

سمپوزيوم فولاد ۹۳ ۵ و ۶ اسفندماه ۱۳۹۳ یزد، مجتمع معدنی و صنعتی اردکان



# Sulfur removal from iron ore concentrate by leaching

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#### Abstract

High Sulfur iron ore concentrates causes several problems in steel making process and hence affect the concentrate price. Also its lead to environmental issues such as sulfur dioxide emissions during the concentrate pelletizing process. The current study is focused on the removal of sulfur from iron ore concentrate using chemical leaching technique. Magnetite iron ore concentrate were chosen for the study. Laboratory results are presented here. These results show that more than 90% of the total sulfur content, can be removed from iron ore concentrate by chemical leaching. The background for the process concept and a summary of the results are presented below. Effect of several parameters such as temperature, particle size on sulfur removal was studied by series of experimental conditions. Experimental results demonstrate that the sulfur removal was enhanced with the increase in temperature and Increasing temperature was more important in sulfur removal than decreasing particle size.

Keywords: sulfur removal, chemical leaching, pyrite removal.

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# Introduction

The high grade magnetite hematite iron ore deposit is in the Golgohar mine, located in Sirjan in the Kerman province in Iran. The geological proven reserve is about 1200 Tg (teragrams) and The Gole-gohar complex with about provides production of 5 Tg/year of concentrates 0. The iron ore mineral is composed mainly by magnetite and hematite, but Many of the iron ore rocks and mines contain sulfide minerals, such as pyrite, chalcopyrite, arsenopyrite, etc. the sulfur content in iron ore concentrate is generally 0.5 to 2%, sometimes more than 0.7%, while the steel industrial permitted limit is 0.1% 0. on the other hand sulfur percentage increase with depth and mine development and hence this problem is more serious at future. thus Sulfur is one of the major important impurity in iron ore and It's presence greatly affect on iron ore concentrate price and will seriously impact the after work iron and steel metallurgical processes, and finally it will lead to excessive sulfur content of steel, thus affecting the quality of steel. Also sulfur in iron ore concentrate causes environmental issues, especially sulfur dioxide emissions during the pelletizing or smelting process. Furthermore by recent developments in direct reduction of concentrate to sponge iron without pelletizing, concentrate with high sulfur content cannot use in direct reduction. For this reasons it is becoming increasingly to remove or decrease sulfur from iron ore or concentrate before they enter the pelletizing process or blast furnace.

Up to now Much research has been done to remove sulfur from iron ore. Sulfur removal can be performed by two main methods: conventional hydrometallurgical method (smelting/converting) and hydrometallurgical method (leaching or bioleaching). The sulfur content reduction in iron ores is conventionally carried out by Floatation after grinding. The research work about sulfur removal from iron ore through floatation by several authors has been carried out in the literature 0, 0, 0. In hydrometallurgical method ore must be broken down by chemical materials or bacterial leaching where the metal-sulfur mineral bond is broken by hydrogenolysis to produce elemental sulfur or metal sulfates or sulfites. Bioleaching usually involves Oxidation of insoluble metal sulphides to soluble metal sulfates by biological process. J. T. Pronk et al and ALAFARA A. BABA et al reported the biological oxidation of pyrite to ferric sulphate and sulfuric acid 0, 0.

Leaching process has often been used to recovery of precious metals from mining ores. Removal of impurities and dissolution of sulfur minerals based on leaching process especially for coal cleaning were reported 0, 0.

The current study is focused on controlling sulfur emissions by pre-treating iron ore concentrate to remove sulfur by leaching technique. Technically chemicals are used to react with the sulfur bearing minerals in iron ore to convert them into a soluble fraction, resulting in easy separation from the insoluble solid phase. Since the amount of iron ore concentrate must be treated is huge, Process should be used with low product loss during the chemical leaching reaction. It must be economically affordable in raw materials and operating costs. Other important parameter is the process operating time that should be low as possible.

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In order to provide an economically viable process for dissolution of mineral sulfur it would be necessary to found a selective and regenerable chemical agent to dissolution of mineral sulfur. The Reasons for nitric acid selection for leaching agent are: (i) Its powerful oxidizing agent, that's strong enough to dissolve sulfide minerals (iii) it's can't dissolve iron oxides (ii) the leaching agent can be regenerated or recycled.

Nitric acid completely dissociates in water and oxidation leaching of sulfide ores may be represented by ovearl reaction:

$$3MeS(s) + 2HNO_3(aq) + 3H_2SO_4(aq) = 3MeSO_4 + 3S(s) + 2NO(g) + 4H_2O$$
 (1)

and several half reactions as follows 0, 0, 0:

| $NO_3^- + 2H^+ + e^- = NO_2(g) + H_2O; E^0 = +0.81 V$  | (2) |
|--|-----|
| $NO_3^- + 3H^+ + 2e^- = HNO_2(aq) + H_2O; E^0 = +0.94 V$   | (3) |
| $NO_3^- + 4H^+ + 3e^- = NO(g) + H_2O; E^0 = +0.96 V$   | (4) |
| $2 \text{ NO}_3^- + 10\text{H}^+ + 8\text{e}_{-} = \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}; \text{ E E}^0 = +1.11 \text{ V}$ | (5) |

Also the return of nitric acid to leaching cycle is possible. 0, 0, 0, 0, 0. Sulfur dissolution of minerals in leaching process is done through an electrochemical reaction between sulfide ion and oxygen. Sulfide sulfur is oxidized either into elemental sulfur, sulfite or sulfate ions 0.

The following research, discusses and investigate the influence of physico-chemical leaching parameters such as temperature, particle size on the dissolution of sulfur minerals in an oxidative medium to find out the optimum conditions.

# Experimental, materials and methods Sample collection and grinding

The iron ore concentrate samples from Gole-gohar complex were used in this study. These samples were taken from conveyor located after ball mill grinder and wet manetic separation where the magnetite iron ore is enriched. After collection, samples dried, homogenized and were used in all of the experiments. to ensure homogeneity and having a representative sample every 8 hours about 300 g sample collected for 10 days. The particle size of the concentrate was -100  $\mu$ m. In order to prevent separation of sulfur minerals by sieving, particle size fraction wasn't done by sieve, instead of this, preparation of smaller particle size was done through ball mill crusher in experiments on the effect of particle size investigation.

#### Solutions, chemicals and experimental procedure

The leach solutions used in this study were prepared by adding the 4 ml concentrate nitric and 0.7 ml sulfuric acid to deionized water before a leaching process. Deionized water was used in the preparation of all aqueous solutions.

The leaching process were done in a 250ml Erlenmeyer flask on electric heater. For each leaching treatment, 20g concentrate sample and 100ml deionized water was conducted in to 250ml Erlenmeyer flask, nitric and sulfuric acid was then added and heating started for time is needed. After leaching time, the solid residues after

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completing the leaching tests were filtered through a  $0.45\mu m$  filter and stored in an desiecrator until were examined. For elemental sulfur removal that produced in leaching process, The filtered sample extract with toluene solvent.

Leaching process efficiency was determined by measuring the amount of sulfur before and after concentrate contact with leaching solution and organic solvent extraction.

#### **Results and discussions**

In leaching process several parameters can affect the process and proposed method efficiency was measured and investigated at various physical and chemical conditions.

#### **Effect of temperature**

Temperature affects the rate of chemical reactions, hence the effect of this parameter on leaching efficiency were investigated. For this purpose the experiments were performed in the 70-100°C range at constant leaching agent concentration and particle size for 3h as shown in table (1). In separate experiments at different temperatures, concentrate sulfur content was measured to determine the optimum temperature. The results were plotted in Fig. 1. According to this results that oxidation of sulfur content minerals increases significantly at elevated temperature .

## Effect of leaching time

To investigate the optimum time for leaching process, sulfur content of concentrate was monitored as a function of leaching time. In the time intervals about 2g sample was taken from leaching flask, filtered and after drying, extracted by toluene, then dried and finally cooled in desiccators and sulfur content was measured. As shown in table (2) and Fig. (2) the concentrate sulfur content was plot against the leaching time. After 3h, sulfur removal is constant.

# Effect of particle size

A series of experiments was done to determine the effect of particle size on sulfur reduction in leaching process. Three concentrate particle size (100 mm, 76mm, 45 mm) were made by grinding in ball mill as explained in section 2.1. the reaction temperature and time was kept constant. The sulfur content of different particle size recorded in Table (3). From this results we found that leaching efficiency

# Effect of organic solvent

As mentioned in introduction section, elemental sulfur is one of the leaching byproducts and it should separate from concentrate. This can be done easily by a magnetic separator in industrial process or Davis tube in laboratory process but we use organic solvent extraction instead of Davis tube in experiments because we want investigate only the leaching efficiency on sulfur removal and hence for prevent sulfur

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removal by magnetization in Davis tube, toluene was used to extraction of elemental sulfur from leached concentrate. As shown in table (4) sulfur removal without solvent extraction is significantly lower than than the process with solvent extraction and this confirms that some of sulfurs in mineral pyrite converted to elemental sulfur through reaction(2-2).

#### Conclusions

In this study leaching process was used for sulfur removal from concentrate in order to having a better quality raw material for steel making industry, increasing concentrate price and finally decreasing environmental issues, especially sulfur dioxide emissions during the pelletizing or smelting process. Also as mentioned in introduction section in direct reduction of concentrate to sponge iron without pelletizing, concentrate with low sulfur can use.

Effect of several parameters were investigated to improve the rate and process efficiency. From the results obtained from temperature effect investigation, sulfur removal rate depend on temperature and significantly increase in elevated temperatures.

In proposed process it can be found that although sulfur removal increase with the decrease of particle size but not significantly. It's interestingly, the sulfur removal has a linear dependence to particle size So that the particle size decreases from 100  $\mu$ m to 45  $\mu$ m, sulfur removal percent shifted only from 91 to 95%. It said that desulfurization lower than 100  $\mu$ m should not depend on the particle size. So the iron concentrate needn't to regrind in leaching process. This fact can be attributed to the Mineralogy studies on leached concentrate show that proposed method leach sulfur from Sulfur minerals which could be separated, associated or inclusion in iron oxide concentrates.

One big advantage of our proposed method is using of mineral pyrites to useful byproducts. as shown in section 2.4 when we use organic solvent, the sulfur removal increases from about 73% to about 91%, thus the some of the sulfur in sulfur containing minerals convert to elemental sulfur that can use as a by-product.

#### Acknowledgements

The financial support of this work by Gole-gohar iron ore complex Research is gratefully acknowledged. Also we greatly acknowledge Mr. Darreh Zereshki whose guides us about the topics.

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| Particle size | Leaching temperature ( <sup>0</sup> C) | perature ( <sup>0</sup> C) Concentrate S content |      |
|---------------|--|--|------|
| -100 µm       | 70                                     | 0.99%  | 40.0 |
| -100 µm       | 80                                     | 0.61%  | 63.0 |
| -100 µm       | 90                                     | 0.42%  | 74.5 |
| -100 µm       | 100                                    | 0.33 %   | 80.0 |

Table 1. Effect of temperature on the sulfur removal from concentratewith 1.65% sulfur comtent.

Table 2. Effect of leaching time on leaching efficiency.

| Particle size | Leaching time (h) | %S after leaching | %S removal |
|---------------|-------------------|-------------------|------------|
| -100 µm       | 0                 | 1.65              | 0          |
| -100 µm       | 0.5               | 0.65              | 60.6       |
| -100 µm       | 1                 | 0.44              | 73.3       |
| -100 µm       | 2                 | 0.25              | 84.8       |
| -100 µm       | 3                 | 0.19              | 88.5       |
| -100 µm       | 4                 | 0.13              | 92.1       |
| -100 µm       | 5                 | 0.12              | 92.7       |

Table 3. Effect of particle size on removal of sulfur from concentrate.

| Particle size | Leaching time (h) | Concentrate sulfur content | %S removal |
|---------------|-------------------|----------------------------|------------|
| -45 μm        | 3                 | 0.08                       | 95.0       |
| -76 µm        | 3                 | 0.12                       | 92.8       |
| -100 µm       | 3                 | 0.13                       | 91.5       |

Table 4. Organic solvent extraction effect on sulfur removalfrom iron ore concentrate.

| Particle size | Leaching time (h) | S content after leaching | %S<br>removal | Extraction agent |
|---------------|-------------------|--------------------------|---------------|------------------|
| -100 µm       | 2                 | 0.71%                    | 57            |                  |
| -100 µm       | 2                 | 0.24%                    | 85.5          | toluene          |

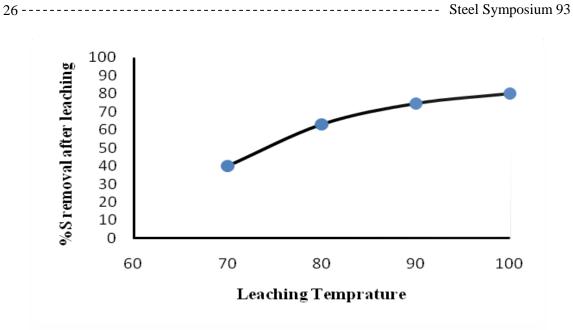


Fig. 1. Temperature effect on the concentrate sulfur removal .

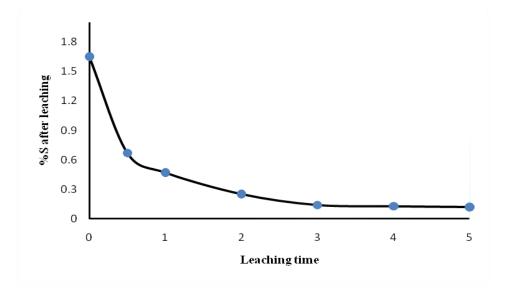


Fig. 2. Leaching time effect on the sulfur content of iron ore concentrate.