

FLOTATION MECHANISM OF FLUORITE AND HEMATITE WITH SODIUM NAPHTHENE SULFONATE^①

Ge, Yingyong Que, Xuanlan

Changsha Research Institute of Mining and Metallurgy, Changsha 410012

ABSTRACT A highly selective collector SNS(Sodium Naphthene Sulfonate)has been developed and flotation behaviours of fluorite and hematite of Baotou complex mine using SNS as collector have been studied. The separation mechanism of fluorite from hematite was investigated by IR, microelectrophoresis, analysis of adsorption on mineral surfaces and solution chemistry. It was found that the adsorption of water glass and SNS on the mineral surface result in the variation of zeta-potential, the adsorption of SNS on the mineral surface is to a great extent a physical process in the acid media, and a chemical process in the alkaline media. There exist different active species of water glass in the solution of different pH and the species have different adsorptability for fluorite and hematite at same pH. In pH=6~9.5, using SNS as collector, the two minerals would be separated because hematite which adsorbed more water glass than fluorite was depressed.

Key words: flotation mechanism sodium naphthene sulfonate fluorite hematite

1 INTRODUCTION

The Bayanobo complex ore of Baotou, China, has various types of valuable minerals with fine dissemination and extremely associated with each other. Therefore, it is very difficult to separate them from the ore. For instance, the concentrate yielded a recovery of 64%~68% hematite with iron grade of 58%, also a very high content of fluorine occurring as fluorite (about 3%), which led to not only severe influence on smelting operation and material quality but also environment pollution to a certain extent.

To improve the separation results and reduce impurities in the iron concentrate for Baotou concentrator^[1], we synthesized an effective collector sodium naphthene sulfonate (SNS)for flotation separation of fluorite from hematite.

The mechanism of their flotation separation using SNS as collector was explained via measurement of Zeta potential on mineral surface and solution chemistry analysis. The results showed that fluorite and hematite can be

successfully separated with SNS as collector and water glass as depressant.

2 EXPERIMENTAL

Raw naphthenic acid from Changlin Oil Refinery was purified to be final naphthenic acid by removing non-saponified materials and fatty acid from it. The naphthenic acid was sulfonated and saponified as to obtain sodium naphthene sulfonate (SNS). Oxidised paraffin soap was purchased from a chemical factory. Sulfatizing oleic acid was prepared in our laboratory. Water glass with modulus 2.1 was supplied by Changsha water glass factory. Sulfuric acid and sodium hydroxide were analytically pure.

Fluorite and hematite were taken from the fluorite-type iron section of Bayanobo Mine, Baotou. The hand-picked high grade ore was crushed and ground before it was treated by low intensity magnetic separation followed by tabling, as to obtain hematite containing 98.37% Fe₂O₃ and fluorite containing 96.93% CaF₂.

① Received Feb. 17, 1994; accepted in revised form May. 30, 1994

Flotation tests were carried out in a lab type flotation cell. The mineral sample for each test was 2 g, and 0.1 mol/L H_2SO_4 and NaOH were used to modify the pH value. An appropriate amount of depressant water glass was added to the pulp sometimes. After adding SNS into the flotation cell, the pulp was mechanically agitated for 4 min. The froth products were scraped out of the flotation cell with a froth scraper until the end of the flotation operation. The concentrate and tailing obtained were dried and weighed respectively and the concentrate yield was used as the recovery.

The electrokinetic mobility of the two minerals was measured with a Japan-made MRK microelectrophoresis instrument. Small amounts of the mineral under investigation were added to the required solutions and conditioned for 10 min prior to each measurement.

The fluorite or hematite sample slice was processed and scanned with an infrared spectrometer in the wave number range of 400 ~ 4 000 cm^{-1} .

The adsorbed amount of water glass on the mineral's surface was determined by spectrophotometric analysis.

3 RESULTS AND DISCUSSION

Considering both the collectivity and selectivity, the fluorite and hematite separation tests were carried out using mixing sodium naphthene sulfonates with various carbon lengths. Moreover, comparative tests were carried out with sodium naphthenate, oxidized paraffin soap, sulfatized oleic acid and SNS, so as to look into the difference in collection behaviour between SNS and conventional reagents. The results obtained are shown in Fig. 1.

From the curves in Fig. 1, it can be seen that at SNS dosage of 1×10^{-5} mol/L, fluorite recovery is 80.0% and hematite recovery only 8.1%. That is to say, selective separation of fluorite from hematite can be achieved using SNS. Sodium naphthenate can not be used as collector because its poor selectivity for the two minerals. Oxidized paraffin soap and sulfatized oleic acid have stronger collectivity and poorer selectivity than SNS. From the above, it can be concluded that in fluorite and hematite flotation, SNS is superior to sodium naphthenate, oxidized paraffin soap and sulfatized oleic acid in selectivity because of its stronger collecting strength for fluorite than for hematite. Fig. 2 shows the curves of fluorite and hematite recoveries varying with pH. It can be seen that the two minerals have a wide pH range suitable for flotation separation

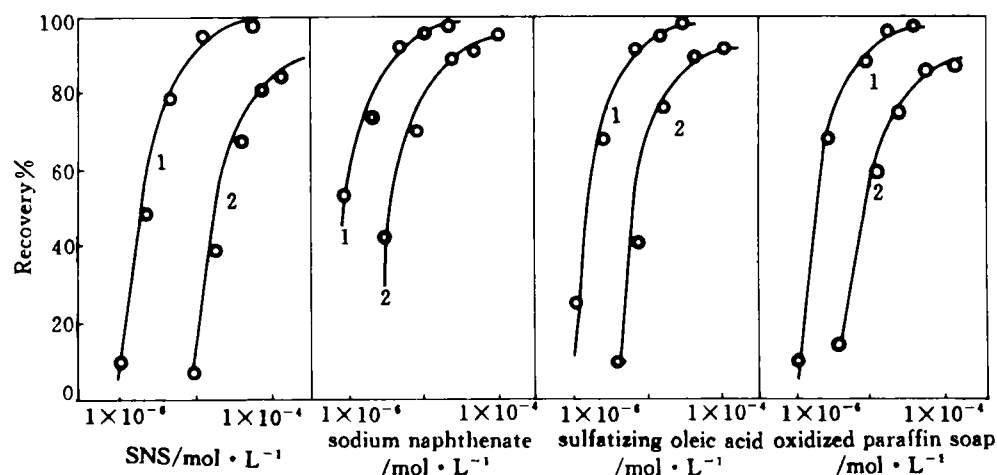


Fig. 1 Comparative tests of fluorite/hematite separation using various collectors

1—fluorite; 2—hematite

and can be floated even in stronger acid medium. This is due to the fact that the active groups-sulfonic groups in the reagent molecules occur as ions in acid medium ($\text{pH} > 3$), improving the electrostatic adsorption between the reagents and mineral surface. The recoveries of the two minerals vary with pH values and have two peak values at about $\text{pH} = 4$ in acid media and $\text{pH} = 10$ in alkaline media. This may be attributed to the SNS's structure of double active groups.

In alkaline media, the chemisorption of SNS's carboxy groups on the two minerals' surface is predominant; in acid media the physical adsorption of SNS's sulfonic groups is predominant; and in neutral media all the above two adsorptions take place. From the curves in Fig. 2, it can be seen that at a smaller dosage SNS has better selectivity for the two minerals with lower recoveries; and at a higher dosage it has poorer selectivity for them with higher recoveries. Therefore, the two minerals can not be fully separated from each other only by conditioning pH and adjusting SNS dosage.

Fig. 3 shows the relationship between the recoveries of fluorite and hematite and pH in the presence of water glass. Below $\text{pH} = 3$ water glass has a slight depressing effect on

hematite, and it increases gradually with increasing pH value; at $\text{pH} > 6$ the recovery of hematite is very small. On the contrary, water glass has strong depressing effect on fluorite in acid media. The flotability of fluorite increases gradually with increasing pH value until its recovery peak value occurs at $\text{pH} 7 \sim 8$ and then reduces with further increasing pH value. Making a comparison between Fig. 2 and Fig. 3, it is clear that it is very difficult to separate the hematite and fluorite at any pH using SNS alone instead of water glass as depressant. In the presence of water glass their separation can be achieved with SNS in pH 6 \sim 9.5 range.

4 SEPARATION MECHANISM OF FLUORITE AND HEMATITE

4.1 Zeta Potential on the Surface of the Two Minerals

Surface charges on oxide minerals and salt minerals have direct influence on their surface adsorption of reagents. It is, therefore, necessary to investigate into the way by which surface charges on the two pure minerals before and after the action of SNS and water glass vary with pH values. The results obtained are showed in Fig. 4 and Fig. 5. It can be seen that isoelectric points of fluorite and

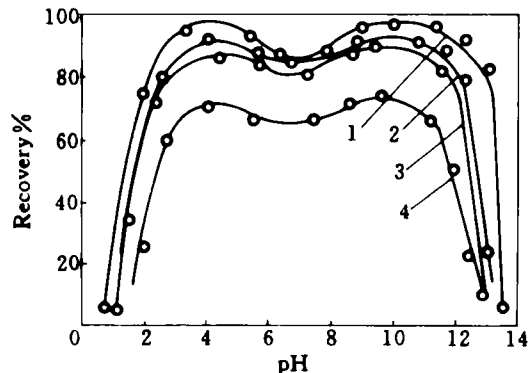


Fig. 2 Effect of pH on fluorite and hematite flotation

- 1—fluorite, SNS 1×10^{-4} mol/L;
- 2—fluorite, SNS 5×10^{-5} mol/L;
- 3—hematite, SNS 1×10^{-4} mol/L;
- 4—hematite, SNS 5×10^{-5} mol/L

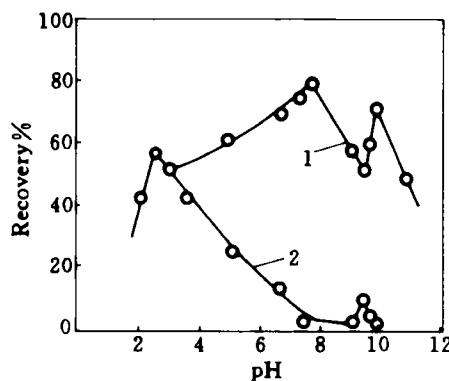


Fig. 3 Effect of pH on the recoveries of fluorite and hematite in the presence of water glass

- (water glass 2×10^{-4} mol/L, SNS 5×10^{-4} mol/L)
- 1—fluorite; 2—hematite

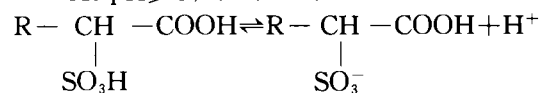
hematite are at pH 4 and pH 7, respectively. Water glass has a slight effect on the isoelectric point of fluorite and a greater effect on that of hematite. At pH 5~8, surface potential changes of the two minerals by the action of water glass are shown as follows:

$$\Delta\xi_{\text{CaF}_2} = 5 \sim 10 \text{ mV}$$

$$\Delta\xi_{\text{Fe}_2\text{O}_3} = 20 \sim 30 \text{ mV}$$

The greater the $\Delta\xi$, the more the anionic ions adsorbed on the mineral surface, resulting in a stronger depressing effect on the hematite. Addition of SNS to the solution containing the two minerals which have been treated by water glass would lead to a different variation of the surface potentials. The zero point charge (zpc) of fluorite shifts to the low pH value, but no obvious change in zpc of hematite takes place in such case. Moreover, since fluorite has far greater $\Delta\xi$ than hematite, the former adsorbs more anions than the latter. All this lead to the fact that fluorite has better flotability than hematite. This is in agreement with the results in Fig. 3.

At $\text{pH} \geq 3$, SNS is ionized as follows^[2]:



Therefore, sulfonic groups can be adsorbed on the surface of hematite at $\text{pH} < 4.7$.

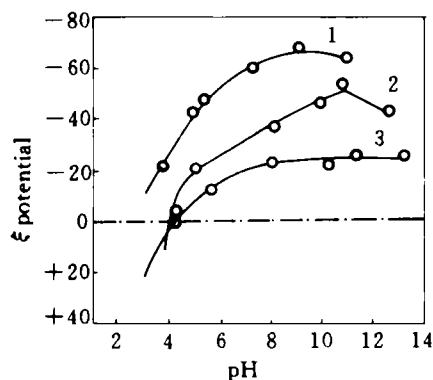


Fig. 4 ξ potential of fluorite as a function of pH

- 1—water glass 1×10^{-4} mol/L,
SNS 1×10^{-4} mol/L, CaF_2 ;
2—water glass 1×10^{-4} mol/L, CaF_2 ;
3— CaF_2

At $\text{pH} < 4$, the same electrostatic adsorption can also take place on the surface of fluorite. It is because of this that the peak values of fluorite and hematite recoveries can be obtained using SNS as the collector in acid media (see Fig. 2).

4.2 Infrared Spectral Analysis

Adsorption mechanism of SNS on the surface of fluorite and hematite in alkaline media was studied by infrared spectral analysis. Fig. 6 shows the infrared spectrograms of fluorite before and after the action of SNS. There are two characteristic peaks forming after the adsorption of SNS on fluorite, representing $-\text{CH}_3$ at 2800 cm^{-1} and 2900 cm^{-1} respectively. At 1700 cm^{-1} there is a small peak where physical adsorption of SNS on fluorite takes place. At about 1600 cm^{-1} the characteristic peak of fluorite after the action of SNS almost coincides with that of the pure fluorite. From the difference in sharpness between the two peaks, it can be seen that chemisorption has taken place. The peak of sulfonic groups at 1200 cm^{-1} has shifted to the lower wave numbers, showing the formation of calcium sulphthene sulfonate.

Similarly, from Fig. 7 it can be seen that

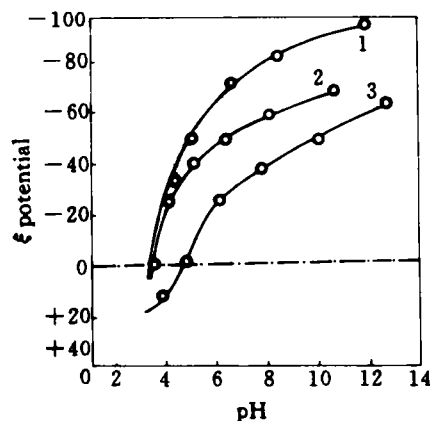


Fig. 5 ξ potential of hematite as a function of pH

- 1—water glass 1×10^{-4} mol/L,
SNS 1×10^{-4} mol/L, Fe_2O_3 ;
2—water glass 1×10^{-4} mol/L, Fe_2O_3 ;
3— Fe_2O_3

the characteristic peaks occur at 2960, 2860, 1700 and 1600 cm^{-1} , and the characteristic peak at 1200 cm^{-1} presenting sulfonic groups has shifted to the low wave numbers. Therefore, it can be concluded that both the chemisorption and physical adsorption of SNS occur on the surface of hematite.

From the above, it is clear that although fluorite and hematite differ from each other in natural flotability in alkaline media, SNS can act chemically on both, forming stable chemisorption together with physical adsorption. It is, therefore, necessary to separate them with a selective depressant.

4.3 Solution Chemistry of Water Glass and Separation of Two Minerals

Dilute solution of water glass has been

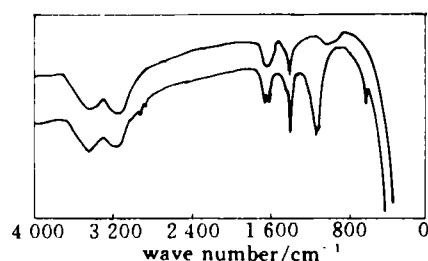


Fig. 6 Infrared spectrograms of pure fluorite and fluorite after the action of SNS

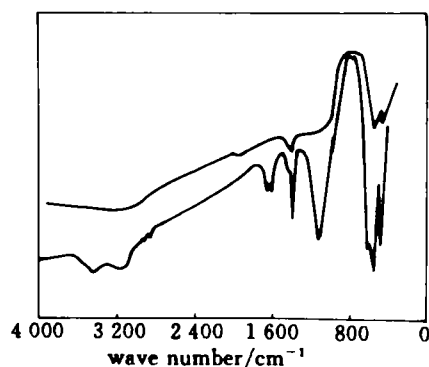


Fig. 7 Infrared spectrograms of pure hematite and hematite after the action of SNS

extensively studied^[4, 5]. The species present in it were varied with pH values.

Taking 1×10^{-4} mol/L SiO_2 solution for example^[6]: $\text{Si}(\text{OH})_4$ is predominant at $\text{pH} < 9.0$, and $\text{SiO}(\text{OH})_3^-$ between $\text{pH} 9.5 \sim 12.5$, and $\text{SiO}_2(\text{OH})_2^{2-}$ at $\text{pH} > 12.5$. $\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$ is not predominant at any pH but its concentration does reach a maximum between $\text{pH} 10.0 \sim 12.0$ ^[7].

In solution saturated with respect to soluble silica polymerization of silica took place. The rate of polymerization is closely dependent on the pH, silica concentration and temperature. Very slow rates are obtained at low and high pH values. The fastest rate would appear to occur at weakly alkalyne pH values. The structure of the various polymeric species is not well defined, but it is known that under certain conditions the polymers or colloid sized particles exhibit a considerable negative charge^[8].

The adsorption measurements of water glass on the surface of fluorite and hematite are shown in Fig. 8. In acid media, hematite adsorbs less water glass, i.e., it has poor adsorbability for $\text{Si}(\text{OH})_4$; in neutral media it can adsorb more water glass, that is to say, it has better adsorbability for SiO_2 colloid which is formed in the solution at this pH value and the hematite flotation recovery is smaller.

With increasing pH, the solubility of

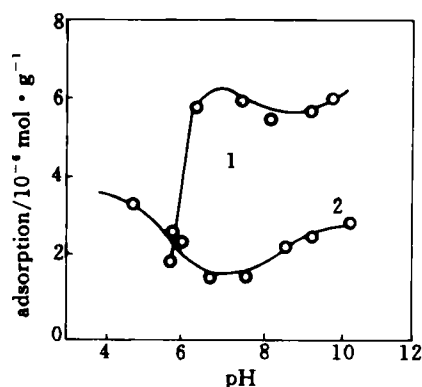


Fig. 8 Adsorption of silica on mineral as a function of pH

(water glass concentration 5.2×10^{-4} mol/L)

1—hematite; 2—fluorite

water glass increases, the amount of SiO_2 colloid decreases, the adsorption amount of SiO_2 on hematite also decreases slightly and the recovery of hematite increases a little (see Fig. 3).

In case of $\text{pH} > 10$, adsorption of large quantities of $\text{SiO}(\text{OH})_3^-$ and $\text{SiO}_2(\text{OH})_2^{2-}$ leads to the increase in the adsorption amount of water glass on hematite, resulting in complete depression of hematite (see Fig. 3).

At $\text{pH} < 6$, fluorite is depressed due to its adsorption of more water glass. This means that it has good adsorbability for $\text{Si}(\text{OH})_4$, and the molecular adsorption has not led to the changes in zero point of charge of fluorite (see Fig. 4). With increasing pH values the concentration of $\text{Si}(\text{OH})_4$ decreases and the flotability of fluorite increases. At $\text{pH} > 9.5$, the fluorite is gradually depressed because it has adsorbed large quantities of $\text{SiO}(\text{OH})_3^-$ and $\text{Si}(\text{OH})_2^{2-}$, resulting in more negative surface charge (see Fig. 4).

Therefore, at $\text{pH} 6 \sim 9.5$, hematite is strongly depressed with water glass as depressant, whereas fluorite remains to have good floatability because of its adsorption of less water glass. In such a case better separation of fluorite from hematite can be achieved with SNS as collector.

5 CONCLUSIONS

This study shows that the reagent prepared using naphthenic acid as main raw material and mainly consisting of SNS is an effective collector for selective separation of fluorite and hematite. It is superior to such con-

ventional reagents as oxidized paraffin soap, sulfatizing oleic acid and sodium naphthenate. Since both chemisorption and physical adsorption of SNS on the surface of fluorite and hematite can take place at the same time. It is necessary to use water glass as depressant for separation. Water glass has different components in aqueous solution of different pH values. Fluorite and hematite have different adsorbability for them. Therefore, it is recommended that pH values should be conditioned in the range of $6 \sim 9.5$. Because in this pH range, hematite is strongly depressed due to its strong adsorbability for SiO_2 colloid and $\text{SiO}(\text{OH})_3^-$, whereas fluorite remains to have better flotability due to a small effect of SiO_2 colloid on it. In such a case the separation of the two minerals can be achieved using SNS as collector.

REFERENCES

- 1 Li, Y T. Mines, 1987, (1): 1—8.
- 2 Wang, D W. *et al.* Anionic surfactants. Publishing House of Hight Industry, 1983.
- 3 Liao, P Y. Applications of Infrared Spectra in Mining and Metallurgy. Central South Institute of Mining and Metallurgy, 1984.
- 4 Bilinskii, H. Acta Scand, 1954, 21: 2503—2510.
- 5 Ingri, N. Acta Chen Scand, 1959, 13: 758—775.
- 6 Marinakis, K I *et al.* Int J Miner process, 1955, 14.
- 7 Marinakis, K I; Shergold, H L. Int J Minter Process, 1985, (14): 177—193.
- 8 Ilser, R K. The Chemistry of Silica. New York: J Wiley and Sons, 1979.