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Posphogypsumwaste valorization by acid attack with the presenceofmetallic iron

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Abstract

In phosphoric acid factories using phosphate rock, the major problem known is the high quantity of produced phosphogypsum “PG” waste. Storage and management of this quantity present a serious problem. The consumption or the re-use of this waste generates several environmental risks due to its composition. Several valorization processes of the PG, economic and environmental, are in phase of development and study. Among the tests of valorization, we can find methods of desulphurization, bacteriological or thermal, allowing to produce sulphur dioxide SO_2 used in the synthesis of the sulphuric acid. The object of our work is to develop an alternative technique to valorize the PG and produce sulphur dioxide “SO_2” following an attack by a strong acid in the presence of a metal catalyst. We have shown that the leaching of the PG with acid alone does not allow reduction of the ions sulphates dissolved to the SO_2. However, if the leaching is made in the presence of the metal elements, the release of gaseous SO_2 is observed. The values of ΔGr and ΔHr calculated allowed us to discuss the possibility of the reactions involved and to argument the experimental results found.

1. Introduction

The demand for phosphate rock is expected to increase and will rise from 176 Mt in 2010 to 262 Mt by 2050. Morocco has more than 70% of basic world reserve in phosphatic rock and occupies the second place in the export of the phosphates estimated at about (15%) and has more than 38% of world reserves in phosphatic concentrate. It has the highest (Reserve/Production) ratio, currently at around 2000 years, which is much higher than the world average of 370 years [1, 2].

The manufacturing of phosphoric acid (H_3PO_4) and phosphate-enriched fertilizers use two different processes starting ore of rock calcium phosphates. The “Wet Process” is the process which uses less energy and has become widely used in several countries. However, its disadvantage is the production of a significant amount of phosphogypsum waste (PG), which is becoming increasingly a serious environmental problem. It is known that the phosphogypsum waste (PG) contains large amounts of toxic compounds like heavy metals, radioactive elements and fluorine. In manufacturing, more than 5 tons of the PG is produced for a 1 ton of acid synthesized [3, 4]. In Morocco, the production of the PG is estimated at 20 million tons a year which is stored near the production site or discharged in the sea [5].

Many researchers use biological, physical, chemical and thermal methods and having potential economic are tested for treatment of PG waste and to reduce its environmental effects [3, 6]. In the thermochemical decomposition of PG the reaction yields to sulfurous gas. The temperature and yield of this process have been the subject of several studies [7, 8]. Another valorization of the PG in the cement industry is given by the Müller-Kühne reaction [9]. This process makes it possible to obtain cement and SO_2 gas used to synthesize sulfuric acid. The decomposition of PG occurs at high temperature (T > 1100 °C) and several additives enhance the decomposition improving the rate of decomposition and decreasing its temperature [10].

The chemical treatment of PG waste is based on the leaching of PG with various solvents such as water, acid and basic solutions. The sulphate leaching rate is higher in an acidic environment and the presence of metallic elements could accelerate the decomposition of sulphates and improve the release of the SO_2 gas used to produce sulfuric acid. In this work we have tried to develop a new method of valorization of PG based on acid attack catalyzed by iron and producing sulfuric acid. The decomposition reactions of PG and the production of the acid occur simultaneously in the liquid phase at low temperature. The mechanism of these reactions and the thermodynamic equations are presented and discussed.

2. Materials and methods

Amounts of 400 g of the raw PG are placed in a reaction chamber, attacked with concentrated hydrochloric acid under boiling temperature. Variable amounts of the metallic iron are added to the PG before the attack step. After dissolving nearly all of solid, we filtered out cold and we kept both the insoluble residue and solution. After, the attack solution was analyzed and the escaped gas was recovered and assayed.

The analytical techniques used are X-ray diffraction 6000 SHIMADZU to characterize structure of initial and solid residues after attack. The X-ray powder diffraction have been recorded using a diffractometer with copper Kα radiation and data were obtained in the 2θ range of 10°-90°. FTIR-8400S SHIMADZU is used as infrared spectrometry to determine vibrational groups in solids. FTIR measurement is done in transmission mode on the pellets prepared by mixing 1% of compound with KBr.

The acid digestion and decomposition of the PG by a strong acid concentrate HCl (variable acid / solid / metal ratios) at the boiling temperature are carried out in a reaction chamber partially isolated from atmospheric pressure. The attack is maintained until complete dissolution of the solid followed by dilution with distilled water. The gas released from the reaction chamber is bubbled through solutions which keep SO_2 gas as described in [11]. The attack product was filtered using Whatman paper N° 0.41. The recovered solid residue is dried at 105 °C, weighed and then, analyzed by DRX and IR. The reagents used for acid attack and assay are all analytical-grade. Concentration of the sulfate ions in the various solutions is obtained by gravimetric determination and by colorimetric method using a (UV-9200 Rayleigh) spectrophotometer. The SO_2 gas which released from the reaction chamber is bubbled through a solution of H_2O_2. The titration of the excess of H_2O_2 by a strong oxidant $KMnO_4$ indirectly gives the amount of SO_2 released.

3. Results and discussion

3.1.*Characterization of Solids*

The PG raw material with a grain size less than 63 µm, was characterized by X-ray diffraction and by infrared spectroscopy. X-ray diagram is presented on figure 1. The result obtained shows that the PG raw material contain essentially calcium sulphatedihydrate $CaSO_4.2H_2O$, brushite$CaPO_3(OH).2H_2O$ and silica SiO_2. This result is in great agreement with what reported by El Ouardi [15] who has demonstrated that the PG raw material may contain unreacted fluoroapatite $Ca_{10}(PO_4)_6F_2$, quartz SiO_2, dolomite $CaMg(CO_3)_2$ and calcite $CaCO_3$. [12].

In addition, there is a solid solution between dicalcium phosphate and calcium sulfate because HPO_4^{2-} ions substitute SO_4^{2-} ions in the gypsum structure. The HPO_4^{2-} and SO_4^{2-} ions have the same sizes, molar masses and the same charges.

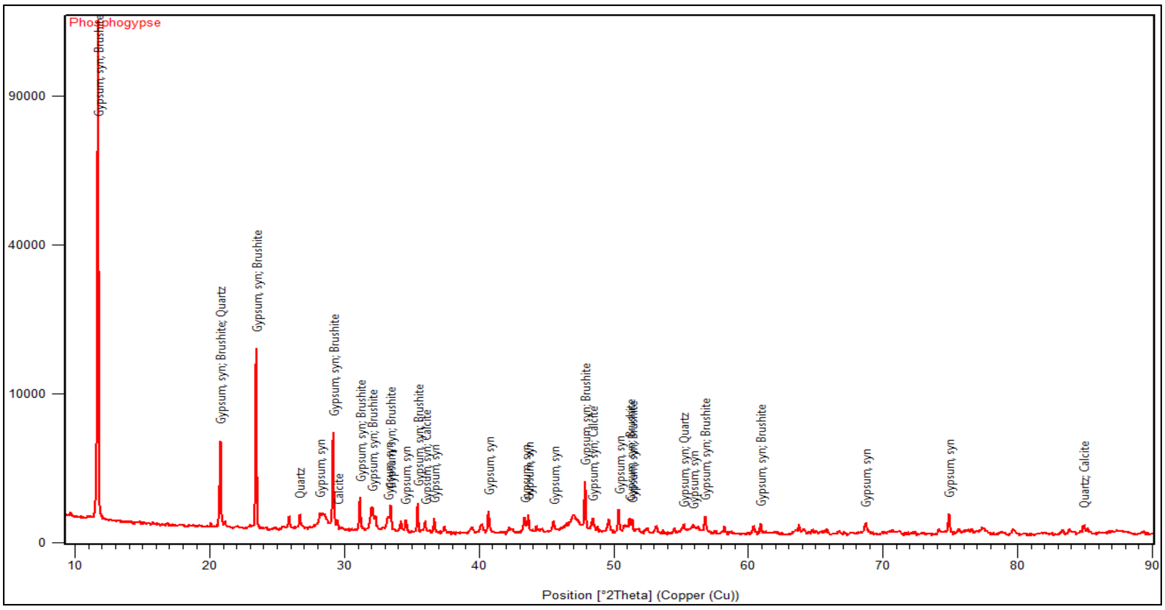

Figure 1: X-rays diagram of PG raw material.

El Issiou has found that the PG raw material contains quartz and/or silicates, fluorides, phosphats, organic materials, iron and aluminum minerals [13]. The chemical analysis of phosphogypsum found by another author indicates the predominant presence of calcium sulphate as well as the presence of some traces of aluminum, phosphorus and sodium respectively from Al_2O_3, P_2O_5 and Na_2O [14].

Becker published the composition of phosphate rock from different origins, including that of Morocco. The main elements mentioned are : (P_2O_5, F, CO_2, SiO_2, CaO) >1% and (Al_2O_3, Fe_2O_3, MgO, Na_2O) <1% [4].

The FTIR spectrum recorded between 4000 cm^{-1} and 450 cm^{-1} of the raw PG is shown in figure 2. This spectrum exhibits several bands. The assignment of the IR absorption bands is shown in table I. These results are in agreement with other studies [5, 15].

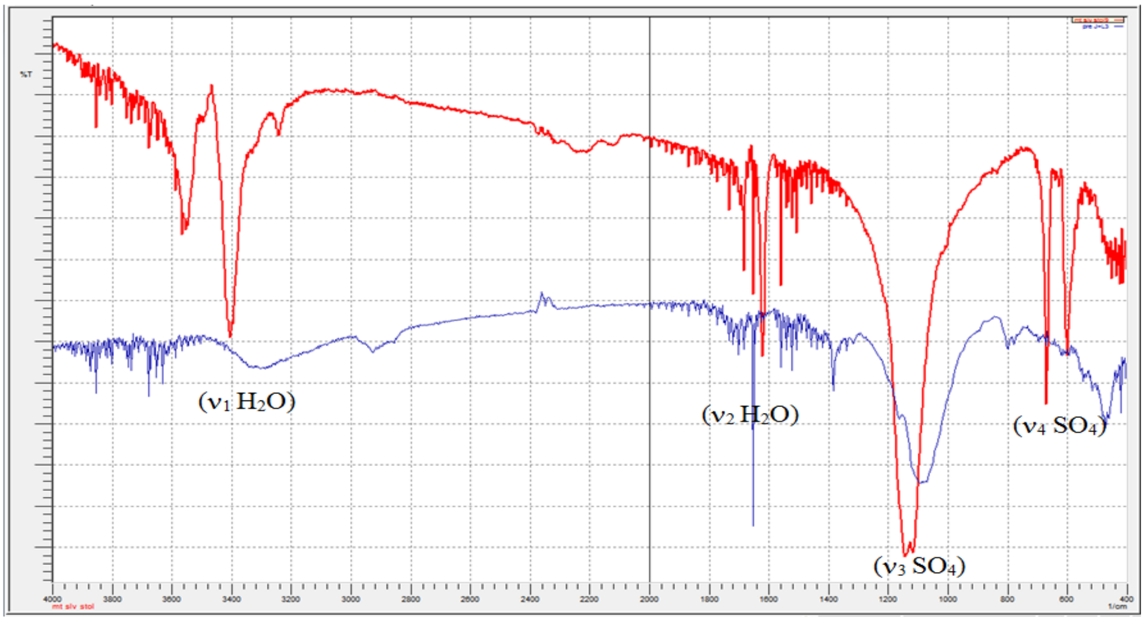

Figure 2: Infrared spectrum of the raw phosphogypsum (top) and the non-soluble residue (bottom)

Table 1 : Assignment of IR absorption bands.

The bands position (cm^{-1})	**Assigning vibration modes**
600 et 669	Deformation antisymmetric of sulphate ($\nu_4 SO_4$)
1117 et 1143	Antisymmetric elongation of sulphate ($\nu_3 SO_4$)
1621 et 1686	Deformation of water molecules (ν_2 H_2O)
3244, 3403 et 3551	Symmetric and antisymmetric elongation of H_2O (ν_1 H_2O)

FTIR spectrum of non-soluble residue which is resistant to acid attack shows absorption bands corresponding to the vibrations attributed to Si-O bond at 1176, 1046 and 456 cm^{-1} [16].

3.2. Characterization of the liquid phase and the gas phase.

The table 2 gives the concentrations of the sulfate ions in the liquid phase and of the concentration of sulfur gas in the gas phase.

Tableau 2 : Analysis of liquid phase and gas phase.

	% SO_2(g) (mass/mass)			**% SO_4^{2-} (mass unreacted in solution)**		
Mixture (Fe:PG)	0:4	2:4	3:4	0:4	2:4	3:4
Min	0	6,395	8,114	77,415	70,371	74,415
Max	0	7,905	8,73	100,333	89,326	80,253
Average	**0**	**7,767**	**8,664**	**89,045**	**83,348**	**78,852**

The quantity of unreacted sulphate ions in the solution is determined by gravimetric analysis. We can observe in table 2 that the content of sulphates ions decreases with the quantity of metal added. It’s known that the solubility of calcium sulphate depends on the temperature, the pH, the presence of impurities in the solution and in calcium sulphate[19, 20]. According to the temperature, the solubility of the gypsum have a maximum value at optimal temperature varying between 30 and 40°C (2.4g/L, pKs=4.58) and it decreases at lower and higher temperatures [17, 20]. The solubility of the PG in a solution is linked to the pH (3.79 g/L with pH = 1.8), it decreases when the pH increases [18].

The following table summarizes some bibliographical data concerning the solubility of calcium sulphates.

Table 3 : Bibliographic data on solubility of $CaSO_4$ (g/l) [19,20]

Parameters		$CaSO_4.2H_2O$	$CaSO_4.1/2H_2O$ α	β	$CaSO_4$ III	$CaSO_4$ II
Temperature	3°C	1.81	8.25	10.06	11.5	3.77
	50°C	2.04	4.26	4.26	4.8	18.4
pH	0	-			14	-
	0.7	-			6.4	-
	1.8	3.79	-			
	11.8	1.55	-			
Water quality	Distilled	2.25	-			
	of sea	3.8				

The Sulfur takes various oxidation steps and its electronegativities (S(0)=2.50, S(-II)=2.55, S(+IV)=2.70, S(+VI)=2.80) are higher than hydrogen (2.2). In a reaction medium, the redox potential of SO_4^{2}/SO_2 is equal to 0.12 V.

$$SO_4^{2-} + H_2(g) + 2H^+ \leftrightarrow SO_2(g) + 2\,H_2O \qquad (1)$$

The theoretical enthalpy calculation of reaction 1 is given by the figure 3.

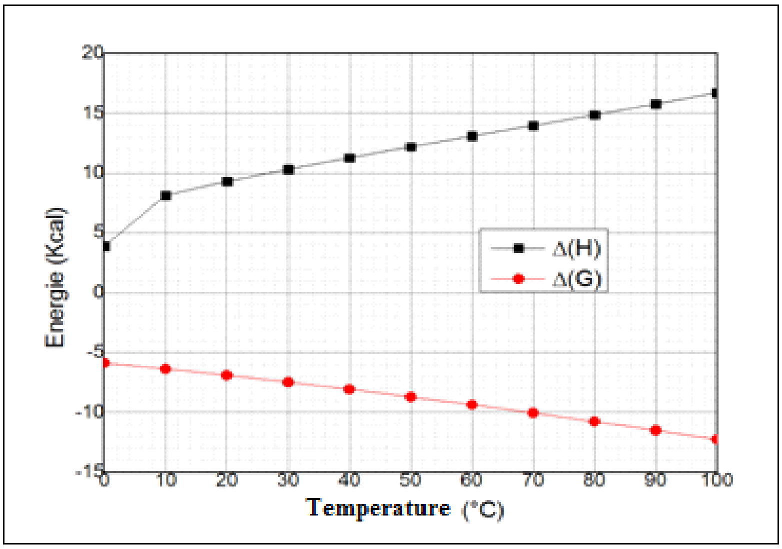

Figure 3: Enthalpies of reaction 1 calculated at different temperatures.

We can observe that the free Gibbs enthalpy ΔG of reaction has a negative value even at very low temperatures. The reaction 15 is a reduction reaction of the S(+VI) to S(+ IV) with takes place in acid medium and in the presence of Hydrogen. The attack of iron by hydrochloric acid generates hydrogen in the solution according to reactions 2 and 3,

$$2HCl + Fe \leftrightarrow H_2(g) + 2Cl^- + Fe^{2+} \qquad (2)$$

$$3HCl + Fe \leftrightarrow H_2(g) + 3Cl^- + Fe^{3+} \qquad (3)$$

The energies reaction calculated at different temperatures are represented by figure 4. It appears that the value of enthalpy of ferric ions reaction is less than that of ferrous ions reaction witch indicates that ferric ions formation is more advantageous than ferrous ions formation.

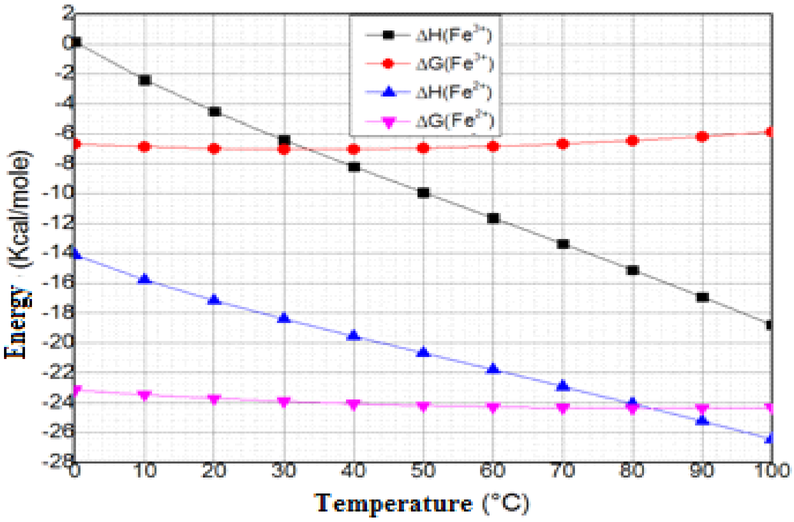

Figure 4: Enthalpies of reactions 2 and 3 calculated at different temperatures.

According to the results obtained, the PG reacts in the hydrochloric medium in the presence of iron and the product formed is SO_2 gas, the possible reaction mechanism involves a reduction reaction of sulfate ions to sulfur dioxide by molecular hydrogen and can be presented by the following reactions 4 and 5:

$$1.5CaSO_4{,}2H_2O + 6HCl + 1.5Fe \leftrightarrow 1.5Ca^{2+} + 6Cl^{-} + 1.5Fe^{2+} + 6H_2O + 1.5SO_2(g) \qquad (4)$$

$$1.5CaSO_4{,}2H_2O + 6HCl + Fe \leftrightarrow 1.5Ca^{2+} + 6Cl^{-} + Fe^{3+} + 6H_2O + 1.5SO_2(g) \qquad (5)$$

We notice that in the absence of iron (Table 2), the content SO_2 recovered is zero. The acid attack causes digestion of the PG in sulphate and calcium ions. This attack does not allow its decomposition into sulfur dioxide. When metal iron is added to the PG, the content of the sulfate ions decreases contrary to the content of SO_2 it increases.

Using simulation and modeling software for simple chemical reactions and unit processes, we have calculated the thermodynamic energies ΔH and ΔG of the various competitive reactions that can take place in the reactor (reaction Eq1, Eq2, Eq3 and reaction Eq4).

$$\begin{aligned}&1.5\ CaSO_4, 2H_2O + 6\ HCl + 1.5\ Fe\\&\quad \leftrightarrow 1.5\ Ca^{2+} + 6\ Cl^{-} + 1.5\ Fe^{2+} + 6\ H_2O + 1.5\ SO_2(g)\end{aligned} \qquad (Eq1)$$

$$\begin{aligned}&1.5\ CaSO_4, 2H_2O + 3\ HCl + 1.5\ Fe\\&\quad \leftrightarrow 1.5\ Ca^{2+} + 3\ Cl^{-} + 1.5\ Fe^{2+} + 3\ H_2O + 1.5\ SO_4^{2-} + 1.5\ H_2(g)\end{aligned} \qquad (Eq2)$$

$$\begin{aligned}&1.5\ CaSO_4, 2H_2O + 6\ HCl + Fe\\&\quad \leftrightarrow 1.5\ Ca^{2+} + 6\ Cl^{-} + Fe^{3+} + 6\ H_2O + 1.5\ SO_2(g)\end{aligned} \qquad (Eq3)$$

$$\begin{aligned}&1.5\ CaSO_4, 2H_2O + 3\ HCl + Fe\\&\quad \leftrightarrow 1.5\ Ca^{2+} + 3\ Cl^{-} + Fe^{3+} + 3\ H_2O + 1.5\ SO_4^{2-} + 1.5\ H_2(g)\end{aligned} \qquad (Eq4)$$

The figure 5 shows the evolution of the energies calculated for the four reactions as a function of temperature.

According to the values of the free enthalpy, the reactions leading to the formation of sulfur dioxide are more advantageous. The reaction (6) giving sulfur dioxide and ferrous ions is exothermic and the most advantageous reaction.

From a thermodynamic point of view, the production of sulphurous hydride (H_2S) can be take place according the reaction (Eq'1) and (Eq'2).

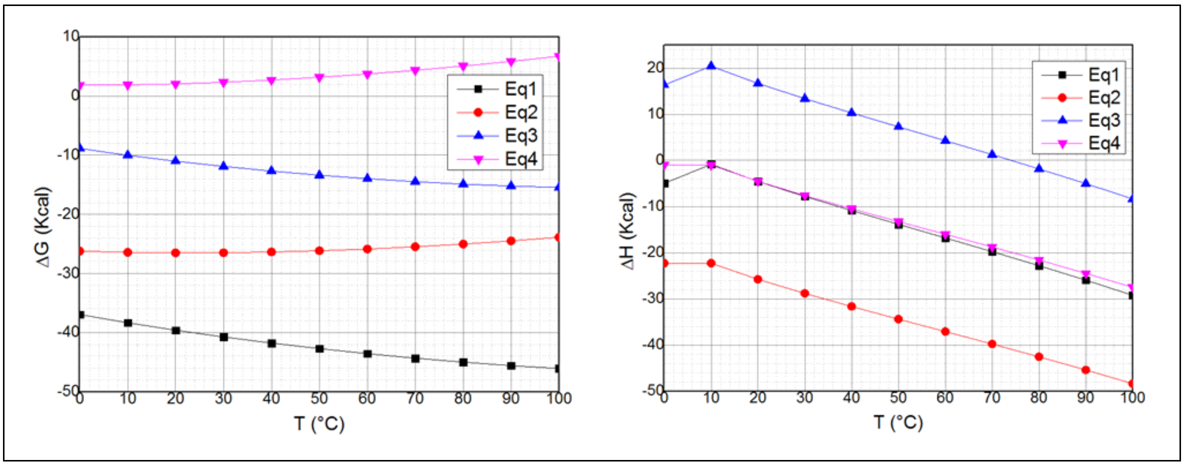

Figure 5: Thermodynamic energies calculated of the reactions (Eq1, Eq2, Eq3 and Eq4).

$$CaSO_4, 2H_2O + 10\ HCl + 4\ Fe \leftrightarrow Ca^{2+} + 10\ Cl^- + 4\ Fe^{2+} + 6\ H_2O + H_2S(g) \qquad (Eq'1)$$

$$CaSO_4, 2H_2O + 10\ HCl + 2.66\ Fe \leftrightarrow Ca^{2+} + 10\ Cl^- + 2.66\ Fe^{2+} + 6\ H_2O + H_2S(g) \qquad (Eq'2)$$

The curves giving the thermodynamic energies of the reactions (Eq’1) and (Eq’2) are shown in figure 6.

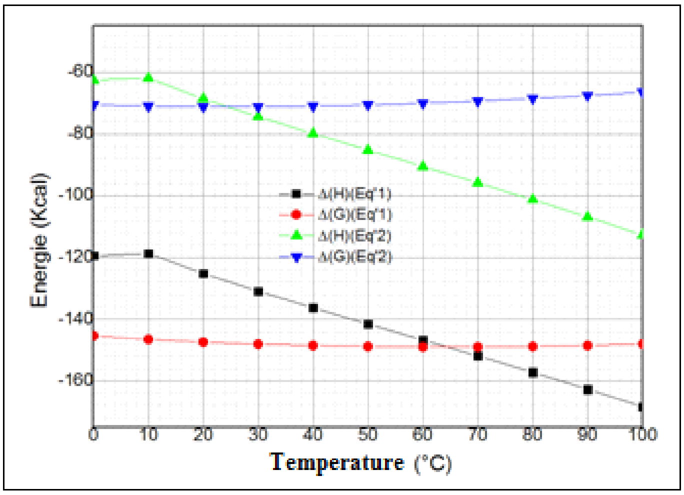

Figure 6: Thermodynamic energies of the reactions 10 and 11.

It seems that the reactions (Eq’1) and (Eq’2) are more energetic. In an oxygenated medium, the sulphurous hydride (H_2S) leads to sulfuric acid. However, the formation of hydrogen sulphide H_2S requires the co-existence of several conditions, namely: presence of water; presence of organic matter, sulfate ions in solutions, absence of air, presence of anaerobic bacteria (*Desulfovibris*, *Desulfotomaculum*), pH 4 to 9 and ambient temperature between 30 and 38 ° C [21]. In our case, these conditions are not fulfilled to favor the reactions (Eq’1) and (Eq’2), which leads us to eliminate this hypothesis.

Conclusions

In this work, we have shown that it is possible to decompose calcium sulphate to sulfur dioxide in an acid medium at low temperatures. We have determined by volumetric measurements that the gas produced when the phosphogypsum is attacked by a strong acid in the presence of metallic iron contains sulphurous gas. The amount of sulfate ions in the medium solution decreases as the amount of iron added increases. This decrease in SO_4^{2-} ions is due to the reduction of this compound to gaseous SO_2. The reactions giving SO_2 were simulated by a computer tool. The calculation of thermodynamic energies shows clearly the possibility of these reactions.

We have shown by this work that phosphogypsum can be valorized in the synthesis of sulfuric acid, which can be used in the phosphoric acid industry from phosphate rock.

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