Desulfurization of magnetic iron concentrates by reverse flotation

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Abstract
The Sarab Mining is an iron concentrate producer located in the Hasanabad Yasukand district of Bijar County, Kurdistan Province. The magnetically separated concentrate product has a particle size (d_{80}) of approximately 42.38 microns, with average sulfur and iron grades of 7.2% and 63.24%, respectively. XRD analysis revealed that the concentrate is composed of magnetite, pyrrhotite, pyrite, grossular, serpentine, and dolomite minerals. Since the presence of sulfur—in the form of pyrrhotite and pyrite—reduces steel's ductility and strength while increasing brittleness, reverse flotation was employed to remove sulfur from the concentrate; parameters such as collector and frother dosages, pulp solids percentage, activator dosage, and pH were investigated using the Design of Experiments (DOE) method. Results obtained under optimal conditions—specifically a potassium amyl xanthate concentration of 1315 g/t, pH of 5.4, frother concentration of 126 g/t, pulp density of 35%, and activator concentration of 210 g/t show a reduction in sulfur grade from 7.2% to 4.1%. By activating pyrrhotite surfaces with 0.004 M oxalic acid in an aqueous solution for one hour prior to flotation, the sulfur content of the magnetic concentrate can be reduced from 7.2% to 1.2% via reverse flotation (under optimal conditions), thereby removing approximately 83.33% of the sulfur present in the concentrate; in other words, simply by pretreating the magnetic concentrate sample with oxalic acid, the sulfur removal efficiency can be improved by 2.9%.

Keywords: Magnetic concentrate, pyrrhotite, reverse flotation, sulfur removal, design of experiments

1-Introduction
There are over 300 types of iron minerals in the Earth's crust, with magnetite (Fe_3O_4), hematite (Fe_2O_3), limonite (FeOOH), siderite ($FeCO_3$), and ilmenite ($FeTiO_3$) being of particular importance [1]. Sulfur, a major harmful impurity in iron ores, primarily occurs in minerals such as pyrrhotite and pyrite; its presence reduces the ductility and strength of steel, rendering it brittle. Higher sulfur content necessitates increased amounts of limestone and coke during the smelting process. Furthermore, harmful gases like sulfur dioxide (SO_2) are generated and emitted in the smelting furnace, contributing to acid rain and air pollution [2, 3]. In other words, impurities in iron concentrate can adversely affect the mechanical and chemical properties of the resulting steel; consequently, iron concentrate used in the steel industry must meet specific standards regarding impurity levels [4]. Pyrrhotite is an abundant iron sulfide that exists in two crystal systems: monoclinic (Fe_7S_8) and hexagonal (Fe_9S_{10}). The lower atomic percentage of sulfur in monoclinic pyrrhotite compared to the hexagonal variety results in higher magnetic susceptibility for the monoclinic form. In terms of magnetic properties, monoclinic pyrrhotite is ferromagnetic, whereas the hexagonal variety is paramagnetic; consequently, monoclinic pyrrhotite is separated alongside other magnetic iron minerals by magnetic separators and enters the iron concentrate, thereby increasing the sulfur content of the magnetic concentrate [5]. Low-intensity magnetic separators are highly effective for the beneficiation and recovery of ferromagnetic minerals in iron ore; however, they are not efficient at separating sulfur when the mineral is monoclinic pyrrhotite [6]. Therefore, reverse flotation is essential for removing or reducing the sulfur present in iron concentrate. In the reverse flotation of iron for sulfide removal, sulfhydryl-type anionic collectors such as xanthates are primarily employed [7]. Although pyrrhotite possesses natural hydrophobicity, its surface oxidizes rapidly upon exposure to air; as oxidation progresses, an iron(III) hydroxide layer forms on the surface, inhibiting the mineral's natural floatability [8]. Some researchers have noted that the oxidation rate of pyrrhotite is 100 times higher than that of pyrite, with ferric ions and oxygen serving as two critical factors in the oxidation process. Furthermore, studies indicate that the surface oxidation rate of monoclinic pyrrhotite exceeds that of the hexagonal variety, a factor that leads to a reduced flotation rate for monoclinic pyrrhotite [9, 10]. parameters such as collector and frother dosages, pulp solids percentage, activator concentration, and pH were evaluated using the design of experiments (DOE) method. The mineralogical composition of iron ores specifically the constituent minerals, their association and liberation characteristics, and the type (pyrite vs. pyrrhotite) and grade of sulfide minerals significantly

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influences the reverse flotation process and its outcomes. Consequently, investigating the parameters affecting pyrrhotite removal via reverse flotation particularly given pyrrhotite's high susceptibility to oxidation and its association with magnetite at sizes below 50 microns—represents a novel aspect of this research.

2- Sampling and Sample Characterization

2-1- Sampling and Sieve Analysis

Samples were collected from the final magnetic separator concentrate at 8-hour intervals over a period of 8 days.Based on the results of this analysis, the d_{80} value (the sieve aperture size through which 80% of the particles pass) was determined to be 42.38 microns.

2-2- XRD Analysis of the Sample

The results of this analysis indicate that the magnetic concentrate is composed of magnetite, pyrrhotite, pyrite, grossular, serpentine, and dolomite minerals.

3- Materials and Experimental Methods

Flotation tests were conducted using a Denver mechanical flotation machine (operating at 1400 rpm) with a 2-liter capacity. sulfur content was analyzed using the equipment available at the Sarab mine (ESI model WF-88). The preparation procedure for all flotation tests followed constant conditions: initial pulp conditioning time of 4 minutes, activator conditioning time of 3 minutes, depressant conditioning time of 3 minutes, collector conditioning time of 4 minutes, frother conditioning time of 1 minute, and a flotation time of 4 minutes. The chemical reagents employed in all flotation tests included potassium amyl xanthate as the collector, copper sulfate as the activator, sodium silicate as the depressant, and MIBC as the frother.

4- Design of Iron Reverse Flotation Experiments

4-1- Parameter Determination and Experimental Design

To investigate the effect of individual parameters and the interactions between them, an experimental design approach using DX7 software was employed. Five parameters such as collector concentration, pH, frother concentration, pulp density, and activator concentration were selected, with their low and high levels determined according to Table 1. Accounting for two replicates, a total of 29 experiments were designed.

Table (1) Selected parameters and levels

Parameters	Unit	Low Level	Symbol	Low Level	High Level
Collector	g/t	900	A	900	1700
pH	-	3.5	B	5.3	5.5
Frother	g/t	110	C	110	150
Pulp density	%	25	D	25	45
Activator	g/t	180	E	180	260

4-2- Comparison of the effect of parameters on the sulfur removal percentage

Figure (1) compares the overall effects of the parameters on the sulfur removal percentage while other parameters influencing the reverse flotation of iron are maintained at their mid-levels. The plot reveals that the parameters exhibit similar trends: the sulfur removal percentage increases with the parameter values, reaching a maximum, after which all parameters exert a negative effect; notably, increasing the pulp density has the most significant negative impact compared to the other parameters.

4-3-Determination of Optimal Conditions for Sulfur Removal

Following the parameter analysis and modeling, the experimental results were optimized using DX7 software. The primary objective of this optimization was to maximize the sulfur removal percentage. To validate the results derived from the experimental design, confirmatory tests were conducted in the laboratory under the optimal conditions. The results obtained under these optimal conditions—specifically a potassium amyl xanthate concentration of 1315 g/t, pH of approximately 4.5, frother concentration of approximately 126 g/t, pulp density of 35%, and activator concentration of 210 g/t—show that the iron grade and recovery reach 65% and 91.16%, respectively, with a sulfur grade of 4.1%.

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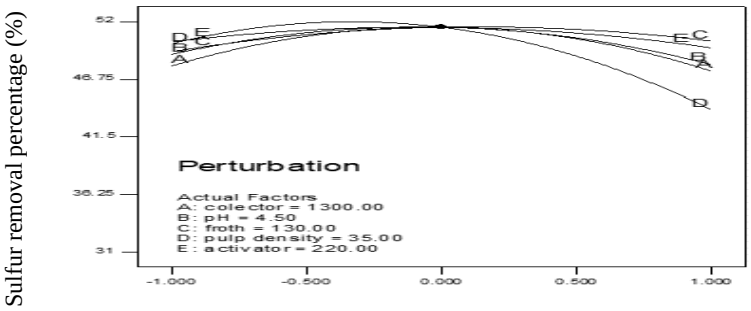

Figure (1) Comparison of parameters regarding sulfur removal percentage.

5- Pyrrhotite Surface Preparation with Oxalic Acid

Studies by Liu et al. (2018) demonstrated that when pyrrhotite is oxidized for 30 days, its recovery rate drops to 32%. To reactivate the oxidized pyrrhotite, they employed sulfuric acid and oxalic acid, finding that the recovery increased to 56% and 84%, respectively, following treatment with these acids [16]. Consequently, oxalic acid was used to activate the oxidized pyrrhotite and to investigate the impact of this preparation on the sulfur removal efficiency during the reverse flotation of iron ore. To this end, flotation feed samples were immersed for one hour in one liter of water containing 0.004 mol/L oxalic acid; this step aimed to remove hydrophilic layers from the pyrrhotite surfaces and enhance collector adsorption for the reverse flotation process. Subsequently, reverse flotation was conducted under optimized conditions.

The results indicated that preparing the pyrrhotite surfaces with oxalic acid successfully removed hydrophilic layers and improved the sulfur removal percentage. The sulfur removal efficiency in the rougher stage reached 83.33%, and the sulfur content in the final concentrate decreased from 7.2% to 1.2%.

6- Conclusion:

Results obtained under optimal conditions show that the sulfur grade of the iron magnetic separation concentrate reaches 4.1%. Furthermore, conditioning the pyrrhotite present in the magnetic concentrate with 0.004 mol/L oxalic acid for one hour prior to flotation reduces the sulfur grade from 2.7% to 1.2% (under optimal reverse flotation conditions); in other words, oxalic acid conditioning improves sulfur removal from the magnetic concentrate by 2.9% under optimal reverse flotation conditions.

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