

Production of Ferrous Sulfate From Steelmaking Mill Scale

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Abstract— Spent pickle liquor from steel manufacturers is usually used to produce ferrous sulfate in the route of acid recovery. This work proposes a new process to be used industrially by which clean mill scale is used as raw material for the production of ferrous sulfate by acid leaching. Process simplicity and abundance of raw material may be invoked as factors that encourage its implementation. In this work, after characterization, a sample of mill scale from a semi-integrated steelmaking plant is leached with sulfuric acid (at concentrations of 5%, 10%, and 15%) inside percolation columns; by recirculation of the acid solution, a liquor rich in Fe²⁺ is produced. Next to the leaching step, the liquor is concentrated by evaporation at the temperature of 80 °C and, in the sequence, is left to cool naturally until room temperature. This procedure allows for the crystallization of ferrous sulfate. To finish, the crystals are collected, purified with ethanol, and characterized by X-ray diffraction. X-ray analysis indicate Melanterite (FeSO₄·7H₂O) as the main compound present in the solid fraction, followed by Szomolnokite (FeSO₄·H₂O) and Rozenite (Fe SO₄·4H₂O).

Index Terms— ferrous sulfate; mill scale; leaching; recycling.

1 INTRODUCTION

A Semi-integrated steel mills are responsible for a large quantity of residues which have to be recycled or properly dispose. In this kind of industry main waste materials are: electric arc furnace dust (EAFD), slags, sludges, and mill scale. They should be recycled, reused or correctly managed in order to avoid environmental damages, minimizing risks and ensuring benefits to the society⁽¹⁾.

Mill scale is a residue from steel hot rolling process and is basically composed of iron oxides and metallic iron with variable oil and grease contents. The specific production of this residue is about 10-20 kg/t of the steel production⁽²⁾. Mill scale can be processed and transformed into environment-friendly concrete blocks (paving products for landscaping area and car parks), eco-bricks, or can be used as iron raw material *e.g.* in self reducing briquettes for the electric arc furnace⁽³⁾. Another possibility – considered in this study – is to employ it as a raw material for the production of ferrous sulfate or Iron (II) sulfate.

Melanterite (FeSO₄·7H₂O) – ferrous sulfate heptahydrate) is the major commercial form of ferrous sulfate and is produced mainly as a by-product of titanium dioxide manufacture⁽⁴⁾ and in steel pickling with sulfuric acid. It has been largely used to control anemia (both in humans and animals), base compound to produce ferric sulfate as well as a reagent for water and wastewater treatment⁽⁵⁾. In Brazil, there is a huge deficit in sulfur-based chemicals, including the Iron (II) sulfate⁽⁶⁾.

The aim of this study is to develop a hydrometallurgical route for the production of ferrous sulfate heptahydrate from mill scale. The study makes use of a sulfuric acid leaching step to dissolve the mill scale and an evaporation/crystallization procedure to produce Melanterite crystals.

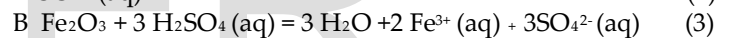
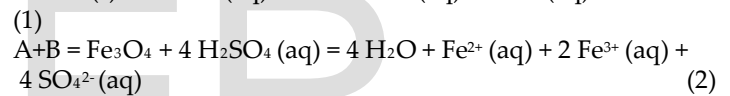
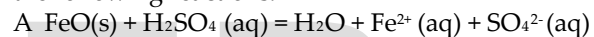
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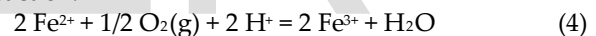
2 THEORETICAL CONSIDERATIONS

2.1 Reactions

With reference to the iron oxides (wustite, hematite and magnetite), acid attack with sulfuric acid can be described by the following reactions:



In presence of oxygen, Fe²⁺ can oxidize to Fe³⁺ by the following reaction:



As indicated by equation (4), the chemical equilibrium that will establish between the ferrous and ferric ions depends on (i) the pH (sulfuric acid concentration) and (ii) the oxygen concentration (redox potential, E_h) in solution. Oxygen (from the atmosphere) is in plentiful supply (at 0.21 atm); nevertheless an anoxic media may establish when oxygen is consumed by chemical or biochemical reactions and no satisfactory renewal takes place (under strongly anoxic condition, its 'partial pressure' can reach very low levels, up to around 1x10⁻⁸³ [atm] – as indicated by the line p_{H₂} = 1 [atm] in Pourbaix diagrams). As expected, pH is manipulated *via* acid addition.

2.2 Thermodynamic Simulation

A thermodynamic simulation based on the software FactSage (version 6.2) was done to anticipate the behavior of the mill scale leaching step in an aqueous solution of sulfuric acid. In this simulation, for the sake of simplicity, only simple iron oxides are allowed as solid phases. Following their self-determining nature, pH and redox potential values varied independently from each other. Values for the logarithm of oxygen pressure ranged from -25 to -50 (with pressure given in atmospheres); the sulfuric acid concentration (molality, m) varied from 0.1 up to 5 (simulation tags along to the following schema: when O₂ pressure varies, molality is kept constant, with m = 3, while, for m as variable, log(pO₂) = -45). For the two conditions surveyed, pH and redox potential were

determined; when displaying these values in a diagram, Figure 1 is obtained. For the sake of completeness, for the conditions studied, the single stable solid oxide phase found in the system is Hematite.

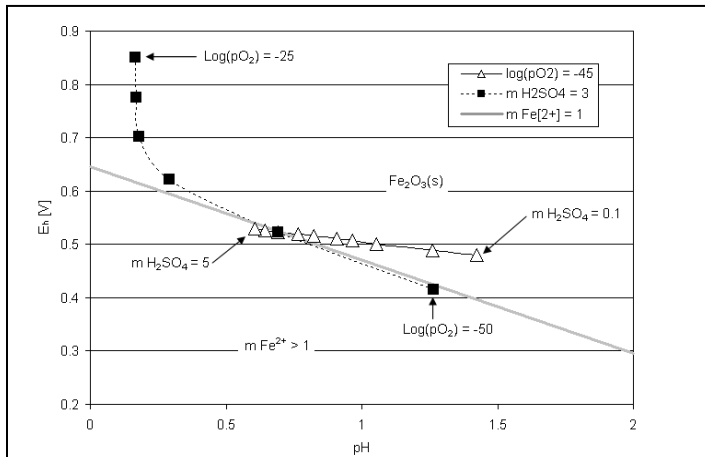


Fig. 1 Diagram displaying redox potential, E_h , and pH result values from thermodynamic simulation (black squares: initial fixed H_2SO_4 molality $m = 3$; white triangles: constant oxygen potential).

In this diagram, concentration of Fe^{2+} in aqueous solution can be seen as a surface which drops from the lower-left to the upper-right corner; for reference, a line was drawn indicating where the concentration equals to 1 mol/kg H_2O (molality $Fe^{2+} = 1$).

Consequently, both effects of lowering the oxygen partial pressure or increasing the sulfuric acid concentration lead to a concentration increase of the ferrous ion in solution; however, solutions which are rich in Fe^{2+} are not easily obtained by varying only one of these factors. As a result, the ideal leaching procedure must be carried out under oxygen deficit and lower pH values.

Therefore, for leaching procedure simulation, the chosen values are: for the logarithm of oxygen pressure -40, -45 and -50 and sulfuric acid molalities up to $m = 10$. Simulation results will be shown later, together with the experimental results. From a comparison between simulation and experiment, it is clear that the chosen ranges were well-located.

3 MATERIALS AND METHODS

3.1 Mill Scale

Sampling of the mill scale used in this study was conducted on-site, at the disposal area of the steel mill. The sample was collected at varying amounts in different parts of the stack, to improve its representativity. The sampling followed procedures described in ABNT Standard NBR 10007:2004. For storage, a plastic barrel with lid was used (sample remained stored in the laboratory for a time period of one week before the beginning of the experimental work).

As the process for the removal of the mill scale is based on jets of water, the amount of oil remaining in the residue used in this study is very low, unable to disturb the leaching process.

3.2 Scale Characterization

After a drying procedure at $105^\circ C$, a particle size analysis of scale was made with a series of Tyler sieves with apertures ranging from 4 to 270 mesh.

A quartered sample of the mill scale was comminuted in a Tecnal orbital disk mill, model TE360 to a particle size -0.074 mm and subjected to a mineralogical and elemental analyses. The majority of the elements present in the mill scale was determined by Inductively Coupled Plasma - Atomic Emission Spectroscopy (sequential ICP-AES, Liberty RL); sample digestion procedure followed the EPA 3050B (7) method.

Mineralogical analysis was performed by X-ray diffraction (Siemens D-500). This analysis was complemented by Mössbauer spectroscopy for a better quantification of iron oxides present in the scale. Finally, a wet chemical analysis of the total iron and zero valent iron was made by the procedure described in ABNT Standard NBR 8577 (8)

3.3 Leaching of Mill Scale

The production of a leachate rich in iron from the mill scale was carried out in the laboratory by means of three Pyrex glass leaching columns (30 cm height, 6,8 cm outer diameter and 6,5 cm inner diameter), each filled with 500 g of scale; a glass frit septum at the base of the column, holds the scale in place, Figure 2.

Mill scale was leached with sulfuric acid (reagent grade Laborsynth) at the following concentrations: 5, 10 and 15 wt.% H_2SO_4 . All of the experiments were carried out at room temperature ($23^\circ C$), in duplicate.

The total volume of leaching solution was kept constant at 1 liter by the addition of deionized water. The leachate recirculation was done by a submerged peristaltic pump (Sarlo Better 300) connected to the leaching system with flexible rubber hoses resistant to acid. The total time of the leaching test was 120 hours each.



Fig. 2 Glass leaching (recirculating) columns.

During the leaching process, the concentrations of Fe^{2+} , Fe^{3+}

and Total Fe was monitored by wet titrimetry ⁽⁹⁾, except for sample digestion, this procedure also followed ABNT Standard NBR 8577:1984. After the leaching step, the solution with 15 wt.% acid concentration was saturated – as small amount of crystallized ferrous sulfate was found on the bottom of the beakers. At the end of the experiment, the mass of scale dissolved by the acid solution was obtained computing the difference between initial and final sample weight.

3.4 Crystallization of Ferrous Sulfate

The leachate was heated to approximately 80 °C (using a heating plate without heating rate control) in order to increase its concentration (with volume reduction up to about 50% of the original volume). In the sequence, the solution was cooled to the room temperature (23 °C) by natural cooling to promote the formation of crystals of iron sulfate, Figure 3 (a) and (b).



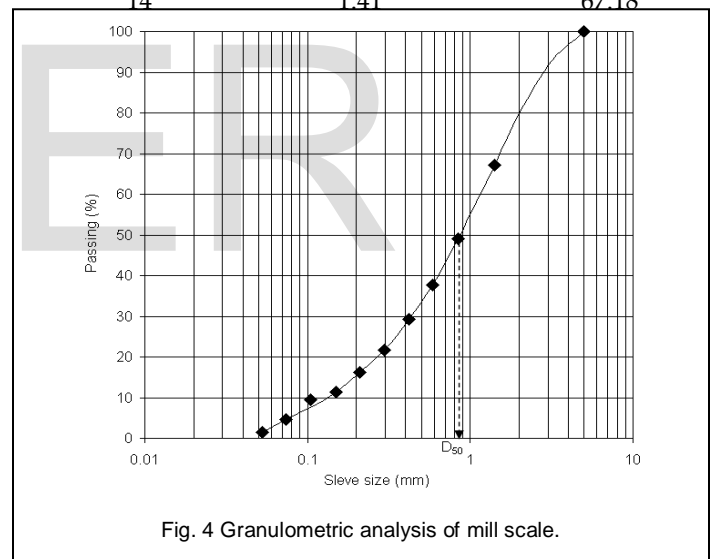
the crystals were characterized by X-ray diffraction.

4 RESULTS AND DISCUSSION

The result of particle size analysis of mill scale used in the experiments can be seen in Table 1 and Figure 4.

TABLE 1
 PARTICLE SIZE CHARACTERIZATION OF MILL SCALE

Tyler scale	Sieve size (mm)	Passing (%)
270	0.053	1.39
200	0.074	4.55
150	0.105	9.38
100	0.149	11.29
65	0.21	16.23
48	0.297	21.71
35	0.42	29.22
28	0.59	37.74
20	0.84	49.02
14	1.41	67.18



Mill scale has the form of platelets and sieve analysis shows that only about 10% of the sample is characterized by having a particle size below 0.1 mm. This low fines content makes the material favorable for application of hydrometallurgical techniques (low clogging danger).

Mill scale is constituted mainly of iron oxides; the chemical characterization of the mill scale by ICP-AES is meant to give an idea of the chemical elements that may contaminate the ferrous sulfate agent; results can be seen in Table 2 (as expected, Fe and oxygen are the most abundant elements).

After rinsing with ethyl alcohol (for the removal of free Fe³⁺, soluble in alcohol ⁽¹⁰⁾ without the oxidation of ferrous ions ⁽¹¹⁾)

TABLE 2.
 CHEMICAL CHARACTERIZATION OF THE MILL SCALE BY ICP-AES.

Elements	WT%
Al	1.95
Cr	0.32
Fe	70.30
Hg	ND
Mn	0.65
Ni	0.10
O	25.80
Si	0.05
W	0.83

TABLE 3
 IRON AND IRON OXIDE PHASES PRESENT IN THE MILL SCALE.

Phase	Amount WT%
Fe ₂ O ₃	6.4
Fe ₃ O ₄	16.5
FeO	67.9
Fe ⁰	2.2
Other	7.0

The results of the mill scale analyses by XRD are presented in Figure 5 and Table 3. XRD analysis detected the following Iron crystalline phases: wustite (predominant), magnetite and hematite. Based on Mössbauer spectroscopy and on the chemical characterization by ICP, Table 1, an adjusted chemical iron and iron oxide composition is presented, Table 2. It can be verified that iron compounds represent 93% of the sample. Wustite (FeO) is found in greatest quantity, followed by magnetite (Fe₃O₄), hematite (Fe₂O₃) and zero valent iron. The non-ferrous compounds, in amounts of about 7% (identified in ICP-AES analysis), are in the form of oxides and their influence was not considered in this work.

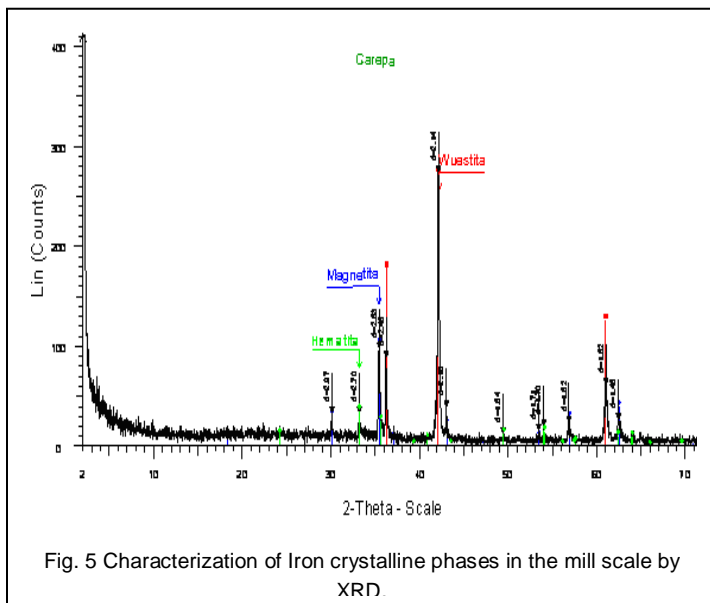


Fig. 5 Characterization of Iron crystalline phases in the mill scale by XRD

next. Figures 6, 7 and 8 show the concentrations of total iron (Fe_{Total}), divalent iron (Fe²⁺) and trivalent iron (Fe³⁺) in the leachate for the three columns during the process of leaching. A gradual increase in ion concentrations during the first 72 hours of testing is clearly seen in all trials; from this point on the values become nearly constant.

This behavior is an indication that the system reached equilibrium, *i.e.*, there will be no more dissolution of the iron mill scale. In this study, this happens for the concentrations of total iron of 36.6, 69.2 and 100 g/L, as shown in Table . These values are applicable for the initial sulfuric acid concentrations of 5, 10 and 15%, respectively.

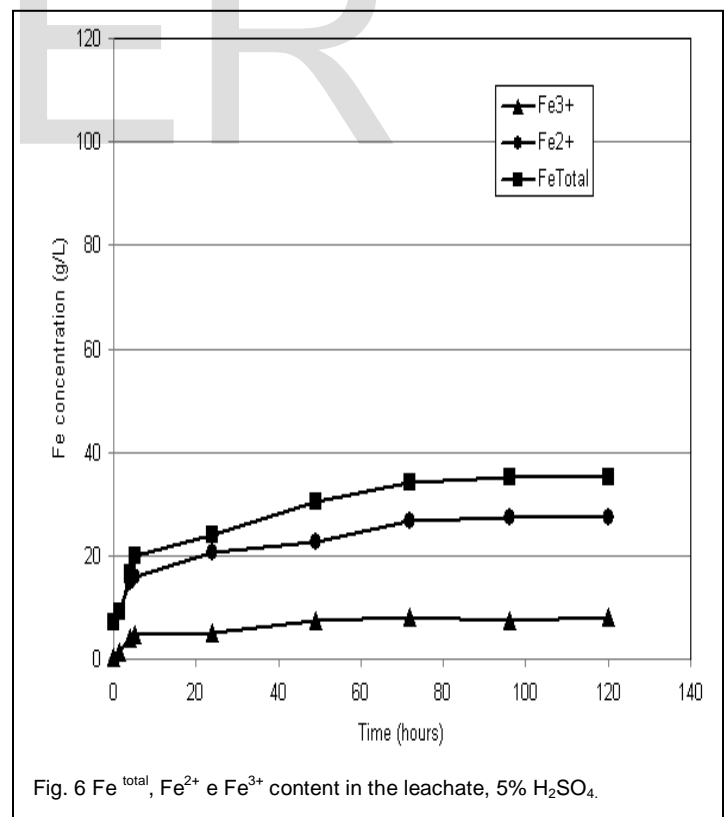


Fig. 6 Fe^{total}, Fe²⁺ e Fe³⁺ content in the leachate, 5% H₂SO₄.

Results from the leaching procedure will be dealt with

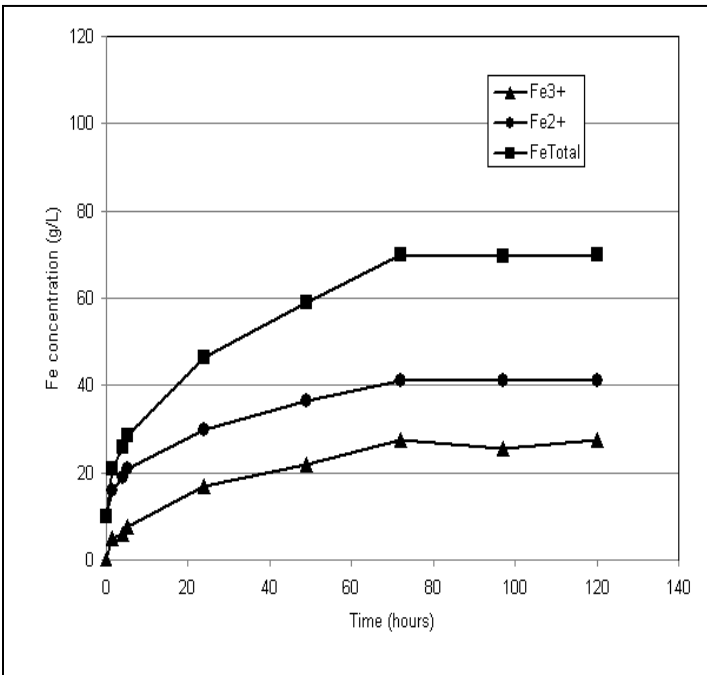


Fig. 7 Fe^{total}, Fe²⁺ e Fe³⁺ content in the leachate, 10% H₂SO₄.

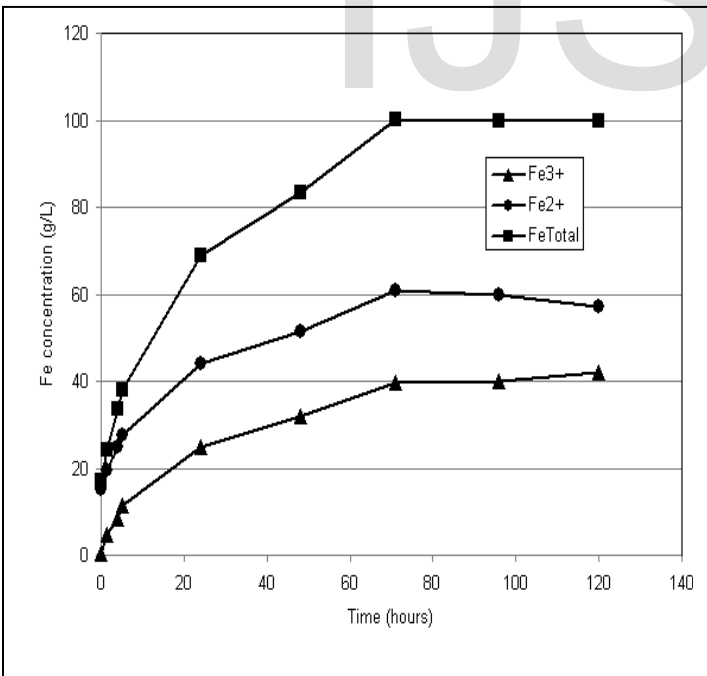


Fig. 8 Fe^{total}, Fe²⁺ e Fe³⁺ content in the leachate, 15% H₂SO₄.

ditions of high acidity and high leaching time, Figure 8. In this case, a relative slight decrease in the concentration of Fe²⁺ over the concentration of Fe³⁺ is observable; this decrease is to be related with the oxidation of Iron (II) sulphate. Table 4 presents the limiting concentration values for the different forms of iron and its percentage at the end of the tests for all the three sulfuric acid concentrations used in the iron mill scale leaching step.

One can also observe from Table 4 that the

TABLE 4
 IRON AND IRON OXIDE PHASES PRESENT IN THE MILL SCALE. LIMITING CONCENTRATIONS FOR DIFFERENT FORMS OF IRON AND ITS PERCENTAGE RELATIVE TO THE END OF LEACHING FOR THREE SULFURIC ACID CONCENTRATIONS.

	Equilibrium concentration [g/L]			Percentage [wt%]		
	H ₂ SO ₄ 5%	10%	15%	5%	10%	15%
Fe _{total}	34.6	69.2	100.0	100.0	100.0	100.0
Fe ²⁺	26.8	42.4	57.5	73.2	61.3	57.5
Fe ³⁺	7.8	26.8	42.5	26.8	38.7	42.5

limiting amount of leached iron increases almost linearly as a function of concentration of sulfuric acid in solution, Figure 9.

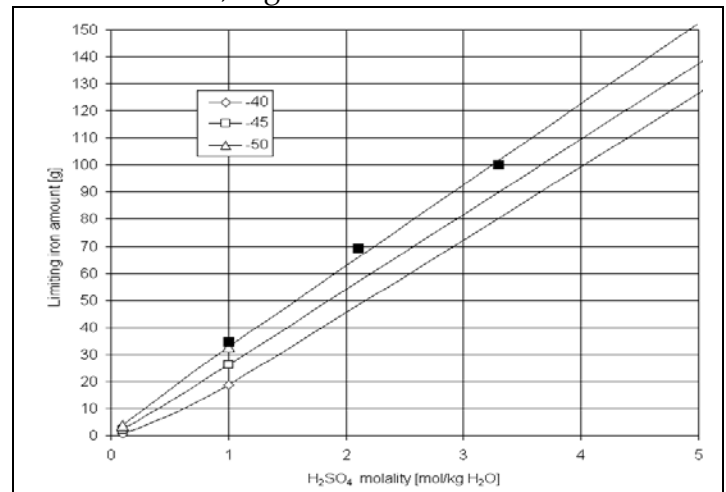


Fig. 9 Limiting amount of iron dissolved in sulfuric acid solution as a function of H₂SO₄ molality for three O₂ pressures; black squares = experimental values.

An exception was observed only under con- dissolved (from thermodynamic simulation) is also

linearly proportional to the molality of H₂SO₄, varying slightly depending on the redox potential.

As observed in Table 4, the ferrous ion despite always being in the majority decreases in proportion to the ferric ion as a function of the increasing concentration of sulfuric acid (given as H₂SO₄ molality), Figure 10. These values fit well the values from the thermodynamic simulation results (Fe³⁺ was taken as the sum of the values of Fe³⁺ and FeSO₄⁺); under strongly anoxic conditions (log (pO₂) = -50) the ratio shows values that greatly favors the formation of *ferrous* ion.

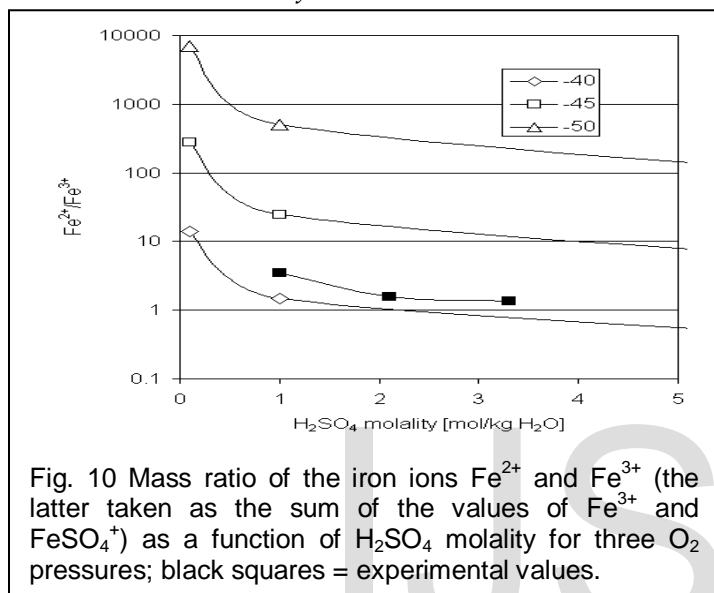


Fig. 10 Mass ratio of the iron ions Fe²⁺ and Fe³⁺ (the latter taken as the sum of the values of Fe³⁺ and FeSO₄⁺) as a function of H₂SO₄ molality for three O₂ pressures; black squares = experimental values.

In addition to the ferrous sulfate crystals, the aqueous phase can also be seen as co-product of the Fe (II) sulfate process, and consists basically of a *ferric* sulfate solution. Ferric sulfate does not crystallize under the experimental conditions; this was confirmed using the thermodynamic tool.

The remaining ferric sulfate solution can be employed, for example, as a coagulant in the treatment of industrial effluents. Upon completion of the tests, the amounts of dissolved mill scale and crystallized ferrous sulfate were determined, Table 5.

In order to characterize and identify the degree of hydration of crystallized ferrous sulfate, an

TABLE 5

AMOUNTS OF DISSOLVED SCALE AND CRYSTALLIZED FERROUS SULFATE AS A FUNCTION OF SULFURIC ACID CONCENTRATION.

	Amount [g]			
	H ₂ SO ₄	5%	10%	15%
Scale dissolved		53.3	72.6	89.0
Crystallized ferrous sulphate		47.7	139.5	197.6

X-ray diffraction analysis of crystals after purification with ethyl alcohol was done. The results, for each of the acid concentrations, are shown in Figures 11, 12 and 13.

For 5% H₂SO₄ the crystalline compound obtained was Melanterite (FeSO₄·7H₂O), Figure 11. At 10% H₂SO₄, in addition to Melanterite, other two phases can be identified: Szomolnokite (FeSO₄·H₂O) and Rozenite (FeSO₄·4H₂O), Figure 12. Under the concentration of 15% H₂SO₄ the predominant crystalline compound is again Melanterite, Figure 13. According to the literature (12) the presence of Szomolnokite and Rozenite may be referred to a certain degree of superheat of the pregnant solution.

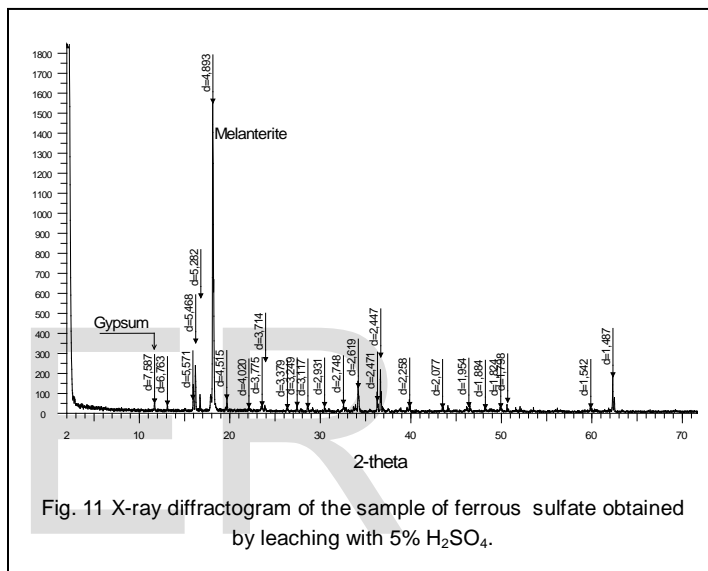


Fig. 11 X-ray diffractogram of the sample of ferrous sulfate obtained by leaching with 5% H₂SO₄.

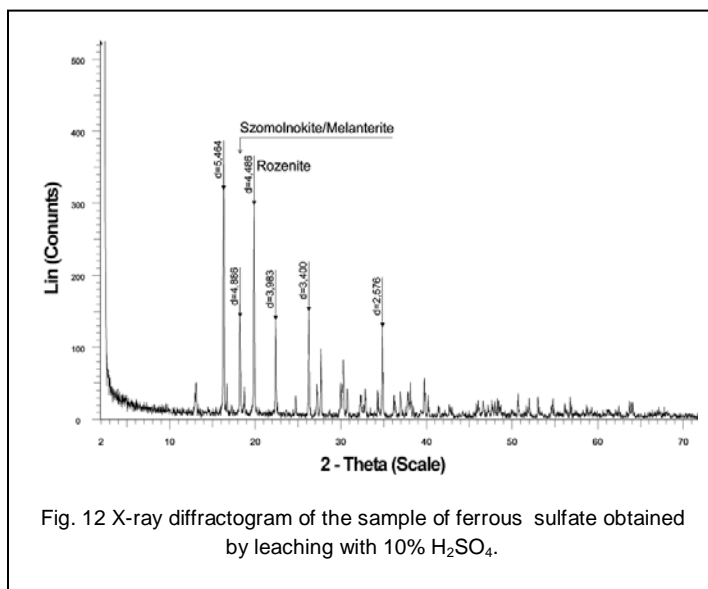


Fig. 12 X-ray diffractogram of the sample of ferrous sulfate obtained by leaching with 10% H₂SO₄.

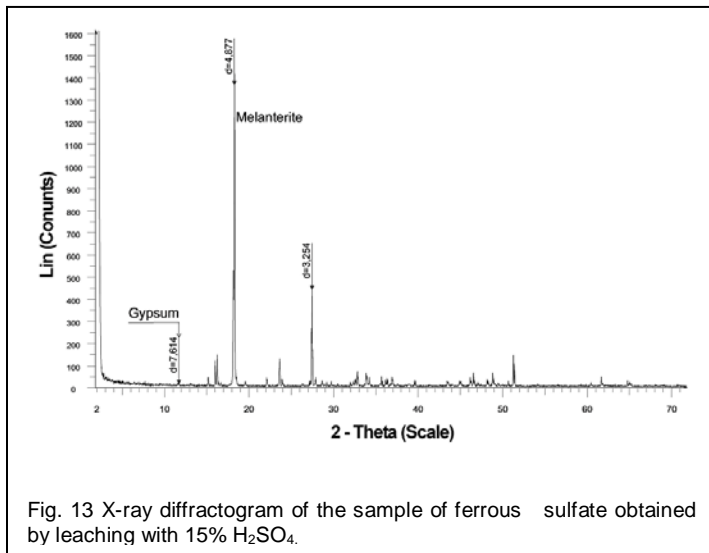


Fig. 13 X-ray diffractogram of the sample of ferrous sulfate obtained by leaching with 15% H₂SO₄.

5 CONCLUSIONS

The results from both experimental and theoretical analyses suggest that Iron (II) sulfate can be produced by the process of mill scale leaching with solutions of sulfuric acid, without the need for special techniques, complex installations or great maintenance.

However, for effective industrial application, complementary studies on a pilot scale are necessary, in order to verify both the technical and economic feasibility of the suggested process.

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