REMOVAL OF SULFUR AND PHOSPHOROUS FROM IRON ORE CONCENTRATE BY LEACHING

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Abstract: Iron ore having high-sulfur content causes problems in the concentrate production, pelletizing, and steel-making processes and environmental issues such as sulfur dioxide emission during the concentrate pelletizing process, and effect on steel quality. The current study was focused on the removal of sulfur from iron ore concentrate using chemical leaching technique. Magnetite iron ore concentrate was chosen for this purpose. The results obtained from the study showed that more than 90% of the total sulfur content was removed from the iron ore concentrate by the chemical leaching. Effects of several parameters, including temperature, stirring speed, particle size, and use of organic solvent on the sulfur removal was investigated by a series of experimental conditions. After optimizing the experimental conditions, it was demonstrated that in addition to sulfur, more than 80% of phosphorus, another important impurity, was also removed from the iron ore concentrate. In addition, one of the major advantages of our proposed method was the transformation of mineral pyrites to useful byproducts such as elemental sulfur.

Keywords: sulfur removal, chemical leaching, iron ore concentrate

Introduction

A high-grade magnetite-hematite iron ore deposit is located in the Gole-gohar mine, Sirjan, Kerman province in Iran. The geological proven reserve is about 1200 Tg (teragram) and the Gole-gohar complex provides the production of 5 Tg concentrates per year. The minerals in the iron ore are mainly of magnetite and hematite, but many of the iron ore rocks and mines contain sulfide minerals such as pyrite, chalcopyrite, arsenopyrite, etc. The sulfur content of iron ore concentrates is generally about 0.5% to 2%, and sometimes more than 0.7%, while the permitted limit of steel industries is 0.1% (Soltanmohammadi et al., 2011). Meanwhile, the percentage of sulfur increases

with the mine development and subsequently the depth, and hence, this problem will be more serious in the future. Accordingly, sulfur is one of the important impurities in iron ore, which greatly affects the price of iron ore concentrate. Moreover, high contents of sulfur in steel decrease its quality. In addition, the presence of sulfur in iron ore concentrates causes environmental issues, especially sulfur dioxide emissions during the pelletizing or smelting process. Furthermore, with recent 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, up to now, 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 (Abzalov et al., 2008; Soltamohammadi et al., 2011; Xiaohui et al., 2013; Weizhi et al., 2015; Sharif and Azizkarimi, 2015).

Sulfur removal can be performed using two main methods: conventional pyrometallurgical (smelting/converting) and hydrometallurgical (flotation/leaching or bioleaching). Reduction of the sulfur content of iron ores is conventionally carried out by flotation after grinding (Weibai, 1983; Changxiang, 2001; Xingwang et al., 2009). In hydrometallurgical method, the ore must be broken down by chemical materials or bacterial leaching where the metal-sulfur mineral bond is broken to produce elemental sulfur, metal sulfates or sulfites. Bioleaching usually involves oxidation of insoluble metal sulfides to soluble metal sulfates by a biological process. Pronk et al. (1990) and Alafara et al. (2007) reported biological oxidation of pyrite to ferric sulfate and sulfuric acid.

Leaching process has been often used to recover precious metals from mining ores. Removal of impurities and dissolution of sulfur minerals based on leaching process, especially for coal cleaning have been also reported (Hamersma et al., 1975; Descostes et al., 2004).
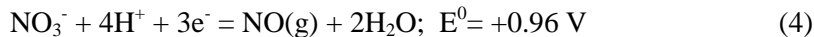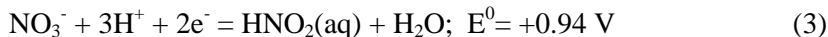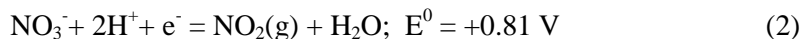
The current study is focused on controlling sulfur emissions by pre-treating the iron ore concentrate to remove sulfur by leaching technique. Technically, chemicals are used to react with the sulfur bearing minerals in the iron ore to convert them into a soluble fraction, resulting in an easy separation from the insoluble solid phase. Since the amount of the iron ore concentrates, which must be treated, is massive, the process should be used with low product loss during the chemical leaching reaction. It must be economically affordable in raw materials and the operation costs. Another important parameter is the operation time which should be as low as possible.

In order to provide an economically viable process for the dissolution of mineral sulfur, it would be necessary to find a selective and re-generable chemical agent. Nitric acid is a suitable leaching agent because: (*i*) it is a powerful oxidizing agent that is strong enough to dissolve sulfide minerals (*ii*) it cannot dissolve iron oxides (*iii*) the leaching agent can be regenerated or recycled.

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

$$3MeS(s) + 2HNO_3(aq) + 3H_2SO_4(aq) = 3MeSO_4 + 3S(s) + 2NO(g) + 4H_2O \quad (1)$$
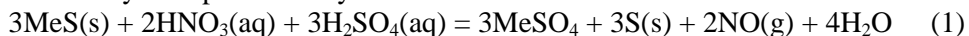
and several half reactions as follows (Anderson, 2003; Gok, 2010):

$$NO_3^- + 2H^+ + e^- = NO_2(g) + H_2O; \ E^0 = +0.81 \ V \tag{2}$$

$$NO_3^- + 3H^+ + 2e^- = HNO_2(aq) + H_2O; \ E^0 = +0.94 \ V \tag{3}$$

$$NO_3^- + 4H^+ + 3e^- = NO(g) + 2H_2O; \ E^0 = +0.96 \ V \tag{4}$$

$$2NO_3^- + 10H^+ + 8e^- = N_2O(g) + 5H_2O; \ E^0 = +1.11 \ V. \tag{5}$$

Oxidation of pyrite mineral with nitric acid is as follows (Gok, 2010):

$$2FeS_2 + 10HNO_3 = 2Fe^{3+} + 2H^+ + 4SO_4^{2-} + 10NO + 4H_2O. \tag{6}$$

Furthermore, the return of nitric acid to the leaching cycle is possible (Queneau and Prater, 1974; Brennecke et al., 1981; Anderson et al., 1994; Anderson, 2003; Gok, 2010). Sulfur dissolution of minerals in leaching process is carried out through an electrochemical reaction between sulfide ion and oxygen. Sulfide is oxidized to elemental sulfur, sulfite or sulfate ions (Rusanen et al., 2013).

The following research discusses and investigates the influence of physico-chemical leaching parameters such as temperature and particle size on the removal of sulfur minerals in an oxidative medium to find out the optimum conditions. After the optimization, the effect of leaching process on removal of phosphorous was also investigated.

Experimental, materials and methods

Sample collection and grinding

The samples of iron ore concentrate were obtained from the Gole-gohar complex. These samples were taken from the conveyor located after a ball mill grinder and wet magnetic separation where the magnetite iron ore is enriched. After the collection process, the samples were dried and homogenized. To ensure homogeneity and representativeness of the sample, about 300 g samples were collected every 8 h for 10 days. The particle size of the concentrate was -100 μm. In this study, a ball mill was used for the preparation of smaller particle size for the experiments.

The chemical content and mineralogy of the sample are shown in Table 1 and Fig. 1, respectively. The contents of iron total and iron(II) were analyzed by titration method (ISO 25971-1, 2006; ASTM, D 3872, 2005). The XRF analysis (ISO 9516, 1992) was used for the elemental analysis of iron ore concentrate.

Table 1. Chemical content of the iron ore concentrate

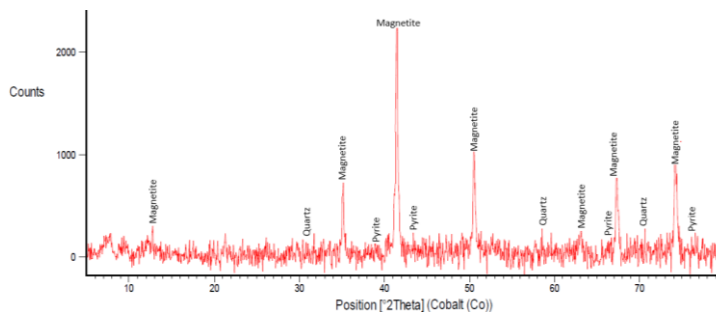| Fe	Fe(II)	S	Si	Al	Ca	Mg
66.8%	21.1 %	1.65%	0.93 %	0.16 %	0.35 %	1.27 %

Fig. 1. XRD patterns for the iron ore concentrate

Solutions, chemicals and experimental procedure

All experiments were carried out in solutions containing 0.7 mol/dm^3 nitric acid and 0.1 mol/dm^3 sulfuric acid. Deionized water (electrical conductivity: 1-3 µSCm^{-1}) was used in the preparation of all aqueous solutions.

The leaching process was carried out in a 250 cm^3 Erlenmeyer flask on an electric heater. For each leaching treatment, 20 g of the concentrate sample along with 100 cm^3 leaching agent solutions were added into the Erlenmeyer flask, and the heating was started for a given time. After the completion of the leaching, the solid residues produced were filtered through a 0.45 µm filter and stored in a desiccator for further experiments. For the removal of elemental sulfur produced in the leaching process, the filtered sample was extracted with toluene solvent. The efficiency of the leaching process was determined by measuring the amount of sulfurs before and after the concentrate contacted with the leaching solution and subsequent organic solvent extraction.

Results and discussion

Several parameters can affect the efficiency of leaching process. Therefore, the process was evaluated under various physical and chemical conditions. Relative standard deviation (RSD%) for the results of sulfur removal was obtained to be lower than 0.1%.

The recycling of the circulating acid in the leaching process is an important goal because the process must be economically affordable in raw materials. Moreover, the second goal in this study was converting pyrite into valuable products like sulfur, with minimal costs. For these reasons, a moderate condition (0.7 mol/dm^3 nitric acid and 0.1 mol/dm^3 sulfuric acid) which produces elemental sulfur was selected. Higher concentrations of leaching agent complicated the regeneration of the stoichiometric amount of circulating acid (Bjorling, 1973). Thus, the optimized result of the previous studies (Gok, 2010) was used to achieve the highest recycling of the leaching agent and production elemental sulfur.

Effect of temperature

Since temperature may affect the rate of chemical reactions, the effect of temperature on the leaching efficiency was investigated. As presented in Table 2, the leaching experiments were performed at different temperatures in the range of 70-100 °C for 3 h at constant concentration of the leaching agents (0.7 mol/dm^3 nitric acid and 0.1 mol/dm^3 sulfuric acid) and constant particle size (-100 µm). For each temperature, the sulfur content of the concentrate was measured to determine the optimum temperature. According to the results shown in Fig. 2, the oxidation of sulfur minerals increased significantly with the increasing temperature because of the possessing at least the activation energy for the sulfide minerals oxidation. Additionally, the reactants move faster at elevated temperatures, resulting in more rapid dissolution of sulfide minerals.

Table 2. Effect of leaching temperature on the sulfur removal

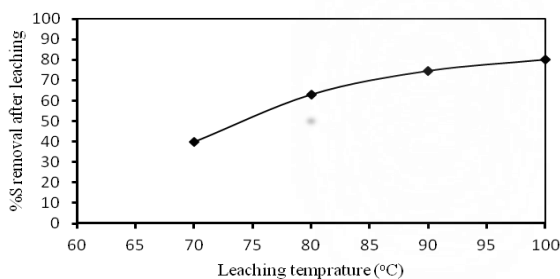| Particle size (µm)	Leaching temperature (°C)	Concentrate S content (%)	%S removal
−100	70	0.99	40.0
−100	80	0.61	63.0
−100	90	0.42	74.5
−100	Boiling	0.33	80.0

Fig. 2. Effect of leaching temperature on the sulfur removal

Effect of leaching time

To achieve the optimum time for the leaching process, the sulfur content of the concentrate was monitored as a function of leaching time. In different time intervals, 2 g samples were taken from the leaching flask, filtered, and after dried, extracted by toluene. After the drying and cooling in a desiccator, the sulfur content of each sample was measured. As shown in Table 3 and Fig. 3, the increasing the leaching time up to 3 h increased the sulfur removal while the sulfur content of the concentrate leveled off after 3 h. 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.

Table 3. Effect of leaching time on the sulfur removal

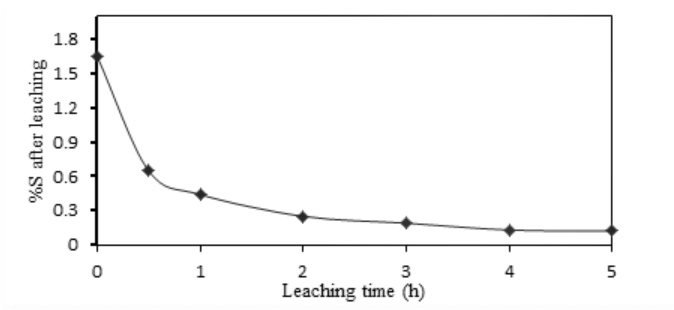| Particle size (μm)	Leaching time (h)	%S after leaching	%S removal
−100	0	1.65	0
−100	0.5	0.65	60.6
−100	1	0.44	73.3
−100	2	0.25	84.8
−100	3	0.19	88.5
−100	4	0.13	92.1
−100	5	0.12	92.7

Fig. 3. Effect of leaching time on the sulfur removal

Effect of particle size

A series of experiments was performed to determine the effect of particle size of the concentrate sample on sulfur reduction in the leaching process. Three particle sizes (100 μm, 76 μm, and 45 μm) were produced by the grinding in a ball mill. The sulfur contents of the concentrate samples with different particle sizes after the leaching in constant reaction temperature (boiling) and time (3 h) are presented in Table 4. From this result, it was found that the leaching efficiency increased with the decreasing the particle size of the initial concentrate sample. Thus, when the particle size decreased from -100 μm to -45 μm, the percent of sulfur removed increased from 91 to 95% because the reaction rate of a solid-liquid phase reaction depends on the surface area particle size) of the solid phase.

Table 4. Effect of particle size on the sulfur removal

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

Effect of stirring rate

Effect of stirring rate on the removal of sulfur from the concentrate was investigated using a magnetic stirrer. A mixture of 20 g of the concentrate (-100 µm particle size) and 100 cm^3 of the leaching solution was treated at optimum conditions of temperature and acid concentration (0.7 mol/dm^3 nitric acid and 0.1 mol/dm^3 sulfuric acid at boiling temperature) for 3 h over a stirring hotplate at different stirring rates from 0 to 600 rpm. As seen from Fig. 4, the sulfur removal is independent of the stirring rate. This may be due to the optimized temperature, and the mobility of mineral particles is enough, and the stirring does not affect the leaching efficiency.
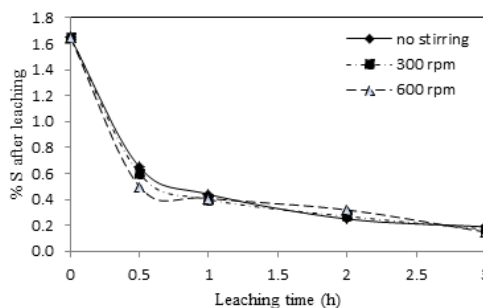

Fig. 4. Effect of stirring rate on sulfur removal

Effect of organic solvent

As mentioned in the introduction, elemental sulfur is one of the leaching by-products, which should be separated from the concentrate. This can be performed easily by a magnetic separator in industrial process, Davis tube in laboratory process or by organic solvent extraction. In this study, an organic solvent (toluene) was used to extract elemental sulfur from the leached concentrate. For this purpose, 100 cm^3 in volume of toluene was used to extract each 20 g sample of the nitric-sulfuric acid-leached concentrate. The extraction was set up to obtain at least 3 cycles for 10 min at boiling temperature in an extractor above a heating mantle. At the end of the extraction procedure, the concentrate was filtered through a filter paper, and then washed with about 20 cm^3 toluene and dried in a drying oven at 120 ^{o}C. As shown in Table 5, the amount of sulfur removed with the solvent extraction were significantly higher than that removed without the solvent extraction for -100 µm particle size, 2 h leaching time in 0.7 mol/dm^3 nitric acid and 0.1 mol/dm^3 sulfuric acid at boiling temperature. Since some of the sulfur in the iron ore converted to elemental sulfur during the process of leaching with acid, toluene dissolves the produced elemental sulfur and as a result the sulfur content of iron ore is reduced. This confirms that some of the sulfur compounds in iron ore were converted to elemental sulfur by nitric acid as mentioned in introduction section. No decrease in the sulfur content was observed

when the sulfur removal process was carried out only by the solvent extraction without the acid leaching.

Table 5. Effect of organic solvent extraction on sulfur removal

Particle size (µm)	Leaching time (h)	%S content after leaching	%S removal	Extraction agent
-100	2	0.71	57	No extraction
-100	2	0.24	85.5	toluene

Effect of leaching on removal of phosphorous and other compounds

Although the main object of this study was to remove sulfur, the results obtained from the experiments indicated that another important impurity in the iron ore concentrate, phosphorus, was also removed after the leaching. It was observed that the amount of phosphorous in the concentrate reduced from 340 ppm to 60 ppm after the leaching for 3 h leaching time in 0.7 mol/dm^3 nitric acid and 0.1 mol/dm^3 sulfuric acid at boiling temperature followed by the organic solvent extraction.

The chemical analysis and mineralogical studies were performed before and after the leaching process. As shown in Figs. 1 and 5, the pyrite peak was removed from XRD pattern after the leaching. In addition, the peak of elemental sulfur could not be seen in the XRD pattern after the leaching because the produced sulfur is an amorphous compound.

The contents of iron total and iron(II) were analyzed by titration method (ISO 25971-1, 2006; ASTM, D 3872, 2005). The chemical results showed that by reducing the impurities such as sulfur and phosphorous, the percentages of total iron and Fe(II) increased as expected (Table 6). XRF analysis (ISO 9516, 1992) was used for the elemental analysis of iron ore concentrate. After the leaching process, the amount of Ca and Mg decreased because Ca and Mg minerals can be dissolved in the acidic leaching solution. An unexpected reduction in Si content was also observed during the leaching process. This could be due to the dissolution of the silica-containing minerals which are soluble in the acidic solution. As demonstrated previously, nitric acid attacks some silicates (Van Loon and Barefoot, 1989).

Table 6. Effect of leaching on the chemical composition of the concentrate

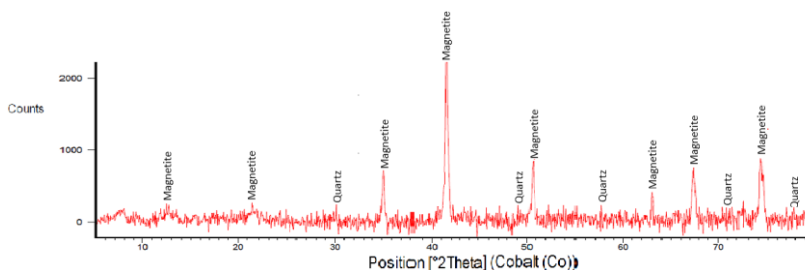| Parameters	Before leaching (%)	After leaching (%)
Fe	66.8	69.2
Fe (II)	21.1	21.8
Si	0.93	0.63
Al	0.16	0.16
Ca	0.35	0.21
Mg	1.27	1.07

Fig. 5. XRD patterns for the iron ore concentrate after leaching

Conclusions

In this study, the chemical leaching process was used for the removal of sulfur from the iron ore concentrate in order to achieve a high-quality raw material for steel-making industry, increasing the price of the concentrate and finally, decreasing the environmental issues, especially sulfur dioxide emissions during the pelletizing or smelting process.

Several experimental parameters were optimized to improve the rate 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 while the stirring of the leaching mixture showed no improvement on the sulfur removal rate and the leaching efficiency. Therefore, there was no need to stirring the leaching mixture and regrind the iron ore concentrate prior to the leaching process.

Finally, one of the main advantages of the proposed method is the transformation of mineral pyrites and other sulfur minerals in the iron ore concentrate to useful by-products. Elemental sulfur is one of these by-products. The produced elemental sulfur which is dispersed in the concentrate matrix may then be separated by magnetic separation of the magnetite concentrate from the produced sulfur by steam or vacuum vaporization or solvent extraction of sulfur. Additionally, the dispersed elemental sulfur can be extracted by flotation or by filtering out the globules formed by melting and re-solidifying the sulfur.

Acknowledgements

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