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To cite this article: Majda Alla, Achraf Harrou, Mohammed Lamine Elhafiany, Dounia Azerkane, Meriam El Ouahabi & El Khadir Gharibi (2022): Reduction of phosphogypsum to calcium sulfide (CaS) using metallic iron in a hydrochloric acid medium, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2022.2052881

To link to this article: https://doi.org/10.1080/10426507.2022.2052881

Published online: 18 Mar 2022.
Reduction of phosphogypsum to calcium sulfide (CaS) using metallic iron in a hydrochloric acid medium

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ABSTRACT

Our study aims to decompose phosphogypsum (PG), mainly composed of CaSO$_4$.2H$_2$O, by reduction in an acidic medium. We evaluated the decomposition of PG by various reaction mechanisms. Sulfate ions from the acid digestion of PG are reduced to sulfide by the hydrogen gas produced in the solution by hydrochloric attack of the metal iron. The solid residues obtained have been determined and monitored by X-Ray Diffraction, Fourier-Transform Infrared spectroscopy and Ultraviolet-visible spectroscopy. The microstructure of residues was observed by scanning electron microscope (SEM). The results show that hydrogen gas formed by hydrochloric acid attack of iron reduces the sulfur from S(VI) to S(-II). CaSO$_4$.2H$_2$O, insoluble in water, gives a residue containing CaS, which is only sparingly soluble in water. The residue also contains anhydrite, bassanite and ferrous chloride. The monitoring of the quantities of residue obtained under varying experimental conditions (temperature, attack time, mass of iron and PG and volume of acid on PG) and volume of HCl showed that the amounts of residue obtained are less than 32% of mass. When the volume of the HCl added increases, the obtained mass of the solid residue decreases sharply. The residue stabilizes at 10% of mass when the volume of HCl added is higher than that required to attack metal iron.

GRAPHICAL ABSTRACT

Introduction

The recovery of industrial and mining wastes, produced in large quantities as phosphogypsum (PG), is a matter of very high industrial and social importance, taking into account the principles of circular economy and environmental protection. Whatever the field of application of by-products, mining waste recycling will be attractive for reduction of solid waste and conservation of finite nonrenewable natural resources.

The synthesis of phosphoric acid, by the dihydrate process at a temperature ranging from 90 to 120 °C, produces P$_2$O$_5$ in amounts between 42 and 52%[3] The synthesis of H$_2$PO$_4$ generates phosphogypsum waste, which is mainly composed of gypsum (CaSO$_4$.2H$_2$O). The quantity of PG produced on an industrial scale is about 5 tons for one ton of phosphoric acid.Rock phosphate also contains fluorite and carbonates, which react with sulfuric acid and increase the content of the phosphogypsum formed.

Morocco is one of the world leaders in the production of phosphoric acid and phosphate fertilizers from phosphate rocks. It is the world’s leading exporter of phosphate in all its forms, with an annual production of twelve million tons. Morocco held second place among the phosphate...
exporters, with 15% of world trade, and has a natural phosphate reserve estimated at 70% and 38% in concentrate. Its operating life is 2000 years, based on the reserve/production ratio of 2014; it has now been estimated at 370 years because of the rise in global demand. In Morocco, the annual production of PG exceeds 20 million tons/year, it is about one tenth of the world production estimated at 250 million tons/year. Various recovery operations of phosphogypsum as a road backfill, fertilizer, additive to cements and source of sulfur dioxide have been studied. However, the presence of harmful elements such as heavy metals (Cd, Zn, Cu and Cr), radionuclides (Ra, U and Th) and fluorine limit the fields of recovery of PG.

Phosphogypsum decomposition has been studied under various experimental conditions, such as reducing gases and reacting with different types of carbon. Thermochromic decomposition of PG to sulfur dioxide and lime provides possibilities to use its main components CaO and S and, at the same time, to solve some environmental problems. Thermal decomposition of PG in air generally occurs at very high temperatures exceeding 1400 °C. PG can also decompose in a reducing atmosphere, under CO for example, at a lower temperature according to the Muller-Khune process. The SO2 gas, produced in amounts ranging between 7 and 10%, is washed and then transported to the sulfuric acid production units.

The addition of FeCl3 a catalyst helped to initiate the decomposition of CaSO4, under CO (g) from 700 °C to give CaS. PG can also be reduced with H2 between 1100 and 1200 °C in a fluidized bed reactor fed with a hydrocarbon fuel and air or by combustion of natural gas. CaSO4 decomposes in the presence of carbon monoxide CO (g) and hydrogen H2 (g), to give sulfur dioxide up to 1150 °C.

The solubility of gypsum in fresh water reaches a maximum value of 2.25 g/L from about 40 °C and decreases at lower or higher temperatures. In hydrochloric acid solution (3 M HCl), the solubility of gypsum reaches 47 g/L at 80 °C. Oumnih et al. studied the possible reactions of PG mixed with Fe and HCl. They demonstrated that the reactions are accompanied by the release of SO2, H2S or H2. The SO2 is thermodynamically the most favorable.

Studies of reductive decomposition of phosphogypsum to SO2 remain limited. Most published results deal with thermogravimetric analysis, which is insufficient to study the decomposition behavior of phosphogypsum to SO2. Problems related to the control of the reaction conditions must be solved, and further insight into the theory of reductive of phosphogypsum to sulfur dioxide and lime is requested.

Calcium sulfide is very difficult to prepare in an aqueous solution due to hydrolysis, and therefore bulk CaS usually prepared in a high temperature environment (1200 °C) and requires toxic H2S gas. Above 950 °C, CaS can be obtained by reaction of SO2 gas with CaO, but it is accompanied by CaSO4 and CaSO3. Likewise, CaS films were coated on micro-slides by the reaction of a solution of (CaSO4), (Na2S2O3.5H2O), distilled water, and EDTA. Iron-doped calcium sulfide nanoparticles were synthesized by co-precipitation in ethanol of Na2S,9H2O and (FeCl2.4H2O, CaCl2).

Our study is part of the sustainable management of phosphogypsum. We seek to evaluate the decomposition of PG mixed with metallic iron and HCl by combining several reaction mechanisms. By hydrochloric attack, metallic iron will release the reducing gas H2 into the reaction medium, the latter will reduce the sulfate ions (SO4 2-) resulting from the dissolution of CaSO4, accelerated by HCl. Sulfur (VI), in the form of SO4 2- ions in solution, is reduced by the reducing gas H2. It can form salts with the lowest possible oxidation state. By X-ray diffraction, we will follow the evolution of insoluble solid residues. The theoretical calculation of the free enthalpies of the reactions will verify the reactions giving the salts evidenced by the XRD.

**Table 1. Labels of raw materials and formulations used for XRD analysis.**

<table>
<thead>
<tr>
<th>Label</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>Raw phosphogypsum (PG).</td>
</tr>
<tr>
<td>E2</td>
<td>Metallic iron (Fe).</td>
</tr>
<tr>
<td>E3</td>
<td>PG (50%) + Fe (50%) before adding HCl.</td>
</tr>
<tr>
<td>E4</td>
<td>Solid residue of PG (50%) + Fe (50%) mixture after the addition of 20 mL of HCl (C = 12.06 M).</td>
</tr>
<tr>
<td>E5</td>
<td>Solid residue after acid attack of 20 mL of HCl (C = 12.06 M) on Fe.</td>
</tr>
<tr>
<td>E6</td>
<td>Solid residue after acid attack of 20 mL of HCl (C = 12.06 M) on raw PG.</td>
</tr>
</tbody>
</table>

**Results and discussion**

**Characterization of raw materials and residues**

The raw materials and the treated samples used for XRD analysis are illustrated in Table 1.

The XRD results of PG, dried at 50 °C for 12 h (E1) and after attack by HCl (E6), show the occurrence of gypsum (CaSO4.2H2O), bassanite (CaSO4.1/2H2O), anhydrite (CaSO4) and quartz (SiO2) (Figure 1A). The total disappearance of gypsum peaks, the addition of FeCl2.4H2O and the formation of calcium sulfide (CaS; JCPDS 01-075-0261) are observed. The XRD characteristic peaks of CaS (2θ = 31.90° and 31.36°) for anhydrite. Quartz is not attacked by acid. HCl reacts with metallic iron allowing the formation of FeCl2.4H2O (Figure 1B).

The spectrum of the solid residue obtained by acid attack of the PG in the presence of metallic iron are illustrated in Figure 1C. The total disappearance of gypsum peaks, the presence of anhydrite, bassanite, iron chloride hydrates (FeCl2.4H2O) and the formation of calcium sulfide (CaS; JCPDS 01-075-0261) are observed. The XRD characteristic peaks of CaS (2θ = 31.4 and 45.08°) clearly appear in E4 but are absent in E3. CaS and FeCl2.4H2O are obtained according to the following reaction:

\[
\text{CaSO}_4.2\text{H}_2\text{O} + 5\text{Fe} + 10\text{HCl} + 14\text{H}_2\text{O} \\
\rightarrow \text{CaS} + 5\text{FeCl}_2.4\text{H}_2\text{O} + \text{H}_2 \\
\Delta H_{298}^o = -450.9 \text{ kJ/mol},
\]
This reaction is strongly exothermic and produces 23.8 L of hydrogen for one mole of CaSO₄·2H₂O. The specific volume of H₂ is 11.9 m³/kg at 20°C,[44] allowing to maintain anaerobic conditions and the stability of the sulfide.[45]

If we consider the dissolution of ferrous chloride tetrahydrate (1600 g/L), the chemical reaction becomes:

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 5\text{Fe} + 10\text{HCl} \rightarrow \text{CaS} + 5\text{Fe}^{2+} + 10\text{Cl}^- + 6\text{H}_2\text{O} + \text{H}_2
\]

\[
\Delta H_{298}^\circ = -538.1 \text{ kJ mol}^{-1}
\]

\[
\Delta G_{298}^\circ = -591.9 \text{ kJ mol}^{-1}
\]

The insoluble solid residue represents a minimum amount of 32% of the mass of the initial solid.

Figure 2 shows the ATR-FTIR spectra of raw PG sample (E1) and solid residue of PG (50%) mixed with Fe (50%) and treated with 20 mL of HCl. The peak at 3688 cm⁻¹ is due to the elongation of the O-H bond of the adsorbed water. PG shows a peak at 3390 cm⁻¹ attributed to symmetrical and asymmetric elongations of the OH bond of gypsum molecule CaSO₄·2H₂O.[46]

The elongation and strain of the SO₄ group of the PG are observed at 1095 cm⁻¹, 663 cm⁻¹ and 591 cm⁻¹ respectively. Peaks due to the elongation of the symmetric and asymmetric O-H bond are observed between 1600 and 1500 cm⁻¹. A small peak at 482 cm⁻¹ is due to the symmetric and asymmetric elongation of the Si-O-Si bond of quartz, present in small amount, is observed in PG.[6] The band at 611 cm⁻¹ can to be assigned to the antisymmetric stretches of the S-O single bonds in the three-membered ring of the C₂ᵥ of the free SO₄²⁻ anion.[47,48]

The solid residue from acid attack of PG in the presence of iron shows the disappearance of the peak at 3688 cm⁻¹ due to the vibration of the extension of the OH bond of the hydrated water molecule of the gypsum. The peaks observed at 3382 cm⁻¹ and 1621 cm⁻¹ correspond to vibrational
elongation of OH group of physiosorbed water and the deformation vibration of OH bond, respectively. The appearance of the peak at 1152 cm$^{-1}$ is likely due to vibrational deformation of Fe-OH bond.\cite{50} The occurrence of two peaks at 3218 and 3180 cm$^{-1}$ is attributed to the vibration of the extension of the P-OH bond of residual P$_2$O$_5$ in PG. The characteristic peaks of CaS are in excess of the medium infrared region, so the FTIR analyzer fails to give the entire spectrum of CaS.\cite{51} However, the small peak observed at 801 cm$^{-1}$ can be attributed to the deformation of the Ca-S bond in CaS \cite{40} or to symmetrical stretching vibration of Si – O.\cite{52,53} The peaks situated at 663 and 591 cm$^{-1}$ are assigned to the asymmetric O-P-O bending ($\nu$4) of acidic phosphate ions (HPO$_4^{2-}$) impurities.\cite{51,54,55,56,57,58}

The UV-Visible spectra of the solid residue, obtained by HCl attack of the PG alone or in the presence of iron, are illustrated in Figure 3. With the presence of Fe, the solid residue have an absorbance between 200 and 500 nm in the UV-Visible region. Optimum photoluminescence occurs at 298 nm, this value is consistent with that given by Barrett et al.\cite{55} Pure CaS shows a strong peak around 220 nm with a small shoulder at 250 nm.\cite{56} CaS sample, prepared by mixing Ca(CH$_3$CO$_2$)$_2$ and Na$_2$S, shows absorbance peak at 405 nm.\cite{57} Natural calcium sulfide (CaS) or oldhamite, from meteorites, is phosphorescent like laboratory-produced compounds. Oldhamite has a high reflectance in the ultraviolet and a weak inflections or shoulders near 360 nm and 375 nm.\cite{58}

![Figure 3. Transmittance (A) and absorbance (B) spectra of solid residue of PG (50%) + Fe (50%) (E4) mixture after acid attack and solid residue after acid attack on raw PG (E6).](image)

![Figure 4. SEM images and EDX spectrum of raw PG.](image)
While, PG alone do not shows any absorbance in the UV-Visible region (Figure 3A). The absorbance between 200 and 500 nm is of low intensity and due to the presence of CaS in solid residue. This low intensity is due to the fact that calcium sulfide is unstable in water, and requires special precautions during preparation and storage. It will hydrolyze to form hydrates and easily dissolves in an acid solution.

In transmittance mode (Figure 3B), the solid residue of PG (50%) + Fe (50%) sample shows an extinction of 56%
from 280 nm. While the extinction is less than 10% for PG attacked by HCl. CaS has a low absorbance ranging from 0 to 0.17, high transmittance ranging from 70 to 100% and low reflectance ranging from 0 to 15% in the ultraviolet. In transmittance mode, by comparing the two products attacked by HCl, we confirm the presence of CaS, which is an excellent phosphor host material.

SEM images show that the micromorphology of PG is in the form of needles (Figure 4). In addition, the crystals of PG are thin, long and overlap to form aggregates. EDX analysis shows that PG consists mainly of Ca and S with low P and Si contents. The presence of P is due to the presence of a small amount of phosphoric acid. While, the presence of Si is due to the presence of quartz from the phosphate bedrock.

After hydrochloric leaching of PG in the presence of iron, two grain forms are present in the residue: rounded grains (M2 10) and agglomerated needles (M2 14) (Figures 5). Calcium sulfate grains, whose the surface is altered, are in the form of agglomerated needles. The rounded grains have a diameter greater than 100 μm. The EDX results (Table 1) of agglomerated needles give Ca/S = 1.00 and O/(S + Ca) = 4.24, which is close to 4 for the agglomerates of gypsum crystals whose anhydrous formula is CaSO₄. Furthermore, the Ca/S and O/(S + Ca) ratios of rounded grains are respectively equal to 1.31 and 1.29. The high concentration of calcium on the surface of the grains can be due to the oxidation of CaS and CaO or by adsorption of OH⁻ ions on the surface of the grains by Vander Walls type bonds with Ca²⁺ cations. Indeed, H₂O molecules activate the decomposition of CaS into CaO and SO₂.

EDX results show the presence of iron and chlorine in small quantities on the surface of the rounded grains (Figure 5). XRD revealed the formation of FeCl₂·4H₂O in the formed residues. The Fe/Cl ratio obtained by EDX is equal to 7 (Table 2), which suggests that there are traces of metallic iron and ferrous chlorides.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass (%)</th>
<th>Standardized mass (%)</th>
<th>Atom (%)</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agglomerated needles (M2 10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5.47</td>
<td>10.9</td>
<td>16.81</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>29.2</td>
<td>58.19</td>
<td>67.33</td>
<td>O/(S + Ca) = 4.24</td>
</tr>
<tr>
<td>S</td>
<td>6.89</td>
<td>13.73</td>
<td>7.93</td>
<td>Ca/S = 1.00</td>
</tr>
<tr>
<td>Ca</td>
<td>8.61</td>
<td>17.17</td>
<td>7.93</td>
<td>Ca/S = 1.00</td>
</tr>
<tr>
<td>Rounded grains (M2 14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>8.59</td>
<td>29.41</td>
<td>50.94</td>
<td>O/(S + Ca) = 1.29</td>
</tr>
<tr>
<td>S</td>
<td>5.77</td>
<td>19.77</td>
<td>17.08</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.44</td>
<td>1.51</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>9.46</td>
<td>32.42</td>
<td>22.41</td>
<td>Ca/S = 1.31</td>
</tr>
<tr>
<td>Fe</td>
<td>4.93</td>
<td>16.9</td>
<td>8.39</td>
<td>Fe/Cl = 7.11</td>
</tr>
</tbody>
</table>

**Figure 6.** Impact of A) time (min) and B) temperature (°C) on acidic decomposition of PG mixed with Fe metallic.

**Figure 7.** Impact of the amounts of PG (A) and Fe (B) added.
Experimental procedures of decomposition of PG

Impact of temperature and time on reactions of decomposition. Figure 6a gives the evolution of the loss of mass of a mixture (mPG = 3 g, mFe = 3 g, VHCl = 25 mL, time = 30 min) as a function of temperature. The loss of mass is very important; it reaches its maximum at 50°C, which corresponds to the temperature of maximum solubility of gypsum in water.[63]

The evolution of the loss of mass of the mixture (mPG = 3 g, mFe = 3 g, VHCl = 25 mL, T = 50°C) as a function of time (Figure 6A) shows a maximum loss of 85% after 30 min of attack followed by a stabilization at 75% after 60 min. This stabilization can be explained by the recrystallization of FeCl₂·4H₂O due to the evaporation of water after a long time at 50°C. Indeed, the solubility of FeCl₂·4H₂O in water is very high in the range of 1600 g/L at 10°C and reaches 4100 g/L at 100°C. In our case, the addition of 3 g of Fe in 25 mL of HCl (12.06 M), the maximum concentration of FeCl₂·4H₂O is 2143 g/L, which is at the limit of supersaturation.

Impact of the amounts of PG and Fe-catalysis on decomposition. When the amounts of PG (mFe = 3 g, VHCl = 25 mL, T = 50°C, Time = 30 min) or that of Fe (mPG = 3 g, VHCl = 25 mL, T = 50°C, Time = 30 min) increases, the loss of mass decreases (Figure 7). For PG, the reduction in mass loss is not significant, compared to that obtained by adding Fe. The influence of the amount of PG added is small because it decomposes to give SO₂ gas, probably H₂S that leaves the reaction medium. The addition of iron allows the formation of the FeCl₂·4H₂O salt.

Impact of acid volume. By varying the volume of the acid (mPG = 3 g, mFe = 3 g, Temperature = 50°C, Time = 30 min), the loss increases sharply from 5 to 10 mL of HCl added (Figure 8). This is probably due to the strong evaporation of HCl, which represents 37% by mass of acid volume. The mass loss stabilizes at 85% when the added HCl content is very high. The saturated vapor of concentrated hydrochloric acid solution (> 12 M) contains more than 72% of HCl at 50°C. This amount of volatile gas increased exponentially at high temperatures.[64]

Conclusion
The decomposition of phosphogypsum by hydrochloric attack and metallic iron catalysis was studied. The solid residue obtained has been determined and monitored. In addition, the impact of experimental parameters as temperature, attack time, mass of iron and PG and volume of acid on PG decomposition were discussed.

Almost complete acid digestion, with concentrated HCl, of PG mixed with iron gave a solid residue consisting of CaS, anhydrite, bassanite and ferrous chloride. The formation of CaS is highlighted by XRD and confirmed by UV-Visible spectroscopy in transmittance and absorbance mode. The decomposition of PG is influenced by temperature, with a maximum decomposition is obtained at 40-50°C corresponding to the maximum solubility of gypsum. Likewise, time affects decomposition of PG that reaches the maximum after 30 min of attack.

The amount of insoluble solid residue increase as the amounts of PG or Fe increases. This increase is more noticeable for iron, allowing the formation of FeCl₂·4H₂O solid, as evidenced by XRD. The increase of the volume of very volatile HCl stabilizes the amount of the solid residue obtained at around 10%. While, the addition of less than 32 wt.% of HCl gives only CaS. This suggests the development of other reactions allowing the formation of volatile compounds such as SO₂.

Experimental

Raw material
The phosphogypsum studied is from the Chérifien Office of Phosphates of the Jorf Lasfar (El Jadida, Morocco). We used powdered metallic iron (Fe) as a catalyst. The concentration of hydrochloric acid used is 12.06 M. Concentrated HCl 36 M is used to compensate any loss during evaporation of this acid.

Experimental procedures
The PG, having a particle size of less than 250 μm, was dried in an oven at 50°C for 12 h, and was mixed in a thermostatic flask with metallic iron (Table 1). The flask, linked to

Figure 8. The influence of hydrochloric acid on decomposition of phosphogypsum.

Figure 9. Schematic overview of the experimental design.
a distillation column, is connected to a condenser, which bubbles the gas leaving in a solution of KMnO$_4$ (0.02 M) the gas continues its way to another bubbler containing a solution of NaOH (0.1 N). The excess gas, escaping from the second bubbler, is tested by a paper impregnated with a solution of KMnO$_4$ (Figure 9). [38]

The temperature was varied from 20 to 70°C, the mass of PG from 1 to 5 g, the degradation time from 15 to 120 min, the mass of Fe from 1 to 5 g and the volume of HCl from 5 to 30 mL. The solid residues were collected, dried in an oven at 110°C for 24 h and then weighed. The weight ratio of the insoluble solid residue relative to the initial mass placed in the reactor ($m_{PG} + m_{Fe} + m_{HCl}$) was determined.

**Characterization techniques**

The X-ray diffraction was carried out on fine crushed powder by a Shimadzu XRD 6100 diffractometer equipped with a Cu X-ray tube (Faculty of sciences, Oujda, Morocco), operating at 40 kV and 30 mA, in the range 200-800 nm (Faculty of Sciences, Oujda, Morocco). The spectra were recorded on diluted aqueous solution of 0.4 cm$^{-1}$ have acquired in a wavelength range of 400–4000 cm$^{-1}$. Powdered samples were mixed with KBr before analysis. UV-Visible spectroscopy was performed by a Jasco V-730 double beam UV/visible spectrophotometer in the range of 200–800 nm (Faculty of sciences, Oujda, Morocco). The spectra were recorded on diluted aqeous suspensions obtained by ultrasonic agitation. The scanning electron microscope (SEM) equipped with energy-dispersive X-ray detectors (EDX), Quanta 200 model, was used to observe microstructure of samples studied.

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**References**


