Sulfur Removal from Wadi Halfa Iron Ore Concentrate by Leaching

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Abstract
In this research an attempt was made to remove sulphur content of Wadi-Halfa low grade iron ore and to concentrate the ore as well, combining of roasting and magnetic separation processes were used to treat the ore. The treated ore was leached with diluted Sulphuric acid. The optimum leaching parameters that effect the sulfur removal such as ore particle size, period of time, temperature, sulphuric acid concentration and solid liquid ratio were obtained by a series of experimental conditions. The results of the mineralogical analysis revealed that Goethite (FeO(OH)) and Quartz (SiO2) were the main minerals present in the ore while Trimagnesium Dihydroxide Phillo-tetrasilicate were present in minute amounts. The leaching result showed that the highest percentages of sulphur removal and Fe2O3 increasing at optimum parameters were 62 % and 40 % respectively. Iron loss during acid-leaching can be negligible, which was less than 0.25\%. The value of pH of liquor solution after leaching with 1% sulfuric acid was about 0.86, which means acid would not be exhausted during the process and it could be reused, and the recycle of sulfuric acid solution would make the desulphrization process more economical.

Keywords: Iron Ore, Roasting, Sulphuric Acid, Leaching.

1. Introduction
A law-grade, oolitic iron ore body which is hematite mineralization is located in Wadi-Halfa town, Northern Province, Sudan. The geological estimated reserve of iron ore deposit is about 1.234 billion tonnage at a head of grade of 41.29\% Fe. The types of iron ore minerals are mainly of goethite and hematite, but all the iron ore rocks and mines contain sulfide minerals. The sulfur content of iron ore concentrates is generally about 0.2\% to 0.5\%, while the permitted limit of steel industries is 0.1\%.[1]

One of the important detrimental impurities in iron ore is sulfur, which greatly affects the iron ore concentrate price. Moreover, high sulfur contents in steel decrease its quality. In addition, the presence of sulfur in iron ore concentrates causes environmental problems, especially sulfur dioxide emissions during the pelletizing or smelting process. Furthermore, with current developments in direct reduction of the concentrate to sponge iron without pelletizing, a concentrate with high-sulfur content cannot be used in direct reduction. For these reasons various studies have been increasingly performed to decrease or remove sulfur from iron ore or concentrate before they enter the pelletizing process or blast furnace [2].

Sulfur with Small amounts in iron have significant deleterious effects on the final properties of products (such as red and hot shortness). In this case, sulphur can exist as either iron sulfide (FeS), which tends to produce cementite leading to a harder iron, or as manganese sulfide (MnS), which hardens the iron [3]. There are minimum specifications for trace elements, including sulphur, phosphorus, and most of the transition metals. These specifications though are not usually applied to...
the ore only, but to the general blast furnace burden. The generalized iron ore specifications for the acceptable contents of sulphur in commercial ores should be lower 0.1% S [3]. The processes of hydrometallurgical have become more significant in metal extraction and production in comparison to pyro-metallurgical processes. In pyro- metallurgical processes the energy consumption is higher than in hydrometallurgical processes and hence energy consumption costs are reduced by using hydrometallurgical processes. Optimized hydrometallurgical processes, are more economical and environmentally friendly processes can be obtained. Several studies have been made regarding hydrometallurgical leaching methods, such as biochemical leaching [4] and acidic dissolution [5].

All metal sulfides are leached for example by using sulfuric acid, iron(III) sulfate or ammonium hydroxide together with air. Leaching can be carried out either in the absence or presence of an oxidizing agent. The solid sulfide is dissociated in the aqueous phase as is described in this equation. MS → M^{2+} + S^{2-}. Acid soluble, alkali soluble and complex forming sulfides may be leached in the absence of oxidizing agents, i.e. under reducing conditions. Depending if the sulfides dissolve in acids or in bases either H2S or S2 is formed respectively. NiS, FeS and CoS are all acid soluble sulfides whereas PbS is an alkali soluble sulfide. ZnS is both soluble in acid and alkali [6].

### 1.1 Chemical Reactions

In general, under oxidant condition and low pH, pyrite oxidation proceeds through two basic steps: In the first step, the dissolution of pyrite to ferrous ions in an acid medium proceeds through the formation of an iron-deficient or a sulfur-rich layer rather than elemental sulfur.

In the second step, further oxidation of this layer occurs, forming sulfides of lower iron content, and eventually are converted to elemental sulfur. In severely oxidizing conditions, the elemental sulfur could be oxidized to oxy-sulfuric species. Anodic reactions, such as pyrite and sulfur oxidations, are sustained by cathodic processes, which could involve oxygen, hydrogen peroxide, or even ozone reduction. The importance of this analysis is based on the fact that, under certain conditions, such as pH, redox potential, temperature, etc., the product layer is protective, thus limiting pyrite oxidation.

Despite the existing discrepancies about the exact composition of the oxidation products, the most well-known general mechanism of pyrite oxidation is described in Eq 1

\[
\text{FeS}_2 = \text{Fe}^{2+} + 2\text{S}^0 + 2e^-
\]  

(1)

Elemental sulfur is stable at low pH and redox potential and could be oxidized to sulfate by molecular oxygen and ferric ions at higher potentials (Eq 2).

\[
\text{FeS}_2 + 8\text{H}_2\text{O} = \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 15e^-
\]  

(2)

The pyrite dissolution has been characterized in the following media:

i. in the presence of oxygen at high pressure and temperature

\[
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4
\]  

(3)

\[
\text{FeS}_2 + 2\text{O}_2 = \text{FeSO}_4 + \text{S}^0
\]  

(4)

ii. in sulfuric acid solutions

\[
2\text{FeS}_2 + 2\text{H}_2\text{SO}_4 + 3\text{O}_2 = \text{Fe}_2(\text{SO}_4)_3 + 3\text{S}^0 + 2\text{H}_2\text{O}
\]  

(5)

When a metal sulfide (MS) is brought into contact with an oxidizing source the following reaction will occur:

\[
2\text{MS} + 3\text{O}_2 \rightarrow 2\text{MO} + 2\text{SO}_2
\]  

(6)

Sulfur dioxide in the presence of oxygen is further oxidized to sulfur trioxide as follows:

\[
2\text{SO}_2 + 2\text{O}_2 \leftrightarrow 2\text{SO}_3
\]  

(7)
An additional or alternate source of sulfur trioxide is obtained by heating sulfuric acid according to the following equation:

\[ 4H_2SO_4 \rightarrow 4H_2O + 4SO_3 \] (8)

Sulfur trioxide in turn reacts with metal oxides as follows:

\[ MO + SO_3 \leftrightarrow 3MSO_4 \] (9)

By combining the above equations one arrives at the overall equation,

\[ 2MS + 4O_2 \rightarrow 2MSO_4 \] (10)

It is evident from the above that in order to obtain complete conversion of a metal sulfide or oxide to the soluble sulfate it is necessary to oxidize the sulfur present into its highest oxidation state, i.e., MS to SO2 to SO3 to MSO4 . For example, higher concentrations or partial pressures of SO2 will result in more SO3 being formed and higher partial pressures of SO3 will result in the formation of more sulfates(1)

The dissolution of Sulfur minerals in leaching process is obtained through an electrochemical reaction between sulfide ion and oxygen. Sulfide is oxidized to elemental sulfur, sulfite or sulfate ions (Rusanen et al., 2013).[9]

2. Materials and Methods

2.1 Sample Collection and Preparation

The sample of the iron ore used for this research work was obtained from Wadi-Halfa low grade Iron ore deposit in Northern State, Sudan. 10kg of the Samples were collected from different points on the deposit by random sampling method. Fore pre concentration of the head samples the ore was crushed and ground respectively. The ground ore was roasted at 800 0C, separated by magnetic separator and sieved by sieve shaker to produce four different particle sizes fractions (-250 +212µm, -212 +180µm, -180 +150µm, -150 +125µm, and -125 +105µm).

2.1.1 Chemical Composition:

The determination of the chemical composition, mineralogy and photo microscopy of the head Sample are shown in Table 1 and Fig. 1, respectively. The XRF was done in the Geological Research Authority of the Sudan, Khartoum, Sudan.

2.1.2 Mineralogical Composition:

Mineralogical characterization of the head sample of the Wadi-Halfa iron ore was carried out using XRD and photomicrography (polishing and thin section) analysis for the rocky head sample were carried out in faculty of mining, Alnelain University, Khartoum, Sudan using transmission and reflection Photomicroscopy model NONAMP - 211M, NXA 0018, made in Russia, to determine the composition and the liberation particle size for the iron oxide in the ore respectively.

2.1.3 Determination of Sulfur Content for the Different Particle Sizes:

The amount of Sulphur content of each particle size was carried out, by using EDS / FP and Elemental Analyzer model G4 ICARUS HF (Manufactured by Bruker). The result obtained was illustrated in figure 3.1.

2.2 Leaching Procedures:

The leaching process was carried out in five stages:

Stage I: The Effect of Particle Size:

15g of -125 +105µm particle size was
transferred into beaker Borocilicate3.3, 100 ml containing 30 ml of 0.7M sulphuric acid at temperature of 65°C. The mixture was put on an electric hot plate heater with magnetic stirrer and agitated at a constant rate of 600rpm. The mixture was leached for a constant time of 1.5hr. After the completion of the leaching the solid residues produced were filtered through a 0.45 μm filter and dried in an oven at 105°C for 24 hours then analyzed. The process was repeated for other the particle sizes of -250 +212µm, -212 +180µm, -180 +150µm and -150 +125µm.

Stage II: The Effect of Time:

From stage I the best particle size for Sulphur removal was determined. The leaching in this stage was carried out at the best particle size of -125 + 105µm and an initial time varying from 0.5, 1.2,3, and 4 hours with the constant of other parameter such as acid concentration (0.7M) of sulphuric acid, agitation of 600rpm, temperature of 65°C after which the solution was filtered and the residue was washed with distilled water thoroughly, dried in an oven at 105°C for 24 hours and taken for analyses.

Stage III: The Effect of Temperature:

With the optimum parameters developed from stages one and two for particle size and time respectively, were used to determine the effect of the variation of temperature from 25 to 1050°C at an interval of 200°C at constant of 0.7M of sulphuric acid concentration and agitation speed of 600rpm was carried out. After which the solution was filtered and the residue was washed with distilled water thoroughly, dried in an oven at 105°C for 24 hours and taken for analyses.

Stage IV: The Effect of Sulphuric Acid Concentrations:

The above process was repeated with different concentrations of sulphuric acid which varying from 0.1 – 1.3M at an interval of 0.3M, at the constant of optimum parameters (particle size, time, temperature and agitation speed) stated above was carried out.

Stage V: The Effect of the Solid Liquid Ratio:

In this stage the effect of the solid liquid ratio of 1:0.7, 1:1, 1:1.5 and 1:2 were investigated, by repeating the same leaching process at a constant of optimum conditions developed above from stages I - IV.

From the above procedures the best leaching parameters were attained thereafter the amount of sulphur removal from the optimum leaching process was determined by measuring the amount of sulfurs before and after the process, by using this equation

\[ RS = \frac{\%SB - \%SA}{\%SB} \times 100 \]

Where: RS = Reduction in Sulphur Content (

\( SA = \) Sulphur content after leaching (%)

\( SB = \) Sulphur content before leaching (%)

3. Characterization the Head Sample

3.1 Head Sample Results

3.1.1 Result of XRF for Head Sample:

The results of the chemical analysis by using XRF (FP), mineralogy analysis by using XRD and photo microscopy of the head Sample are shown in Table 1, Figure. 1, Figure 2a Figure 2b and respectively.

Table 3.1: XRF analysis of head sample showing constituent oxides and percentage composition.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>% result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe2O3</td>
<td>47.68</td>
</tr>
<tr>
<td>SiO2</td>
<td>54.31</td>
</tr>
<tr>
<td>MgO</td>
<td>0.20</td>
</tr>
<tr>
<td>Al2O3</td>
<td>2.37</td>
</tr>
<tr>
<td>MnO</td>
<td>1.10</td>
</tr>
<tr>
<td>S</td>
<td>0.36</td>
</tr>
<tr>
<td>CaO</td>
<td>2.48</td>
</tr>
<tr>
<td>K2O</td>
<td>0.95</td>
</tr>
</tbody>
</table>

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The percentage of total iron in the ore is 47.68% and SiO2 is 54.31%. The minor elements in the ore are Mn, Ca, Mg, Ti, Al, Cr, K, and S. ZrO2 is recorded at trace levels. So this ore is low grade high silica and sulphur content.

3.1.2 Result of XRD for Head Sample:

From the result presented in Table 3.1 and Figure 3.1, it was indicated that iron ore under study is low great and high silica and sulphur content [10].

3.1.3 Result of Photomicroscope (Mag.X40) for Head Sample Analysis:

The Figure 3.2a illustrated that the iron ore composed from these compounds, medium to coarse grain sand courses of quartz 60% (mono crystalline and poly crystalline), feldspar5%, mica2% and iron oxide 22% these minerals cemented by iron oxide(ferruginous), the matrix about (15-75) % greywacke and this rock immature (physically and chemically) and there is sorting moderately to poorly sorted. These results agree very well with the data of chemical compositions of these ores.

The Figure 3.2b: illustrated the particle sizes of the two main components (iron oxide and quartz), witch facilitated the measuring of iron ore average liberation particle size, so it was about 5mm.

Table 3.2: Result of Elemental Sulphur after receiving Analysis:

<table>
<thead>
<tr>
<th>particle sizes µm</th>
<th>Sulphur content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>-212 +180</td>
<td>0.2069</td>
</tr>
<tr>
<td>-180 +150</td>
<td>0.2093</td>
</tr>
<tr>
<td>-150 +125</td>
<td>0.2152</td>
</tr>
<tr>
<td>-125 +105</td>
<td>0.2312</td>
</tr>
</tbody>
</table>

The result of elemental analyzer revealed that the Sulphur content increases as the particle size decreases. So the highest content is in +125 -105 µm sieve size, which was taken for the leaching process.
Result of XRD after Pre Concentration of the Head Samples:

![XRD Pattern](image)

**Figure 3.3 XRD Pattern for Pre Concentrated (after Roasted) Iron Ore**

The chemical analysis and mineralogical studies were performed before and after the roasting process. As shown in table 4.1, Figure. 4.1 and Figure. 4.2, illustrated that the iron peak was increased from 26.4% to 34.3% from XRD pattern after roasting, this is due to converting of hematite to magnetite under heating condition. In addition, the peak of quartz witch is big impurity was decreased from 58.2% to 53.3% and the impurity peak of silicate component was also decreased from 5.5% to 3.3%. These results emphasized that the importance of roasting process as a pre concentrate for iron ores.

The result of leaching process: As the leaching process was carried out in five stages, so their results were:

**The result of stage I:** (The effect of particle size) was shown in figure 3.3.1, at the constant of sulphuric acid concentration at 0.7, temperature of 45 0C, period of time at 1.5 hour and solid liquid ratio of 1:10.

For each particle size, the sulfur content of the concentrate was measured to determine the optimum particle size.

![Graph](image)

**Figure 3.3.1: The effect of particle size on the % degree of Reduction of Sulphur using H2SO4.**

From the result presented in Figure 3.3.1, it was found that the leaching efficiency increased with the decreasing the particle size of the pre concentrate sample. Thus, when the particle size decreased from -212 µm to -125 µm, the percent of sulfur removed increased because the reaction rate of a solid-liquid phase reaction depends on the surface area particle size of the solid phase, indicating that large particle sizes do not favour the reduction of sulphur content.

**The Result of stage II:** (The effect of time) was shown in figure 3.3.2 at the constant of sulphuric acid concentration at 0.7, temperature of 450C, Particle size of (-125 + 105), and solid liquid ratio of 1:10.

For each period of time, the sulfur content of the concentrate was measured to determine the optimum period of time.

![Graph](image)

**Figure 3.3.2: The Effect of Time (hr.) on the % degree of Reduction of Sulphur using H2SO4**
As shown in Figure.3.3. 2, the increasing the leaching time up to 3 hr increased the sulfur removal while the sulfur content of the concentrate leveled off after 3 hr. The sulfide minerals in the iron ore concentrate contacted longer with the leaching agent with the increasing leaching time, hence the leaching reaction efficiency increased.

**The result of stage III:** (The effect of temperature) As it was shown in figure 3.3.3, at the constant of sulphuric acid concentration at 0.7, period of time at 1.5 hour, particle size of (-125 + 105), and solid liquid ratio of 1:10.

For each temperature, the sulfur content of the concentrate was measured to determine the optimum temperature.

![Figure 3.3.3](image1.png)

**Figure 3.3.3:** The effect of temperature $^0$C on the % degree of Reduction of Sulphur using H$_2$SO$_4$.

According to the results shown in Figure.3.3. 3, the oxidation of sulfur minerals increased significantly with the increasing temperature because of the enhancing the activation energy for the sulfide minerals oxidation. Besides, the reactants move faster at elevated temperatures, resulting in more rapid dissolution of sulfide minerals. But at temperature above 850 $^0$C, evaporation problem of leaching agent appeared.

**The result of stage IV:** (The effect of sulphuric acid concentration) was shown in figure 3.3.4, at the constant of temperature at 45 $^0$C, period of time at 1.5 hour, particle size of (-125 + 105) and solid liquid ratio of 1:10.

![Figure 3.3.4](image2.png)

**Figure 3.3.4:** The effect of acid concentration (M) on the % degree of reduction of sulphur.

The figure 3.3.4 showed the amount of sulphur removed increasing significantly with the increasing of sulphuric acid concentration this is due to the increasing pressure of SO$_3$ in the solution which promote the formation of dissolved iron sulphate.

**The result of stage V:** (The effect of solid liquid ratio) was shown in figure 3.3.5, at the constant of sulphuric acid concentration at 0.7, temperature of 45 $^0$C, period of time at 1.5 hour and, particle size of (-125 + 105).

![Figure 3.3.5](image3.png)

**Figure 3.3.5:** Effect of Solid Liquid Ratio on the % degree of Reduction of Sulphur using H$_2$SO$_4$.

As a result, from Figure. 3.3.5 the amount of Sulphur removed increasing significantly with the increasing of solid liquid ratio till a certain ratio after that the amount of Sulphur removed
still constant, this is due to the increasing the availability of contacting between solid phase and liquid phase, which enhances the rapid dissolution of sulphide minerals.

**Leaching effect on removal of other impurities:**

In addition to the main object of this research was to remove sulphur from iron ore concentrate, the experiments results showed that CaO was also decreased from 2.482% to 0.223% because CaO mineral can be dissolved in the acidic leaching solution.

**4. Conclusion**

In this research work, the chemical leaching process (acid leaching) was used for the removal of sulfur from the iron ore concentrate in order to achieve a high-quality iron ore for steel-making industry, adding value to iron ore concentrate and finally, decreasing the environmental problems, especially sulfur dioxide emissions during the pelletizing or smelting process.

Several experimental parameters were optimized to improve the rate of sulfur removal and efficiency of the process. The results obtained from this study showed that sulfur removal was higher at elevated temperatures. The sulfur removal was observed to have a linear dependence upon the particle size of the concentrate with a gentle slope.

One of the important advantages of the proposed method is the transformation of mineral pyrites and other sulfur minerals in the iron ore concentrate to useful by-products such as elemental sulfur. After leaching process, the produced elemental sulfur which is in the concentrate matrix may then be separated by magnetic separation of the concentrate.

The large deposit of Wadi-Hafa iron ore which was initial adjudged as not suitable for the production of Direct Reduced Iron (DRI) and for the usage at the Blast Furnace due to the harmful nature of the ore because of high sulphur of 0.35% could be drastically be reduced.

**References**


