Comparison Between Different Conditions of Iron Mineral Sulfur Removal in Gol-E-Gohar Mine by Reverse Flotation

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Abstract

Removal of sulfur from iron oxide minerals, mainly as a form of pyrite, which is usually done by reverse flotation. In this work, reverse flotation was performed at pH=8 using potassium amyl xanthate (PAX) and MIBC as collector and frother respectively on iron ore from Gol-e-Gohar mine. For comparison between different conditions, fatty acid and copper sulfate ($CuSO_4$) were used. XRD, XRF and SEM analysis were conducted to evaluate the flotation performance. The results showed that the addition of copper sulfate cannot remove sulfur well due to the formation of copper xanthate and the use of the collector. Because at pH=8, the surface of pyrite has a negative charge, fatty acid could not be effective in removing it. It was shown that two rougher stages in flotation reduced its efficiency.

Keywords: *pyrite, potassium amyl xanthate, reverse flotation, copper sulfate, fatty acid*

Introduction

Sulfur is one of the harmful elements found in steel and causes a decrease in its mechanical properties and corrosion resistance. One of the effective ways to reduce sulfur is to remove it in iron ore before iron making. Pyrite (FeS_2) is one of the main sulphide minerals in iron ores, and sulfur is mostly found in the form of pyrite [1,2]. Therefore, the removal of pyrite is one of the important goals in the production of iron concentrate. Pyrite removal is usually done by physical, physico-chemical, chemical and thermal methods [3]. Flotation is the most attractive method of removing impurities and especially pyrite from iron ore. In this method, which is based on the surface properties of minerals (hydrophilicity and hydrophobicity), chemical reagents are used to improve the performance of the process. In reverse flotation of iron ore, pyrite floats and simultaneously iron oxides (hematite or magnetite) are depressed. Therefore, air bubbles play an important role [3,4].

Collectors used in pyrite flotation, usually have two main portions in their structures. Polar and non-polar parts which are hydrophilic and hydrophobic portions respectively. It is noteworthy that polar parts can attach to minerals [5]. Xanthates are common collectors for pyrite in froth flotation which are reported in numerous articles [6-8].

One of the approved mechanisms in the hydrophobicity of pyrite is that in the presence of oxygen, xanthates combine with pyrite and make pyrite floatable by creating a dixanthogen composition.

Some depressants like sodium silicate, sodium co-silicate, starch, amylose, amylopectin, humic acid and tannin have been used according to literatures [9,10].

Gol-e-Gohar is a famous iron mine in Iran with high sulfur content [3]. Gol-e-Gohar is located in southeastern Iran in Kerman province where its deposits include

more than 1.3 billion tons [11]. Sulfur species are mainly present as pyrite and chalcopyrite in this mine. These kinds of sulfur minerals are usually removed from iron mines like magnetite by reverse flotation [12]. In this work, different reverse flotation tests have been compared under different operating conditions to remove pyrite content from the magnetite feed of Gol-e-Gohar mine in the presence of PAX.

Experimental

The feed used in this work was prepared from Gol-e-Gohar mine with a particle size of -70+45 µm. Potassium amyl xanthate (PAX) and fatty acid were used as collectors in reverse flotation.

In addition, methyl isobutyl carbinol (MIBC), sodium silicate (Na_2SiO_3) and copper sulfate ($CuSO_4$) as frother, iron ore depressant and activator in flotation, respectively, were used in industrial grade. NaOH and HCl as pH modifiers were purchased from Merck.

Chemical and phase analysis of feed were determine by X-ray fluorescence (XRF, Philips X-Unique-II,Germany) and X-ray diffraction (XRD, Panalytical, Netherlands), respectively. Table 1 shown that feed contains about 48.26% Fe and 3.1% S. Based on the XRD pattern in Figure 1, the main component of feed in this study was Fe_3O_4.

Table 1. Chemical analysis of the feed

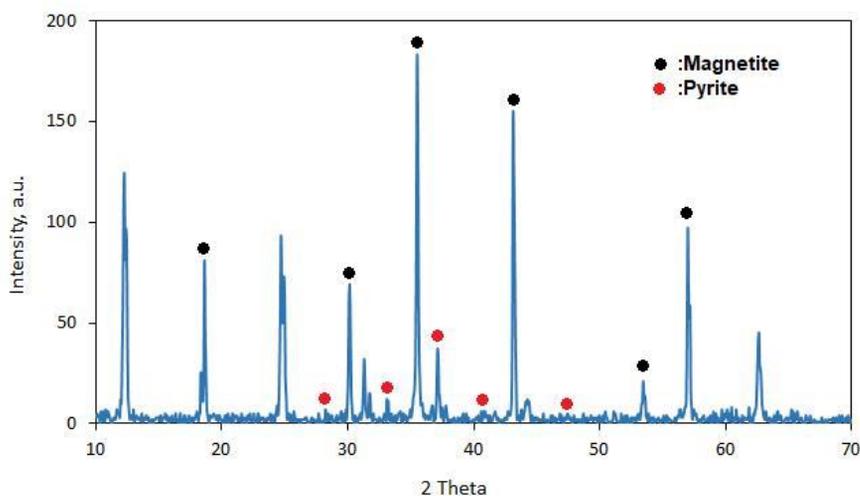| component	Fe	P	S	Si	Mg	Ca	Cl
wt%	48.26	0.20	3.10	5.60	8.83	0.38	0.08

Fig. 1. A XRD pattern of the feed

Flotation tests were carried out in a Denver laboratory flotation cell by 20% solid in pulp and 1500 rpm. Details of the conditions for flotation tests are provided in Table 2. After addition of 500 g of feed and then sodium silicate (600 g/t) in cell, and 2 min conditioning time, NaOH and HCl were used to adjust the pH of pulp in 8. Then the collector and frother were added to the pulp.

In the experiments, the dose of depressant was the same, but different dosages of collector and frother and rougher steps were used. In test C1RC, after adjusting the pH, $CuSO_4$ was added as an activator. After 2 min conditioning time, PAX and MIBC were used. The general flowchart of flotation tests is shown in figure 2.

Table 2. Flotation tests in this research

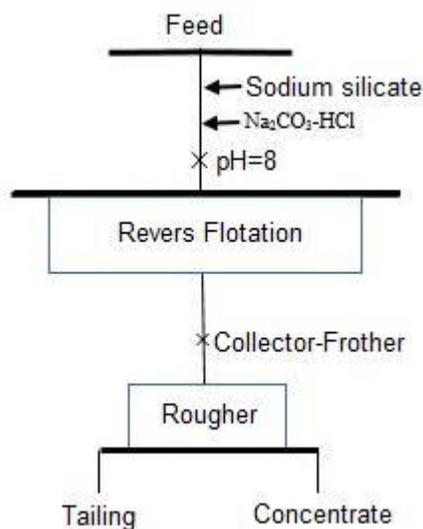| Test	Collector	Frother	Activator	Conditioning time Collector-frother	Flotation time	Rougher steps
C1R	PAX, 150 g/t	MIBC, 70 g/t	-	6 min	5 min	1
C2R	PAX, 70 g/t	MIBC, 35 g/t	-	Rougher 1 = 3 min	Rougher 1 = 3 min	2
				Rougher 2 = 3 min	Rougher 2 = 2 min	
C1RC	PAX, 150 g/t	MIBC, 70 g/t	$CuSO_4$, 50g/t	6 min	5 min	1
C1RF	PAX (150 g/t), Fatty acid (50 g/t)	MIBC, 70 g/t	-	6 min	5 min	1

Fig. 2. General flowchart of flotation tests

Finally, CS (ELTRA-CS2000, Germany) and XRF analysis were used to determine the chemical composition of concentrate and tailings.

Result and Discussion

In this work, optimization of flotation conditions was done based on sulfur removal and recovery and iron grade when PAX was used in flotation as a collector and MIBC as a foaming agent. Table 3 and Figure 3 show the results of different tests. In the C1R test, which is a one-step test, the rapid absorption of xanthate and simultaneous oxidation on the surface of pyrite causes good selectivity. While in two-stage flotation (C2R test), the results were not suitable.

In some studies, the effect of the number of stages on the recovery of the flotation circuit has been investigated and they showed that the configuration of the flotation circuit is not very sensitive to the number of stages [13,14]. But some researchers showed that this is not always true. Using simple numerical examples, Radmehr et al. [15] showed that the assumption of insensitivity of the general flotation circuit to stages is not correct in all cases. Using a large number of stages does not necessarily increase the performance of the circuit and in some cases may impose additional costs and make the circuit inefficient.

In the C1RC test, copper sulfate activator is used and the consumption of xanthate collector is increased. The sulfur in the concentrate has been reduced, but it has not reached the ideal level. Because more tailings have been removed, due to more iron loss, iron recovery is low. Research has shown that potassium amyl xanthate in the pulp reacts with copper sulfate to form copper xanthate. The use of potassium amyl xanthate reduces the flotability of pyrite, and as a result, copper xanthate can be absorbed by bonding with sulfur on the surface of pyrite. Adsorption of copper xanthate on pyrite surface is strong. On the other hand, a redox reaction occurs with copper sulfide adsorbed on pyrite. The main hydrophobic factor is copper xanthate, which changes the surface's electrical properties and wetting properties. Therefore, the absorption of xanthate ions on the surface of pyrite and the chemical reaction of oxidation of xanthate

ions and conversion to xanthogen and iron(III) xanthate occur on the surface of pyrite [16,17].

The results show that the removal rate of pyrite increases with the increase of copper xanthate. On the other hand, xanthate in solution reacts with copper sulfate and forms copper xanthate, thus increasing the consumption of the xanthate collector and leading to less flotation of pyrite. Under strong alkaline conditions, pyrite recovery is reduced in copper xanthate systems. These results are consistent with previous works [16].

Addition of copper sulfate at high pH reduces the contact angle on the pyrite surface. The reason is that the surface of pyrite tends to form hydrophilic substances such as $Cu(OH)_2$, which increases the hydrophilicity of the surface [18]. In fact, the adsorption of copper xanthate on the surface of pyrite at high pH increases the contact angle. Deng et al showed that pyrite pretreated with copper xanthate shows more hydrophilicity in acidic solution than in alkaline solutions [16].

In the C1RF test, where fatty acid was used as a collector, the results were not suitable. Obviously, the presence of fatty acid compared to the C1R test caused these results. Certainly, the zero charge point (ZCP) on the mineral surface and the value of the zeta potential are very important to attract collectors to the mineral surface. The ZCP for pyrite is at pH 6.0, so the value of zeta potential at pH above 6 is negative [19, 20]. At the test pH, fatty acid ions cannot be directly adsorbed on the pyrite surface. Because in this pH range, the surface of pyrite has a negative charge [21], so the adsorption of fatty acid ions on the surface of pyrite is resisted by electrostatic repulsion. Therefore, C1RF has not shown a favorable result compared to C1R. In the interaction of sulfhydryl collectors with pyrite surface, pyrite is oxidized and turns into disulfide. At the same time, Fe^{3+} is reduced to Fe^{2+}. This is associated with a decrease in zeta potential and an increase in surface hydrophobicity [22]. The addition of PAX leads to an increase in the value of negative zeta potential of pyrite particles, which indicates the dissolution of surface iron hydroxides and recovery of bare pyrite. A problem associated with the use of fatty acids in flotation is that these reagents have low solubility and often require heat to increase their activity, which significantly increases the cost of the process [23].

Table 3. Results of flotation tests

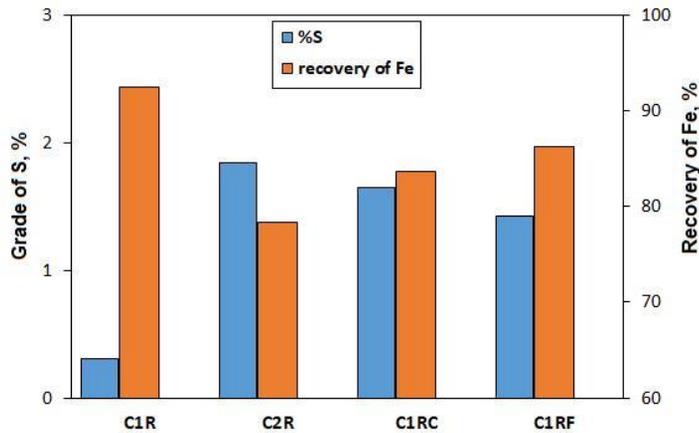| Sample	Assay, %		Fe recovery, %	Tailing ratio
	Fe	S		
C1R	63.86	0.31	92.5	0.30
C2R	54.2	1.84	78.4	0.31
C1RC	61.92	1.65	83.6	0.35
C1RF	61.43	1.42	86.2	0.32

Fig. 3. Degree of sulphur in concentrate and recovery of iron from different flotation tests

Figure 4 shows the XRD pattern of the concentrate obtained from the C1R test. As can be seen, the peaks of magnetite have been identified and there are no peaks of pyrite phase. This means that the amount of sulfur has decreased appreciably. Figure 5 shows SEM and map images of C1R feed and concentrate. As can be seen, there is a large amount of sulfur in the feed and it is completely dispersed in the sample. In the concentrate, in addition to the significant reduction of sulfur, its distribution is uneven. This non-uniform distribution is due to the degree of freedom and the difference in the dimensions of the feed particles.
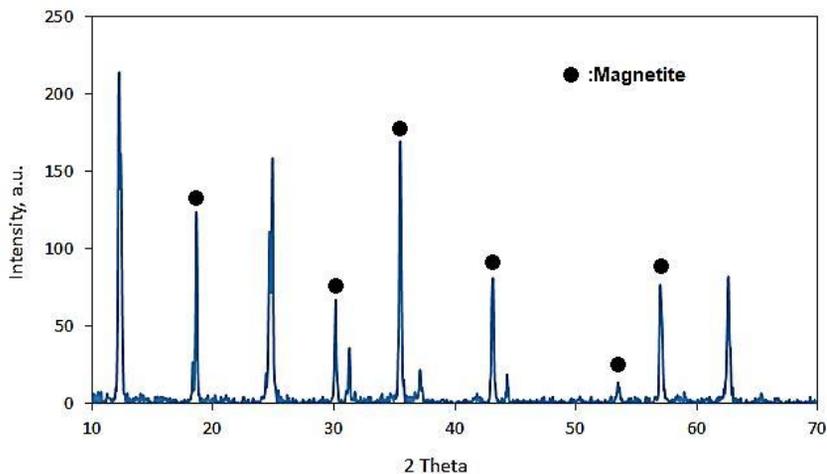

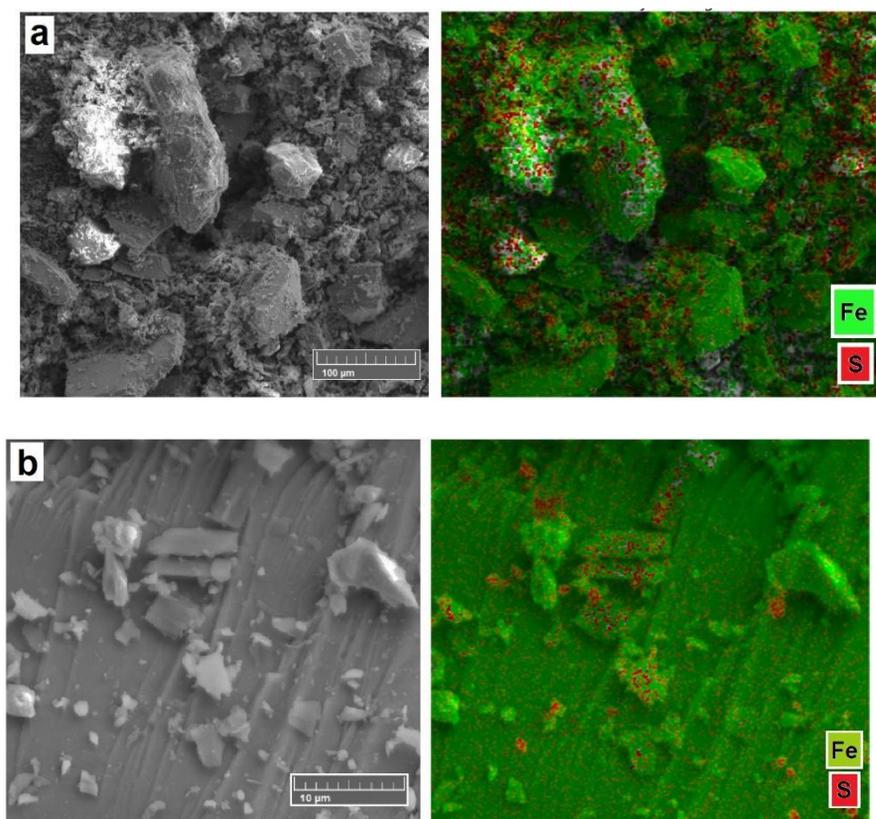**Fig. 4.** XRD pattern of concentrate of C1R test

Fig. 5. SEM and map images of a) feed and b) concentrate of C1R test

Conclusions

In this work, reverse flotation was performed to remove sulfur from iron oxide ore in Iran's Gol-e-Gohar mine. Examining the results of real industrial tests showed:

1. Two rougher stages are not suitable everywhere and sometimes it can weaken the flotation performance.

2. In the presence of PAX, the copper sulfate activator cannot give acceptable results due to the high consumption of the collector.

3. At alkaline pHs where the pyrite surface has a negative charge, fatty acids cannot contribute significantly to the PAX collector and thus cannot improve the flotation efficiency.

Acknowledgement

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