Technology Section

Pak. j. sci. ind. res., vol. 32, no. 10, October, 1989

RECOVERY OF SULPHUR FROM SULPHUR REFINERY WASTE

R.A. Gohar, K. Hussain and N. Sheikh
PCSIR Laboratories Complex, Lahore-54600

(Received June 7, 1989; revised November 7, 1989)

Elemental sulphur has been recovered from sulphur refinery waste containing 16% sulphur, by the flotation technique. The sulphur concentrate, assaying 81% sulphur at a recovery of 90% has been obtained. Flotation parameters such as pH, percent solids, feeds size, and reagents for obtaining optimum grade and recovery have been studied.

Key words: Sulphur, Flotation technique, Parameters.

Introduction

Sulphur deposits have been known to occur in the Koh-i-Sultan area of Baluchistan for a long time [1]. Smaller sulphur deposits, however, have been reported in Chitral, D.I. Khan, Kalat, Khairpur and Peshawar Divisions [2].

Presently there is a sulphur refining unit at Quetta (Baluchistan Sulphur Private Limited, Mustung Road), which is exploiting Koh-i-Sultan sulphur ore. The refinery uses the autoclave technique to purify the sulphur ore and treats it at a rate of 10 tonnes per day. The refining technique results in a low yield of refined sulphur, leaving behind a waste containing around 16 percent of recoverable sulphur.

For the recovery of sulphur from ore, froth flotation is generally used whenever the Frasch process cannot be employed profitably. The natural hydrophobicity of sulphur helps its recovery by allowing flotation with the use of frothers only. Petrov [3] reported the use of kerosine oil and pine oil for the flotation of a sulphur ore containing10.5% elemental sulphur, resulting in a recovery of 75%. Narayanan and Subramanyam [4] employed diesel oil and cresylic acid to recover sulphur from clays. In the Chemico Sulphur Recovery Process [5], a sulphur ore containing 40% sulphur is treated in two steps. About 1/3rd of the originally contained sulphur is recovered by a gangue separator while the rest by flotation. A Sulphur ore containing 24.7-26.7% sulphur was floated with 30-40 g/t turpine oil, 600 g/t kerosine oil, and 2000 g/t water glass to obtain a concentrate containing 95% sulphur at a recovery of 72% [6]. In another study Jamusz [7] reported the flotation of marl and clay sulphur ores using 3-4.5% solutions of $NaCl$, $MgCl_2$, or $CaCl_2$ to act as a pulping medium. The recovery for marl sulphur ore was 95%, whereas for the clay ore it was 85%; 150 g/t emulsified kerosine oil was used as a collecting agent.

A pilot plant process was optimised in Colombia for the processing of sulphur ore containing 27-32% sulphur. Pine oil was used at a rate of 50 g/t and a flotation concentrate assaying 73% sulphur and a recovery of 91% was obtained. A recent study [8] deals with the use of monoquaternary ammonium salts for the flotation of finely divided sulphur (0.8μm). Other studies [9,10] deal with the effect of particle size and the stability of a surface film in the flotation of sulphur. Adamache[11] obtained a patent on the recovery of elemental sulphur from its contaminants such as fire clay, sand, and pebbles by the process of froth flotation. The starting material, containing 47.6% sulphur, was grounded with 1 kg/t Na_2SiO_3. The slurry was conditioned for 2 minutes with 80 g/t MIBC and 80 g/t kerosine oil. A rougher flotation stage and two cleaning stages resulted in a concentrate grade of 98.8% and a recovery of 97.21%.

The present study is aimed at recovering elemental sulphur from the refinery waste, by flotation, to make the existing sulphur recovery process more economical.

Sample description. A 40 kg sulphur waste sample was received from the refinery for the development of a recovery process for elemental sulphur. The material was mostly in the form of a granular powder. Some of the material was in the form of agglomerates. The chemical analysis of the sample, as received, is shown in Table 1.

TABLE 1. CHEMICAL ANALYSIS (%)

S	15.70
SiO_2	69.24
Fe_2O_3	2.80
Al_2O_3	4.52
CaO	4.60
MgO	1.79
Moisture	1.35

Experimental

Sample preparation. The feed material for flotation tests was prepared by using a laboratory roll crusher and porcelain jar mill with flint balls. For this purpose the rolls products were dry ground in the jar mill. Samples of ground ore were drawn from the mill from time to time and sieved till the desired size (determined microscopically) was obtained.

Flotation tests. A Denver D-12 flotation cell was used for processing of the sulphur waste sample. Tests were conducted to optimize grade and recovery by varying the following flotation parameters.

pH, PERCENT SOLIDS, FEED SIZE, AND REAGENTS.

Effect of pH. The effect on the recovery of sulphur was studied over a range of 2 to 8, using sulphuric acid and lime to achieve the desired pH. The other parameters (i.e., feed size, percent solids in the pulp, and reagents) were kept constant. The results of these tests have been given in Fig. 1.

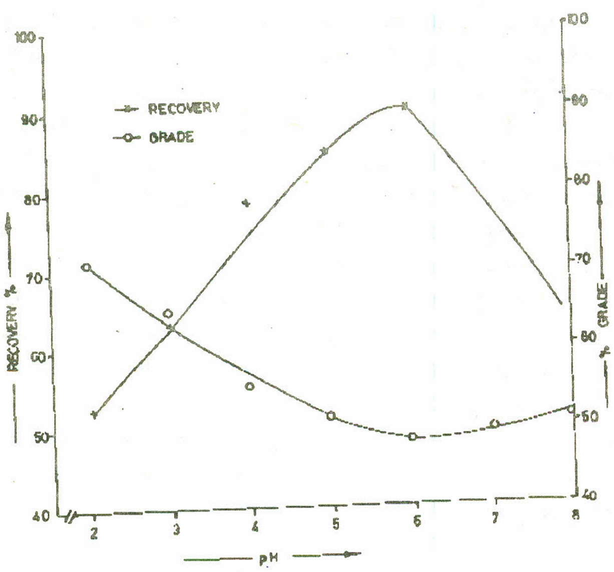

Figure 1. Effect of pH on the grade and recovery of sulphur

Effect of feed size. The effect of feed size was studied by preparing feed of different sizes as described earlier. The feed so prepared was then pulped with an appropriate quantity of water in the flotation cell and subjected to flotation. The other parameters, (i.e. pH, pulp density and reagents) were kept constant (at 6, 40% and pine oil 0.27 kg/t and sodium silicate 0.23 kg/t.) The results have been given in Fig. 2.

Effect of pulp density. Keeping the feed size at 0.833mm, pH at 6, and reagent combination of pine oil 0.27 kg/t and sodium silicate 0.23 kg/t constant, a set of experiments were carried out to study the effect of percent solids on the recovery of sulphur. The results of these tests are plotted in Fig. 3.

Effect of reagents. At a feed size of 0.833 mm, in a pulp containing 40% solids at a pH 6, various reagent

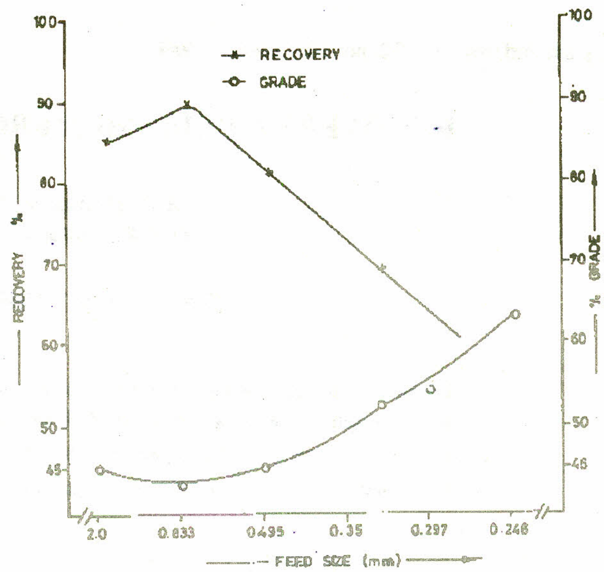

Figure 2. Effect of feed size on the grade recovery of sulphur

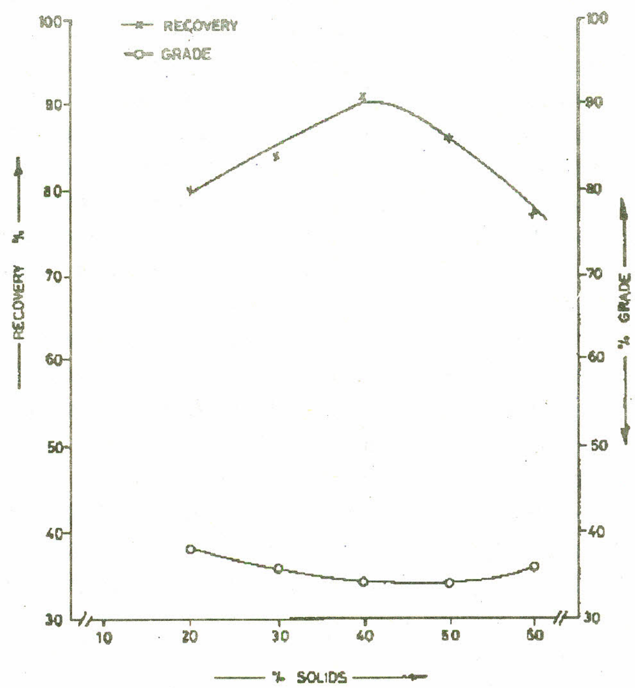

Fig 3. Effect of Percent solids on the grade and recovery of sulphur.

Table 2. Effect of Reagents on the Recovery of Sulphur

Reagents		Grade %	Recovery %
Pine oil	0.27 kg/t	55.61	89.58
Sodium silicate	0.23 kg/t		
K-Amyl Xanthate	0.05 kg/t	64.40	80.92
Sodium silicate	0.23 kg/t		
Cresoles/Kerosene	0.022/ 0.05 kg/t	44.05	83.15

combinations were used as given in Table 2.

Metallurgical balance: A test was carried out using one kg of the waste, reducing it to a size of 100 percent passing 0.833 mm and floating it at a pulp density of 40% with pine oil and sodium silicate in quantities of 0.27 kg/t and 0.23 kg/t respectively. The metallurgical balance of the process of floation of the elemental sulphur from the waste under these conditions is given in Table 3.

Cleaning tests. The rougher concentrate obtained was subjected to three stages of cleaning, using a small quantity of sodium silicate only, resulting in a grade of 81 percent sulphur. The metallurgical balance of the process of flotation is given in Table 4.

TABLE 3. METALLURGICAL BALANCE

Products	Wt. %	Grade %	Distribution %
Rougher concentrate	37	41.21	89.69
Rougher tail	63	2.78	10.31
Calculated heads	100	16.99	100.00

TABLE 4. METALLURGICAL BALANCE

Products	Wt. %	Grade %	Distribution %
III Cleaner Conc.	9.0	81.94	43.38
III Cleaner Tail	5.0	58.06	17.07
II Cleaner Conc.	14.0	72.42	60.46
II Cleaner Tail	9.0	34.41	18.21
I Cleaner Conc.	23.0	58.15	78.68
I Cleaner Tail	14.0	13.38	11.01
Rougher Conc.	37.0	41.21	89.69
Rougher Tail	63.0	2.78	10.31
Calculated Head		16.99	

Results and Discussion

The metallurgical balance given in Table 3 indicates that about 90% of the elemental sulphur contained in the waste material can be recovered by flotation. This recovery has been obtained at a feed size of 100 percent passing 0.833 mm, a pulp pH of 6, pulp solids 40%, sodium silicate 0.23 kg/t, and pine oil 0.27 kg/t of the feed. Table 4 shows that a final concentrate, assaying 81.94% sulfur, can be obtained after subjecting the rougher concentrate to three stages of cleaning.

The results of the test work have been shown in Fig. 1-3. Figure 1 shows that under constant conditions of particle size, percent solids, and reagent quantities, the recovery of sulphur increases from about 52% at a pH of 2 to a maximum of about 90% at pH 6 after which it falls to about 68% at a pH of 8.

In order to explain the flotation response of sulphur it may be pointed out, that sulphur is a nonpolar mineral and falls in the category of naturally floatable minerals (graphite, molybdenite, boric acid, coal, talc) with a net hydrophobic character and exhibits contact angles approaching 90•. Inspite of its natural attributes, the mineral surface may have a significant number of hydrophilic sites resulting in a surface charge and a tendency to adsorb ions from the surrounding medium. Since we have employed a non-polar Oil as frother which also acts as a weak collector, chemisorption reaction should not be expected but an adsorption resulting from coulombic and/or hydrogen bonding process may be anticipated.

It appears from the experimental results that as the pH increases beyond the PZC (2 for sulphur) [12], the zeta potential of the mineral particles becomes more and more negative (a condition necessary for the dispersion of mineral particles) offering an increased number of discrete particles for collector coating and the build-up of the collector coating to a monolayer thickness. After the attainment of maximum negative zeta potential at a pH 6, and the build up of the collector monolayer, further addition of collector or increase of pH increases only the bulk stress [13] of the suspension resulting in reversal of zeta potential (a condition indicating agglomeration of mineral particles) and hence lowered recovery.

An extrapolation of the recovery curve, Fig. 2, on the coarser sizes side shows that the sulphur yields would generally be better as compared to those on the finer sizes side, the maximum recovery occuring at 0.833 mm.

It has been shown [14] that specific flotation rate decreases with size to a few microns. Coarser sizes are favoured (upto 28 mesh) increasingly for early recovery. It appears, therefore, that there must be an optimum size where, under a set of given conditions, maximum recovery is obtained. It has been argued [15] that the flotation of larger particles may be aided by copious aereation in which coursing bubbles give an extra lift. Denser pulps give extra bouyancy to the floating particles but this is somewhat offset by friction, turbulence and gravitational pull. The sharp fall of recovery, in the finer size may be due to the presence of slimmery material in the pulp. In that case the particle-bubble encounter probability is low [16] and the flotation response becomes that of mineral flocs rather than mineral particles.

Figure 3 summarises the results of the effect of pulp density on the recovery of elemental sulphur. It is seen that the recovery increases gradually in pulps increasing in percent solids upto 40 percent when it starts falling.

It may be pointed out that in practice pulp density is always controlled in a grinding/classifying circuit. It is rare that a flotation feed would be independently adjusted in pulp density unless obtained from a source not requiring grinding. It has been shown [17] that the effects of variations of pulp density, however obtained, are important in that increasing recovery and decreasing grades are obtained with increasing solids concentration.

It is generally recognised that rougher flotation should be carried out at as high a solids content as possible. This practice helps in the flotation of coarser particles due to high pulp viscosity resulting in the mechanically entrained load of the froth. It also helps in saving water, increasing the capacity of the flotation machine and reducing reagent consumption. This yields a high recovery but the concentrate is not clean, i.e. it is low in grade. The cleaning is conducted in dilute pulp in which case it has been shown [18] that the recovery decreases but at the same time the rejection increases.

In the present case it has been seen that the constraints imposed by pH, feed size and pulp density on the optimum recovery of elemental sulphur, may be removed by carrying out the rougher flotation at a feed size of 0.833mm, pH 6 and pulp density of 40 percent using sodium silicate as dispersant and pine oil as frother.

Conclusion

The test work reported here indicate the possiblity of recovering elemental sulphur from the sulphur refinery waste.

It has been shown that about 90% of the sulphur may be recovered using 0.23 kg/t sodium silicate as dispersant and 0.27 kg/t pine oil as frother. This recovery was obtained by carrying out flotation at a pH of 6, pulp density 40% and a feed size of 0.833 mm.

It has been reported[19] that sulphur flotation is carried out in acid proof flotation cells at a pH of about 2. In the present study, the optimum recovery has been obtained at a pH of 6. It may be concluded that the sulphur from the refinery waste may be recovered in the usual flotation equipment without fear of equipment detrioration.

References

1. Z. Ahmad, *Geology of Mineral deposits of Baluchistan*, p. 136 (1975).
2. Z. Ahmad, *Directory of Mineral deposits of Pakistan*, p. 158 (1969).
3. S.S. Petrov, Reports on concentration of non-metallic ores. Pt. 1. (1930) p.p. 114-23
4. G.V. Subramanyam and P.I.A. Narayanan, Indian J. Sci. Ind. Res., **11** B, 423 (1952).
5. T.P. Forbath, Trans. Am. Inst. Mining Eng., **5**, (9), 881 (1953).
6. J. Barcicki, Przemysl Chem., **42** (8), 442 (1963).
7. J. Barcicki. Przemysl Chem., **43** (1), 39 (1964).
8. T.Z. Sotskova, Yu. F. Bzhenov and G.A. Golik. Khim, Tekhnol Vody, **9** (2) 121 (1987)
9. N.G. Bedran and L.M. Skorobogatova. Soversh Tekh. Tekhnol Grubozer mistoi, 99 (1986).
10. Janczuk, Bromislow. Przemysl Chem., **65** (8), 433 (1986).
11. I.A. Damache, "Recovery of elemental sulphur from products containing contaminated elemental sulphur by froth flotation." Can. CA 1,223, 373, CCI 803 D 1/02, 23 Jan. (1987).
12. G.A. Parks Aqueous surface chemistry of oxide and complex oxide minerals. Isoelectric point zero point of charge, in Equilibrium concepts in Natural Water System, Advances in Chemistry Series No. 17 American Chemical Society, 121-160 (1967).
13. T.M. Riddick, *Control of colloid stability through zeta potential*, p. 34, (1968).
14. A.M. Gaudin, R. Schulmann, Jr. and A.W. Schlechten J. Phy. Chem., **46**, 902 (1942).
15. E.J. Pryor. *"Mineral Processing"*. (Elsevir Publishing Co. London, 1965), p 153.
16. A.M. Gaudin. *"Flotation"* (Mc Graw Hill Book Co. Inc. New York, 1957) p.p. 369-391.
17. G.A. Parks. Chemicals Reviews, **65**, 177 (1965).
18. A.M. Gaudin. *"Flotation"*. (McGraw Hill Book Co. Inc. New York, 1957) p. 366.
19. S.M.Z. *"Mineral Processing Hand Book"*. (Ed. N.L. Weiss, 1985) Vol. 2, Sect. 28, p. 7.