss (g) versus time at different temperatures.

a function of time at different temperatures. From the figure, it can be easily seen that there is rapid weight loss in the first 10 min, a slower weight loss in the next 20 min, and a very slower weight loss thereafter.

The first part can be interpreted by fast dehydration that is the portion of the dehydration curve that has a sharp slope, which corresponds to the transformation of gypsum into semihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$). It represents the loss of 1.5 moles of water by the gypsum; the next portion of the curve (at a moderate slope) corresponds to the loss of 1/2 mole of water

remaining and leading to the formation of anhydrite. At 220 °C, the anhydrite is soluble and capable of rehydrating quickly to a semihydrate by absorption of water vapor from the air. By heating the raw phosphogypsum to 105 °C, the humidity obtained is 20.8%, while it is 37.5% at 220 °C. The water of crystallization is then 16.7%. The second method of dehydration was carried out using differential scanning calorimetry (DSC), high-pressure DSC, –120 to 500 °C, Model 90/39324 (Setaram). The experiment was carried out under a helium atmosphere with crucibles of aluminum in a cylindrical shape containing 14.1 mg of raw phosphogypsum. The reference sample is calcined alumina. The DSC curve represents two endothermic peaks, which are more or less well separated according to the heating rate. Figure 2 shows the results at a heating rate of 10 °C/min. As shown in Figure 2, there are two endothermic peaks in the temperature range of 87–175 °C. It can be seen that the dehydration of the dehydrated calcium sulfate is detectable from 87.95 °C. Other studies have reported the start of dehydration of calcium sulfate at 86 °C.^{15,16}

In Figure 2, the first peak (max 105 °C) appears in the interval 88–125 °C. This is related to the loss of 1.5 moles of water and corresponds to the endothermic transformation of dihydrate into hemihydrate. With a further increase in the temperature, a second endothermic peak appears (maximum 158 °C) in the temperature range of 127.1–175 °C, less intense, corresponding to the loss of 0.5 mole of water from the hemihydrate with the formation of soluble anhydrite. It can be noted that the dehydration of phosphogypsum takes place in two stages, first giving hemihydrate and then anhydrous sulfate. This can be expressed in the form of chemical eq 2.



This behavior seems to be linked to the proper structure of gypsum where the two modes of binding of water molecules can be distinguished.¹⁷ The next stage of dehydration is the formation of sulfate anhydrite. The progressive removal of water followed by the complete dehydration ultimately leads to the destruction of the hemihydrate with the formation of the anhydrite network. It can be noted that at fairly high temperatures ($T > 390$ °C), the soluble anhydrite changes to insoluble anhydrite.



If the calcination is continued over 1200 °C, it forms an overcooked anhydrite. Hongjing *et al.*¹⁷ proposed the following global chemical reaction for the dehydration of gypsum

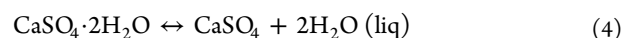


Figure 3 shows the scanning electron microscopy (SEM) picture of the phosphogypsum sample used in this study.

To obtain the transformation into a stable “insoluble” anhydrite, it is indeed to be heated to much higher temperatures close to 350 °C.^{18–20}

The diffractogram presented in Figure 4 shows the scenario where all different additives together are used with PG. The overall mixture (phosphogypsum–reducers–additives) is calcined at high temperatures (1000, 1150, 1300, and 1400 °C). The residual product is analyzed by X-ray diffraction. For a better comparison, the four diffraction patterns are shown in the same Figure 4. The thermochemical decomposition of calcium sulfate is the most important aspect to be analyzed

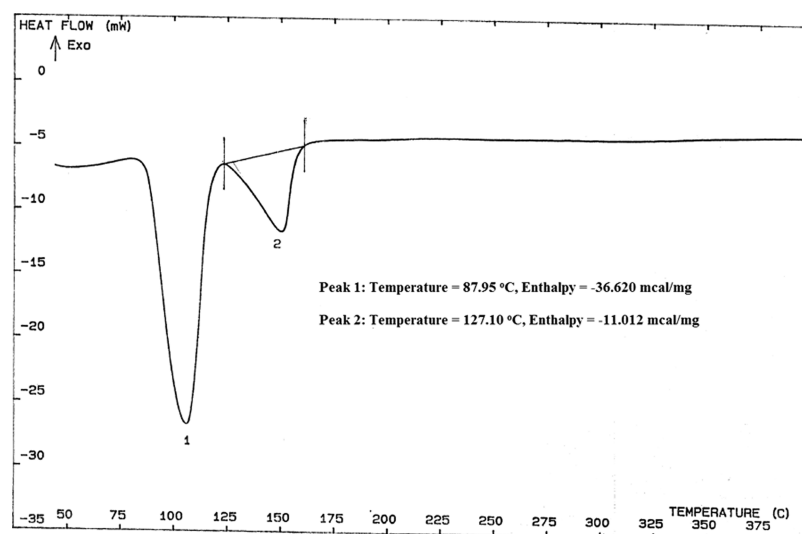


Figure 2. Dehydration of phosphogypsum using DSC.

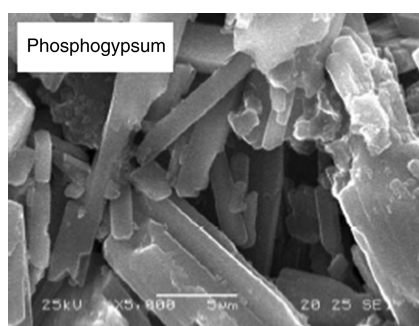


Figure 3. SEM micrograph of the sample.

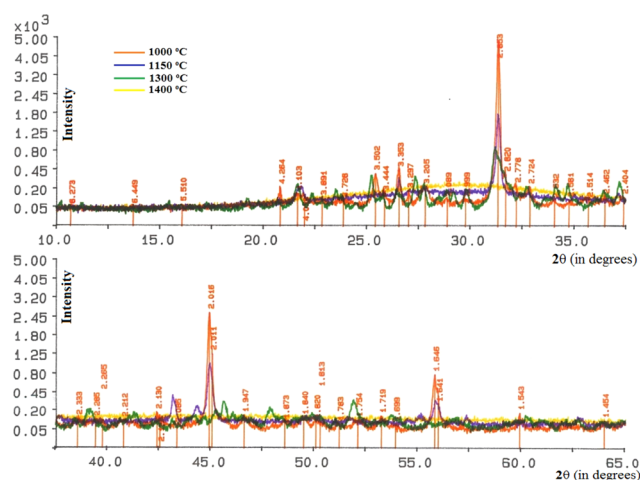
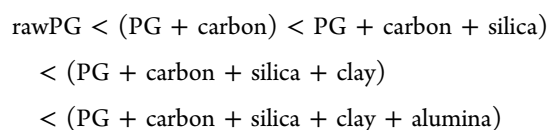
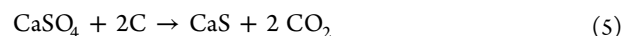


Figure 4. X-ray diffraction patterns of the mixture phosphogypsum-carbon-clay-silica alumina at different temperatures.

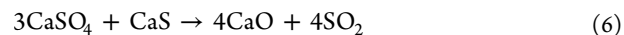
using this figure. From Figure 4, it can be deduced that the increasing order of thermochemical decomposition is as follows



X-ray diffraction analysis confirms the results obtained by the conventional chemical analysis. It also shows that the thermochemical decomposition of calcium sulfate is not complete and that the sulfur present in the residue exists in the form of sulfate and calcium sulfide. It can be concluded that the step in the phosphogypsum conversion scheme then includes the reduction of calcium to calcium sulfide according to the reaction given by eq 5.



The peaks relating to CaSO_4 ($d = 3.50 \text{ \AA}$), CaS ($d = 2.85 \text{ \AA}$), and CaO ($d = 2.40 \text{ \AA}$) appear on the diffractograms, respectively, at angles 25.5° , 31.5° , and 37.5° , in agreement with the results reported by Baraka *et al.*²¹ As temperature increases, the intensities of the CaSO_4 and CaS peaks decrease. On the other hand, it can be noted that the peak of CaO increases with temperature. The more the calcium sulfide decreases, the more sulfur dioxide is released. The only solid-solid reaction that interprets this observation is reaction 6



It is concluded that CaSO_4 decomposes at high temperatures to give CaO and SO_2 . Calcium sulfide is obtained as an intermediate product. The decomposition of calcium sulfate then happens according to eqs 5 and 6. These results from the XRD analysis are in agreement with the results reported by Tewo *et al.* and Ghazel *et al.*^{18,19} In the desulfurization, we have studied the influence of some additives such as charcoal, silica, alumina, and clay. All of the experiments were carried out in a "Heuracus" noodle oven at a temperature of 1000°C , using 10 g of phosphogypsum. The influence of charcoal on the desulfurization of phosphogypsum has been studied. The charcoal used was dried at 350°C , ground, and sieved. Only particles of diameters in the range of $0.08\text{--}0.125 \text{ mm}$ were used. The charcoal used is of the low ash type (5% ash). Calcination of phosphogypsum in the presence of different quantities of charcoal varying from 0 to 1.4 g has been carried out under the conditions mentioned above. The obtained results are shown in Figures 5 and 6. The conversion $X\%$ is presented as a function of the molar ratio N , which is defined as the ratio of the number of moles of charcoal to the number of moles of CaSO_4 .

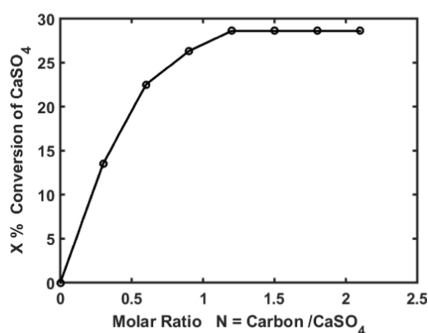


Figure 5. Conversion of CaSO_4 as a function of molar ratio N .

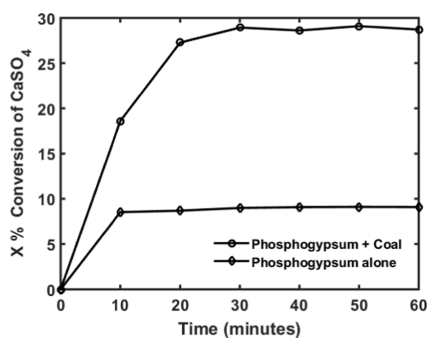


Figure 6. Conversion of phosphogypsum as a function of time.

Figure 5 shows that the conversion reaches a steady state for molar ratios greater than 1.2. Hence, the optimal molar ratio N is equal to 1.2. By controlling the amount of charcoal, the referential reaction can be carried out to give essentially the products SO_2 and CaS . In the presence of small amounts of charcoal, the sulfate is broken down into CaO and SO_2 . On the other hand, in the presence of quaternary coal deposits, the reaction products are CaS and CO_2 .²² It has been found that by increasing the ratio N up to 3, the rate of decomposition and the rate of conversion have increased enough to obtain calcium sulfide.²³ The percent conversion X is calculated as $[(S_i - S_f) / S_i] \times 100\%$, where S_i and S_f are the initial and final contents of sulfur in CaSO_4 , respectively. X was calculated, and the results of the calcination of phosphogypsum alone and with coal at 1000°C are presented in Figure 6.

The mixture phosphogypsum–carbon is calcined at 1000°C for different residence times in the oven for which the corresponding conversions are estimated. Figure 6 shows a comparison of conversion of phosphogypsum as a function of time with coal and alone scenarios.

Figure 6 shows that the phosphogypsum conversion rate is fairly rapid during the first quarter of an hour, less rapid during the second quarter of an hour, and constant thereafter. However, the figure shows that the conversion rate is very low for the case of phosphogypsum alone compared to the case where coal is used as an additive. At a temperature of 1000°C , for 1 h of calcination, the presence of the reducing agent (coal) considerably increases the conversion rate of phosphogypsum. The steady-state conversion achieved is 28.6% in the presence of the reducer against 8% in its absence. It clearly shows that carbon has a significant influence on the thermochemical composition of calcium sulfate present in PG. For the experiments related to the additives, different masses of silica, alumina, and clay varying from 0 to 2.8 g, are added to the PG–coal mixture and calcinated at $T = 1000^\circ\text{C}$. Figure 7

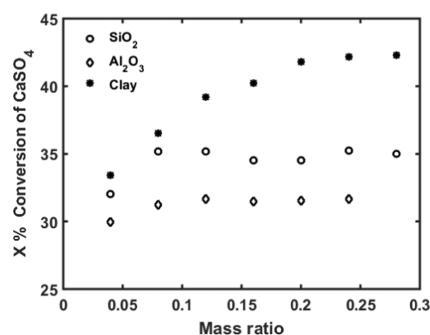


Figure 7. Calcination of phosphogypsum in the presence of additives at $T = 1000^\circ\text{C}$.

shows a comparison of conversions obtained for silica, alumina, and clay as a function of mass ratio, which is the ratio of mass of additive to the mass of PG. From Figure 7, it can be clearly seen that the optimum ratios for silica, alumina, and clay are 0.1, 0.08, and 0.2, respectively, for which the corresponding conversions are 35.21, 31.66, and 42.3%. The highest conversion is achieved with clay as additive compared to silica and alumina.

For each of the additives, the conversion rate of the mixture phosphogypsum–charcoal–additives as a function of time at $T = 1000^\circ\text{C}$ is obtained, and the results are shown in Figure 8. It

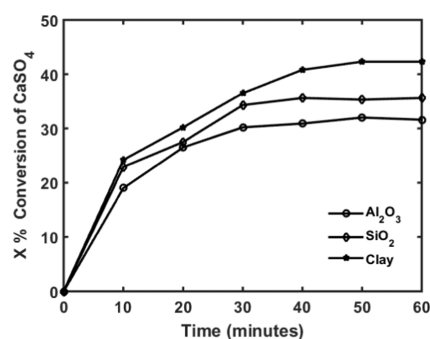


Figure 8. Variation of the conversion of the mixture as a function of time at 1000°C .

can be seen that the conversion rate of calcium sulfate is quite high when using each of the constituents. It is 32, 35, and 42% using alumina, silica, and clay, respectively, at 1000°C for 1 h of calcination. It seems that bentonite clay is an adjuvant that promotes, in a remarkable way, the decomposition of calcium sulfate. It follows from these tests that, through appropriate additives, it is possible to speed up the thermochemical process of calcium sulfate present in the phosphogypsum. From the tests carried out, it can be noted that the conversion rate increases with the calcination time up to $t = 40$ min. Beyond this value, the conversion rate remains constant; hence, the optimum time for thermochemical treatment of phosphogypsum is 40 min (as shown in Figure 8), after which the change in conversion is very minimal.

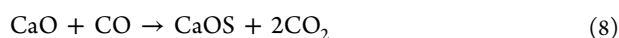
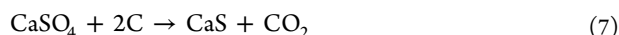
To a mixture of phosphogypsum, charcoal, and bentonite clay, various quantities of silica ranging from 0 to 1.4 g is added. The results showed that by adding an optimal amount of silica equal to 0.1 g, the conversion rate of CaSO_4 achieved is 46%. Further to this mixture, various amounts of alumina are added and calcined. The results of the calcination for a period of 40 min led to achieving a conversion of 53%. The

calcination of phosphogypsum in the presence of all additives at 1000 °C for a period of 40 min showed that the desulfurization is remarkable. Table 1 shows the steady-state conversions achieved when the additives silica, alumina, and bentonite clay are used individually and together in the mixture.

Table 1. Steady-State Conversions Achieved for Different Additives

additives	SiO ₂	Al ₂ O ₃	bentonite	mixture
conversion (%)	35.21	31.66	42.3	53

Table 1 shows that the overall mixture gives a better conversion rate compared to the individual additives. It is found that it is possible, by adding appropriate quantities of silica and alumina to the mixture phosphogypsum + coal + clay, to obtain a notable increase in the yield. At a temperature of 1000 °C, a remarkable desulfurization is obtained using different additives, while the pure calcium sulfate does not begin to decompose until around 1500 °C. Therefore, these results confirm the usefulness of using these additives to lower the reaction temperature and thus facilitate the decomposition of the calcium sulfate present in the phosphogypsum. The various additives and carbon do not enter the main chemical reactions given by eqs 7, 8, and 9 but have a significant accelerating effect on the desulfurization rate by promoting other reactions.



The overall optimal composition of the mixture obtained as a product is shown in Table 2

Table 2. Mixture Composition

compounds	phosphogypsum	bentonite clay	silica	aluminate
% weight	72	15	7	6

The effect of temperature on desulfurization is studied by calcining the mixture phosphogypsum + charcoal + additives at different temperatures for 40 min. The residual products have been analyzed, and the results obtained are shown in Figure 9.

Figure 9 shows that the sulfur content of the mixture phosphogypsum + coal + clay decreases with an increase in

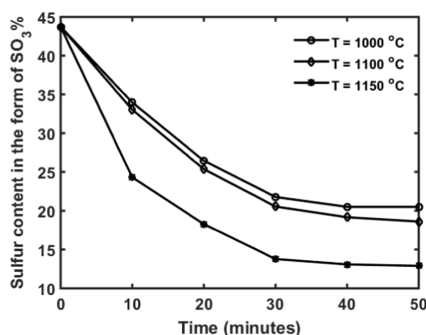


Figure 9. Sulfur content as a function of time at different temperatures.

calcination time. It is clear that, as the calcination temperature increases, greater thermochemical decomposition of calcium sulfate occurs. The corresponding conversion rate of calcium sulfate for these mixtures at different temperatures is also calculated, and the results are shown in Figure 10.

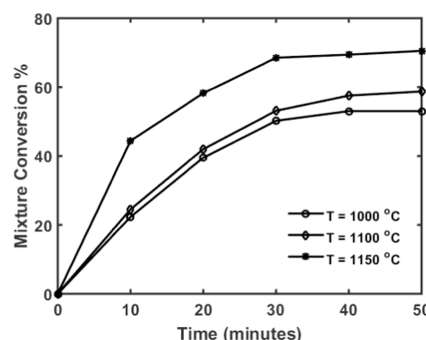


Figure 10. Mixture conversion percent versus time at different temperatures.

From Figure 10, as the temperature increases, higher conversion rates are achieved, which is due to higher decomposition rates. The steady-state conversion rates corresponding to Figure 9 are shown in Table 3 for a period of 40 min.

Table 3. Conversion Rate at Different Temperatures

temperature (°C)	1000	1100	1150
conversion (%)	53	59	70

3. CONCLUSIONS

Phosphogypsum releases are detrimental on two levels (in particular on fauna and flora) and cause economic loss (due to loss of sulfur). The investigation in this study demonstrated a method of alleviating the problem by valorization of this byproduct. For this, the sulfuric acid gypsum process was used to process the Algerian phosphogypsum, and it was shown that a significant amount of sulfur can be recovered from the process. Experiments carried out in this research have enabled us to recover the sulfur in the form of SO₂ using appropriate additives such as silica, alumina, clay, and charcoal as the reducing agent. These additives accelerated the desulfurization process and decreased the decomposition temperature of calcium sulfate. As a result, these additives allowed the reduction of energy used with an increase in the concentration of SO₂. It was found that using all additives with the phosphogypsum mixture gave the maximum conversion of 52% at 1000 °C, which increased to 70% when the temperature was increased to 1150 °C. X-ray diffraction analysis showed that the thermochemical decomposition is not complete and that the sulfur present in the residue exists in the form of CaSO₄ and CaS at 1150 °C. It was also found that the residues obtained after calcination of phosphogypsum has a chemical composition identical to clinker, which can be used for the commercial production of cement. This possibility of using the clinker in cement has to be explored as a futuristic work.

Table 4. Chemical Composition of Phosphogypsum

compounds	CaO	SO ₃	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	P ₂ O ₅	F	H ₂ O
% weight	35.98	43.71	0.43	0.16	0.48	0.39	1.64	0.6	16.70

Table 5. Bentonite (Clay) Composition

compounds	SiO ₂	Al ₂ O ₃	FeO ₃	CaO	MgO	TiO ₂	Na ₂ O	K ₂ O	MnO	PO ₅	S
% mass	66.00	14.20	2.42	3.86	3	0.34	1.42	1.30	0.03	0.07	0.10

4. EXPERIMENTAL SECTION

Aluminate powder, silica, and charcoal were obtained from Sigma-Aldrich, Inc. The phosphogypsum used in this study was obtained from Asmidal, Algeria. Its chemical composition is shown in Table 4.

The morphological analysis of the phosphogypsum was performed using a scanning electron microscope. The clay used is Mostaganem bentonite supplied by the Algerian national company SONAREM. The chemical composition of this bentonite is shown in Table 5.

The sample was dried, ground, and sieved, which is followed by dehydration. Dehydration was conducted using the classical dehydration technique and using differential enthalpy analysis. X-ray diffraction is used to reveal the chemical composition information of the residual mixture. This technique is useful for evaluating minerals, polymers, corrosion products, and unknown materials. In most cases, the samples are analyzed for element by powder diffraction using samples prepared as finely ground powders. The analysis was carried out using a Phillips diffractometer with geometry PW 1820. The operating conditions used are a generator voltage of 40 kV and an intensity of 30 mA, the set of slits in spectrometer with a divergence of 1° and repector of 0.1 mm, rotation speed of 0.02° (2θ/s), a scan of 5–70°, and for a duration of 54 min. The obtained residual product of the calcined phosphogypsum at 1000 °C for 40 min with each of the additives is analyzed using X-ray diffraction.

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Notes

The authors declare no competing financial interest.

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