Pak. J. Sci. Ind. Res. 2008 **51**(1) 45-51

Technology

Beneficiation Studies on Low-Grade Stibnite Ore of Chitral, NWFP, Pakistan

M. Arif Bhatti*, K. R. Kazmi, M. Sharif Nizami, M. Shafique Anwar and M. Habib

PCSIR Laboratories Complex, Ferozepur Road, Lahore-54600, Pakistan

(received March 3, 2007; revised January 17, 2008; accepted January 20, 2008)

Abstract. Antimony ore of Chitral in North West Frontier Province (NWFP) of Pakistan, containing stibnite as an economical mineral, was upgraded by froth flotation technique. Through optimizing the flotation parameters, the grade of the final antimony concentrate produced was raised to 62% Sb with 95 % recovery.

Keywords: stibnite, beneficiation, flotation, antimony, Chitral, Pakistan

Introduction

Stibnite (Sb_2S_3), being the main source of antimony metal and its compounds, is the principal mineral ore. It is found in veins with quartz and occasionally with various antimony minerals resulting from the decomposition of stibnite (Blackburn and Dennen, 1988). Of less commercial importance are the senarmontite (Sb_2O_3 cubic) and valentinite (Sb_2O_3 rhombic), kermesite (Sb_2S_2O) and stibiconite ($H_2Sb_2O_5$). Antimony ores and their concentrates are used as sources of antimony metal and its salts. Antimony metal is used in the manufacture of various alloys such as type metal (Pb,Sb,Sn), bearing metal (Pb,Sb,Sn,Cu) and white metal (Cu,Sb,Sn,Zn). Crude antimony is used on the striking surface of safety match boxes and in detonating caps for ammunition. It is also used in lead storage batteries while its compounds are used in medicine, as mordant in dying, as opacifier in vitreous enamels and glazes, as refining agent in optical glasses, as flame retardant in polymers like P.V.C, for vulcanizing and colouring rubber and also as paint pigments (Johnstone and Johnstone, 1961).

Stibnite deposits are found at various places in Pakistan. However, economically important and sizeable reserves are found at Krinj area of Chitral which contain significant amount of antimony content (Ahmad and Siddiqi, 1993). Although, the ore containing 5-10% Sb content is considered feasible for the recovery of metal but it is better to beneficiate such an ore as it improves the production economics to a great extent. Generally, low-grade ores are beneficiated into concentrates containing 40-65% Sb before the production of chemicals and extraction of metal (Wang *et al.*, 2001). Depending upon the nature of ores, various gravity and flotation techniques are used on lean antimony ores. Gravity concentration technique is mostly used for coarse-grained ores. While on the other hand, fine-grained and disseminated ores require more grinding for the liberation of minerals and can only be beneficiated economically by froth flotation technique (Jain, 1986).

The undertaken beneficiation work is so important that several researchers have been engaged in it under different parameters. Liu (1988) separated antimonite and boulangerite by flotation from lead containing antimony ores. Lead was leached from boulangerite with aqueous $AlCl_3$ for its recovery by crystallization. Peng *et al.* (1991) studied the beneficiation of 81% oxidized antimony ore from Yunnan province, China and obtained antimony sulphide concentrate by flotation and antimony oxide concentrate by gravity separation with an overall 74% recovery. Kursun *et al.* (1994) performed bulk and selective flotation experiments for the beneficiation of Etibank Halikoy antimonite ore and were able to produce an antimony concentrate containing 61%Sb with 95% recovery, using Aero 3477 as collector and NaCN as depressant. While, Solozhenkin *et al.* (1994) improved the grade and recovery of antimony ore containing antimonite, senarmontite, hydromardite, kermesite, stibiconite and other antimony containing minerals by using a combined flotation agent, consisting of dialkyldithiocarbamate and butyl xanthate. Later on, Wang and Lei (2000) treated low-grade antimony ore (15-35%) by bath smelting continuous fuming process, in a furnace using coal, limestone and iron ore and produced antimony oxide containing 76.4% Sb with 90% recovery. Wang *et al.* (2001) applied another method for the separation of antimony from ore, involving smashing, milling, classifying, flotation and dewatering. They used lead nitrate as activating agent, xanthate as collecting agent and terpineol as frothing agent. Yin and Long (2003) attempted the direct leaching of sodium antimonate from antimony ore, using sodium sulphide and a mixture of sodium sulphide and sodium hydroxide, followed by solid liquid separation, washing and drying. Zhang (2004) studied three different methods

*Author for correspondence

to recover antimony from the ore of Lu'erba Mine. Their experimental results indicated that the process of flotation and acid leaching was a better method. They first beneficiated the ore by flotation and then recovered antimony from flotation concentrate by acid leaching.

The objective of the present study was selection and development of a suitable process for concentration of indigenous antimony ore. For this purpose, the stibnite ore of Chitral, NWFP, Pakistan, was beneficiated, on bench scale, to produce antimony concentrate by froth flotation technique. Following is the comprehensive account of the experimentation and the results in this regard.

Materials and Methods

The flow sheet developed for preparing antimony concentrate has been shown in Fig.1.

Sample preparation. A bulk sample of the ore, weighing about 10 tonnes was supplied by Sarhad Development Authority (SDA). The bulk sample consisted of lumps of 100-250 mm in size from which about 100 kg of the ore was collected by random sampling. Some of the ore was kept for mineralogical study while the remaining ore was comminuted by primary crushing using laboratory jaw crusher set at 20-25 mm and by secondary crushing using roll crusher set at 5-6 mm. A representative sample for chemical analysis and further processing was obtained by coning-quartering and riffling of the crushed ore.

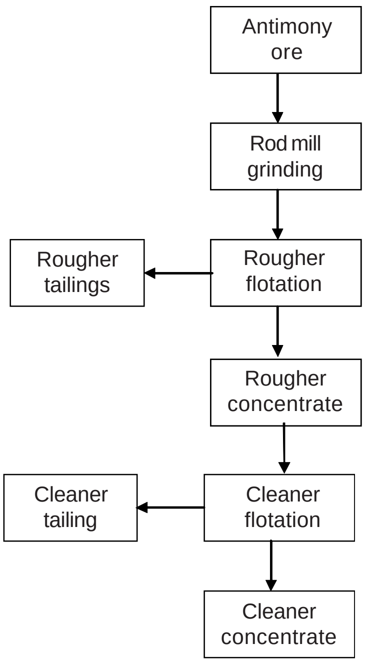

Fig. 1. Flow-sheet for the beneficiation of stibnite ore of Chitral.

Chemical analysis. Representative sample was pulverized to 100% minus 200 mesh size (74 µm) and its chemical analysis was performed by gravimetric and volumetric methods (Jeffery, 1989). Silica, alumina, lead and sulphur were determined gravimetrically, antimony by iodometric titration, iron by oxidation reduction titration, calcium and magnesium by complexometric titration, while sodium and potassium were estimated using flame photometer (PFP7, Jenway Ltd., England).

Mesh of liberation. The product of roll crusher was subjected to sieve shaker (International Combustion, England) for size analysis using different sieves. The fraction retained on each sieve, was analyzed for the liberation of stibnite grains using microscope particles counting method. The percentage liberation at various size fractions was calculated by the following relation (Atiq *et al.*, 2005):

Stibnite liberation (%) = Free stibnite (%) ×100/ [Free stibnite (%) + locked stibnite (%)]

Flotation tests. Flotation tests were carried out in a Denver flotation machine (Model: D-12), using stainless steel cells of 1, 2 and 4 l capacity. The flotation parameters such as grain size, pulp density, pH of the pulp, type of reagents, their consumption and the conditioning time were optimized. The ore was ground from 85% to 100% passing 100 mesh to study the effect of grinding. Flotation feeds were prepared by dry grinding of roll crusher product in rod mill (Denver, USA) and grinding time was adjusted according to the required size of feed. The effect of pulp density was studied by varying the solid to liquid concentration from 20% to 35% and similarly the effect of pH was studied by varying it with soda ash from 7.0 to 8.5. Sodium silicate was added to depress the silicate gangue minerals and its quantity was varied from 100-400 g/ton. Impeller speed was increased from 900-1200 rpm to study the effect of aeration. Potassium amyl xanthate was used as anionic collector and its dosage was varied from 100-200 g/ton while, polypropylene glycol was utilized as frother and its dosage was varied from 30-60 g/ton. Lead acetate was employed to activate stibnite and its amount was varied from 500-2000 g/ton. Optimum conditions and metallurgical balance of the typical tests are recorded in Table 3 and 4 separately.

Results and Discussion

The results of the chemical analysis of the representative sample are given in Table 1. The percentage of antimony in head sample was found to be 19.05. The obtained grade is sufficient to exploit the ore. However, the presence of silica appeared to be the main impurity. It was decided, in this perspective, to involve the flotation technique which has the potential to reduce it effectively.

Percentage liberation of various sizes of stibnite particles is given in Table 2. As flotation technique is very selective and the success of the froth flotation depends upon the nature and size of mineral particles distributed in the ore, therefore, ore is ground to such an extent that all of the mineral grains are fairly liberated from the matrix. The average size of stibnite grains in Krinj, Chitral ore was observed to be around 150 µm. It is evident from the Table 2 that about 98 % mineral grains (phases) are liberated around 100 mesh (150 µm). Therefore, the ore under study was ground in rod mill to 100 mesh sieve so that it may have a fair proportion of free valuable mineral particles in subsequent flotation operation.

The results of flotation tests are presented in Table 3 and Table 4. Our findings in this respect are in good agreement with the above referred researchers. Beneficiation of the antimony ore, on the bench scale, showed very encouraging results, particularly with reference to the percentage recovery. The flotation tests showed that this ore can be easily enriched to a high-grade concentrate containing over 62% Sb by a very simple flotation operation. It is clear from the results that the flotation operation proved to be successful in reducing the silica content of the ore significantly. The production of chemical and metallurgical grade antimony concentrate in two step flotation with 95% recovery of antimony from an ore containing around 19% metal content is quite reasonable. It is evident from the Table 4 that better grade antimony concentrate was produced after cleaning stage of flotation.

Table 1. Chemical composition of ore

Constituents	Percentage
SiO_2	64.00
Pb	1.55
Sb	19.05
Al_2O_3	0.50
Fe_2O_3	4.5
CaO	1.40
Na_2O	0.18
K_2O	0.15
S	8.21

Table 2. Mesh of liberation of stibnite

Mesh No. (BSS)	Particle Size of ore (µm)	Liberation of mineral (%)
60	250	75
70	212	80
85	180	92
100	150	98

It is obvious from the chemical analysis of the final concentrate (Table 5) that the antimony content of the investigated ore was raised from 19.05% to 62.02%.

The data generated regarding particle size versus grade and recovery has been shown graphically in Fig.2. It is clear from the Fig. that the grade and recovery of antimony was improved by decreasing the particle size and maximum recovery was obtained at feed size of 95% passing 100 mesh (150 µm). This,

Table 3. Antimony flotation parameters/conditions

Parameters	Conditions	
	Rougher	Cleaner
Particle size	95%-100#	95%-100#
Impeller speed	1100 rpm	900 rpm
Pulp density (%solids)	30%	20%
pH of the pulp	~8.0	~8.0
Gangue depressant (sodium silicate)	300 g/t	50 g/t
Stibnite activator (lead acetate)	1500 g/t	Nil
Collector (potassium amyl xanthate)	150 g/t	Nil
Frother (polypropylene glycol)	50 g/t	Nil
Conditioning time	20 min	10 min

Table 4. Metallurgical balance for antimony flotation

Product	Weight (%)	Grade (%) Sb	Recovery (%) Sb
Cleaner concentrate	29.12	62.02	95.05
Cleaner tailings	2.40	16.30	2.06
Rougher concentrate	31.52	58.54	97.11
Rougher tailings	68.48	0.82	2.89
Head sample	100	19.00	100

Table 5. Chemical analysis of final concentrate

Constituents	Percentage
SiO_2	2.15
Pb	2.68
Sb	62.02
Al_2O_3	0.12
Fe_2O_3	2.55
CaO	0.54
Na_2O	0.06
K_2O	0.02
S	27.88

being the maximum liberation limit of stibnite, was considered as optimum feed size and selected for further investigation. It is interesting to note that the grade and recovery of antimony sharply decreases on further grinding of ore. On excessive grinding, the generation of slimes might have lowered the grade and recovery; Parsonage (1985) pointed out that the particles in the size range of 20 µm and below have a deleterious effect on the process of flotation.

The percentage of solid feed in the pulp is another very important factor in recovery. The data for solid percentage versus grade and recovery is given in Fig. 3 from which it is clear that the increase in pulp density decreases the grade slightly but recovery is increased. Maximum recovery was achieved at 30% solids beyond which it decreased because coating by collector is not proper due to excess amount of solids. Therefore, this value was selected for the remaining study. It was observed that lower pulp density at rougher stage although produced higher grade but recovery decreased.

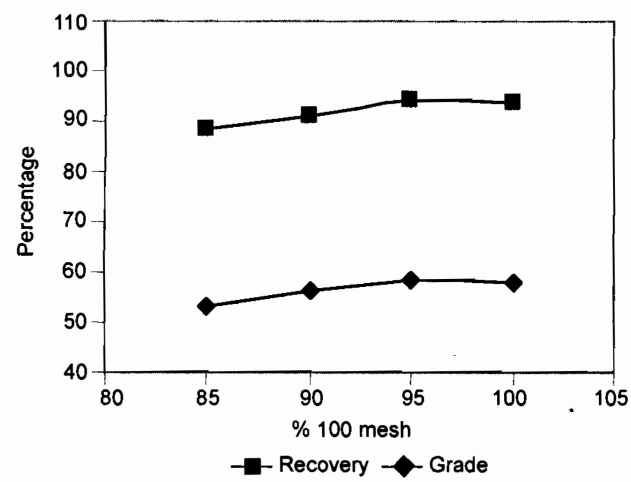

Fig. 2. Effect of particle size.

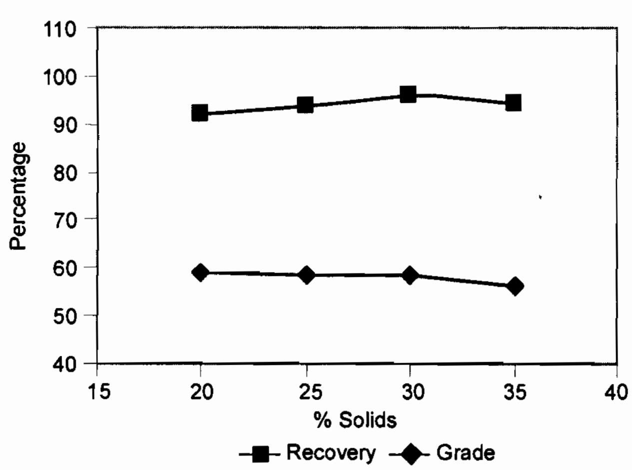

Fig. 3. Effect of pulp density.

While at cleaning stage of flotation, a pulp density of 20% produced a concentrate with good grade and recovery.

The pH of pulp is very critical factor during the flotation of sulphide minerals. The results obtained, at various pH values, are presented in Fig. 4. It is clear that under constant condition of particle size and solid to liquid ratio, the grade and recovery increase with increase in pH from neutral to slightly alkaline medium and then decrease. It was observed that the maximum recovery of antimony is obtained at a pH 8.0, at rougher and cleaner stages. It was also noted that practically a small variation in pH showed a significant change in the grade and the recovery. This effect may be attributed to the maximum stability of xanthates in specific alkaline pH (Weiss, 1985).

Another important factor affecting the purity and recovery of antimony is the impeller speed. Data collected regarding the effect of impeller speed is shown in Fig. 5. It is obvious that an aeration speed of around 1100 rpm gave better results at rougher stage. It is due to the fact that this rpm makes the collector-coated mineral particles containing liberated as well as some partially exposed mineral particles float by attaching onto air bubbles and thus increasing the recovery. While on the other hand, at cleaning stage, a lower aeration speed of 900 rpm improved the grade and recovery because it allows the middling as well as gangue particles to remain in pulp thus producing a cleaner concentrate of greater purity.

It was observed that stibnite mineral did not float satisfactorily with xanthate until it was activated. However, it readily floats after activation with lead ions. Activation is, in fact, due to formation of more stable molecules of lead sulphide at the mineral surface by the adsorption of lead ions on the crystal lattice of stibnite (Pen'kov, 2001). The lead

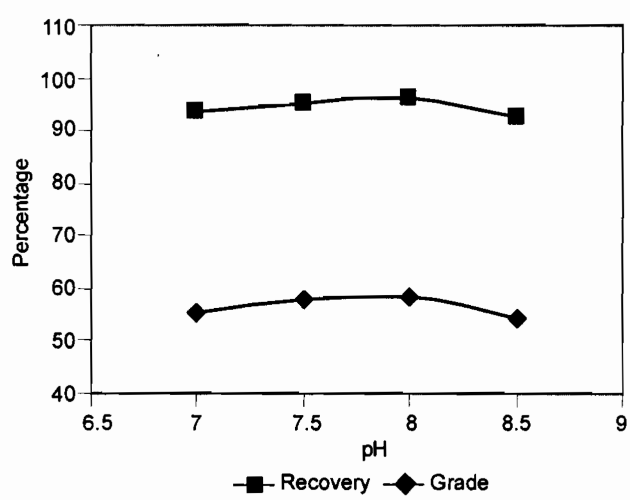

Fig. 4. Effect of pH.

sulphide, so deposited at the mineral surface, reacts readily with xanthate to form insoluble lead xanthate which being hydrophobic, can easily attach with air bubbles. Results obtained using different quantities of activator are given in Fig. 6. It is obvious that the grade and recovery increase with increase in the amount of activator up to 1500 g/ton and further increase is not effective. It is due to the fact that, with less amount of activator, all the stibnite minerals present in the ore are not activated and as the quantity of activator is increased, the grade and recovery increase until all the stibnite minerals are activated.

Results obtained using different quantities of depressant are presented as Fig. 7. Stibnite was readily floated by potassium amyl xanthate after activation but the problem was to keep down the gangue material. This difficulty was overcome by

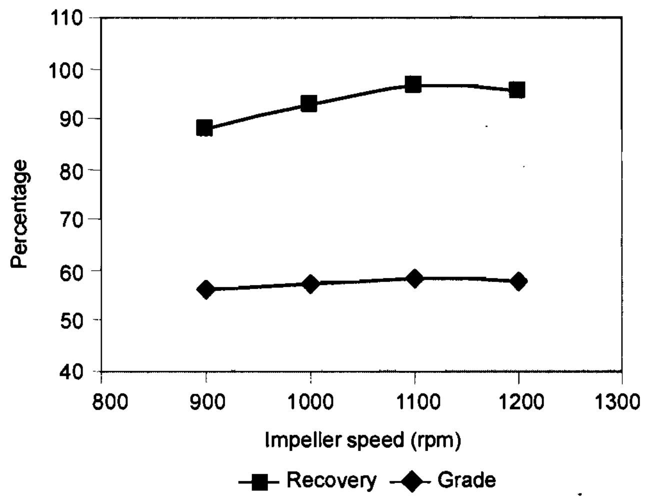

Fig. 5. Effect of impeller speed.

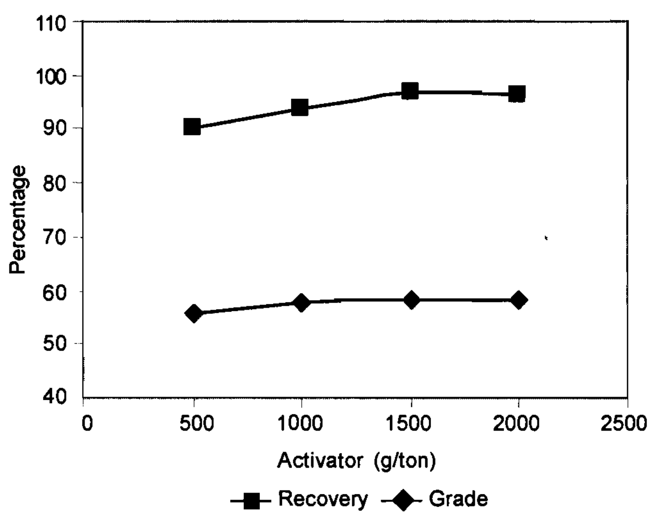

Fig. 6. Effect of activator.

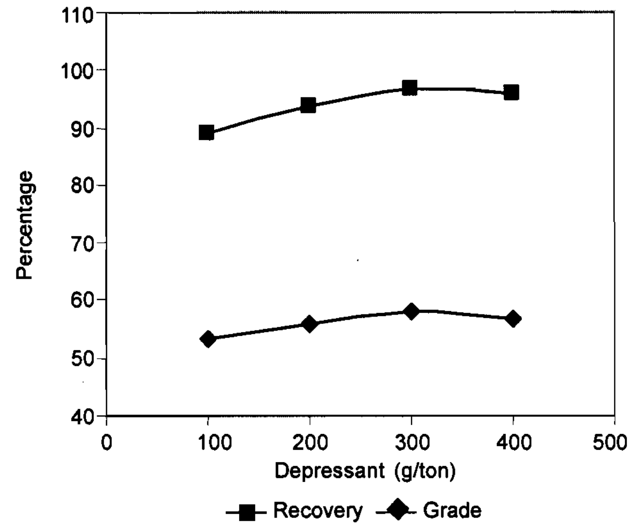

Fig. 7. Effect of depressant.

using sodium silicate as gangue depressant. It increases the selectivity of flotation by rendering the gangue minerals hydrophilic, thus preventing their flotation. It was observed that, quartz, the main gangue mineral present in antimony ore of Krinj, along with other gangue minerals such as clay and silicates were depressed by it. However, it was noted that with the increase in the amount of depressant, initially the grade improved but after 300 g/ton, the grade and recovery decreased probably due to the over coating of some middling particles. Larger amount of depressant was required at rougher stage, as the gangue minerals were present in excess, while, only slight amount of it gave better results at the cleaning stage.

The amount of collector used for antimony flotation and its effect on grade and recovery is presented in Fig. 8. It is evident that better results were achieved at a dosage of 150 g/ton. The reason is that the collector ionizes in solution and produces positively charged ions of alkali metals and negatively charged xanthate ions which are then adsorbed on the surface of the sulphide minerals to form a monomolecular layer due to the chemical forces between the polar group of the collector and the mineral surface resulting in insoluble metal xanthates which are hydrophobic and aerophilic (Wills, 1992). It is notable, on the other hand, that excessive amount of collector adversely affects the grade and recovery of stibnite minerals due to the development of multi-layers of collector on the mineral particles which reduce the selectivity (Crozier, 1992). It was observed that at rougher stage, potassium amyl xanthate coats all the liberated as well as partially exposed particles. But at cleaning stage, there was no need for the addition of collector as mineral particles were already coated.

Frother, being heteropolar, is adsorbed on the air-water interface due to its surface active action thus reducing the surface tension of water and stabilizing the mineralized air-bubbles. Results obtained using different quantities of frother are presented in Fig. 9. It is apparent that a dosage of 50 g/ton gives reasonable grade and recovery; further increase shows no significant improvement in this regard.

Conditioning time has a pronounced effect on the grade and recovery of the concentrate. It allows the surfaces of the mineral particles to react with the reagents (Zhang and Shang, 2002). Results obtained for the effect of different conditioning time intervals are shown in Fig. 10. A conditioning time of 20 min was found to be sufficient for the contact with the mineral particles for optimum recovery and grade. It appears that on prolonged conditioning, the conditioner coating on the mineral particles gets peeled off resulting in lower flotation grade and recovery. It was also observed that short conditioning time requires more collector as it remains unable to coat all the mineral particles present in the pulp, in a short time.

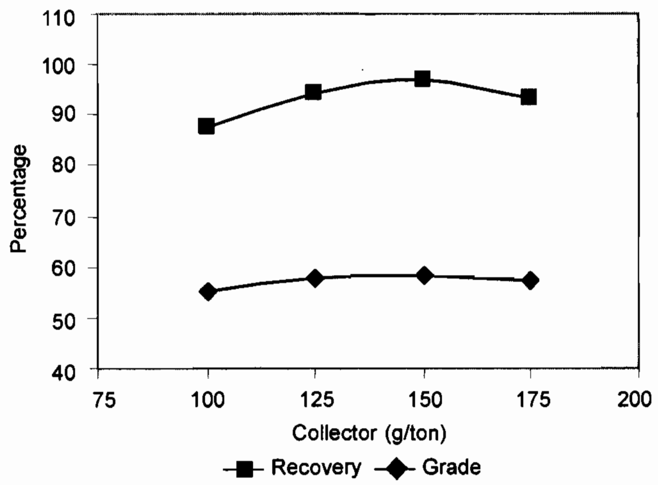

Fig. 8. Effect of collector.

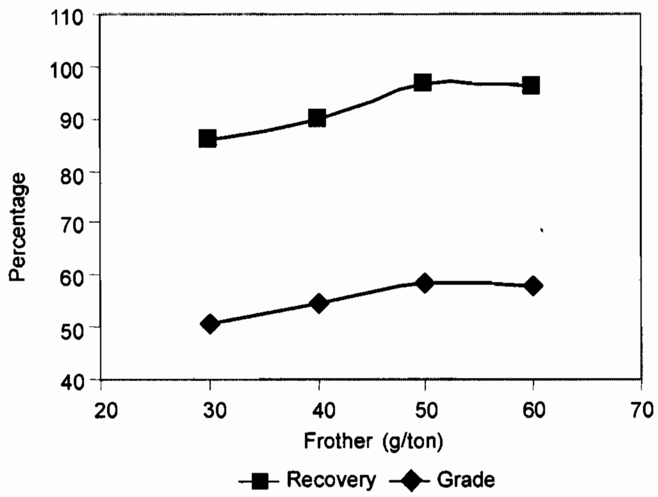

Fig. 9. Effect of frother.

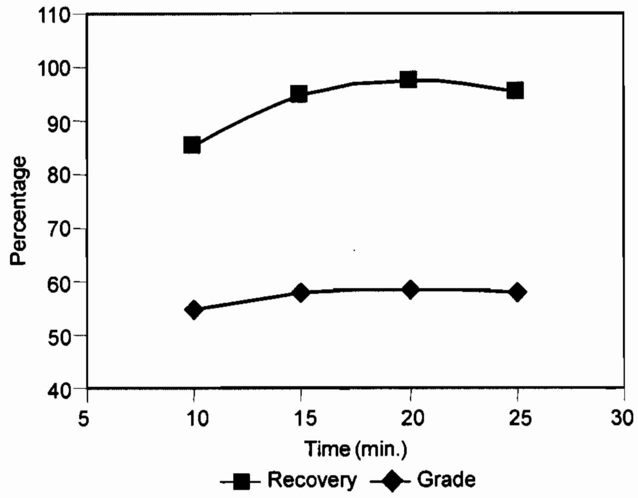

Fig. 10. Effect of conditioning time.

Conclusion

Antimony ore of Krinj area of Chitral comprises mainly of stibnite as economic mineral. Depending upon its nature, the antimony ore of this area can be upgraded by two stage flotation technique to produce antimony concentrate of required grade with acceptable recovery. Gravity concentration technique cannot be applied to this ore consisting of finely disseminated grain texture. The flotation technique is the most suitable for its upgradation. Antimony content of this ore is large enough to be exploited and flotation can produce antimony concentrate of about 62% Sb with 95% recovery. The obtained concentrate can be utilized for the production of chemicals and extraction of metal.

References

Ahmad, Z., Siddiqi, R. A. 1993. *Minerals and Rocks for Industry*, Geological Survey of Pakistan, Quetta, Pakistan.

Atiq, S., Hafeez, I., Khan, K., Malik, M. A. 2005. Beneficiation studies on low-grade chromite ore of Muslim Bagh, Balochistan, Pakistan. *Pak. J. Sci. Ind. Res.* **48**: 86-89.

Blackburn, W. H., Dennen, W.H. 1988. *Principles of Mineralogy*, pp. 247-248, 1st edition, W. C. Brown Publishers, Dubuque, Iowa, USA.

Crozier, R. D. 1992. *Flotation, Theory, Reagents and Ore Testing*, 5th edition, Pergamon Press, Oxford, UK.

Jain, S. K. 1986. *Ore Processing*, 1st edition, Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi, India.

Jeffery, G. H., Bassett, J., Mendham, J., Denney, R.C. 1989. *Vogel's Text Book of Quantitative Chemical Analysis*, 5th edition, ELBS, Longman Group, Oxford, UK.

Johnstone, S. J., Johnstone, M.G. 1961. *Minerals for Chemical and Allied Industries*, 2nd edition, John Wiley & Sons Inc., New York, USA.

Kursun, I., Arslan, F., Perek, K. T., Gurkan, V. 1994. Beneficiation of Etibank Halikoy antimonite ores by flotation and removal of arsenopyrite. In: *Proc. 5th Int. Miner. Process. Symp., Prog. Miner. Process. Technol.*, pp. 161-166, Capodica, Turkey.

Liu, R. 1988. Separation of antimony from ore containing lead. *Kuangye Gongcheng* **8**: 24-28.

Parsonage, P.G. 1985. Effect of slimes and colloidal particles on the flotation of galena. In: *Flotation of Sulphide Minerals*, K. S. E. Forssberg (ed), vol. **6**, Elsevier Science Publishing Company, New York, USA.

Peng, M., Wang, P., Chen, R. 1991. Mineral processing technology for a highly oxidized antimony ore. *Kuangchan Zhonghe Liyong* **2**: 15-17.

Pen'kov, N. 2001. Chemical activity of minerals: genetic and technological aspects. *Zap. Vseross. Mineral. O-va.*, **129**: 29-37.

Solozhenkin, P. M., Ivanova, N. K., Ibragimova, O. I., Stoyanov, A. F., Tkachova, K. I. 1994. Reagent regime improvement in flotation of antimony ores. *Tsvetn. Met.* **7**: 63-65.

Wang, J., Liu, Y., Chen, W., Zhang, S. 2001. Flotation separation of antimony and mercury from antimony-mercury paragenetic sulphide ore. *Faming Zhuanli Shenqing Gongkai Shuomingshu* CN 1, 308, 988.

Wang, J., Lei, T. 2000. Treating low-grade antimony ore by bath smelting-continuous fuming process. *Youse Jinshu*. **52**: 44-48.

Weiss, N. L. 1985. *SME Mineral Processing Hand Book*, Society of Mining Engineers, New York, USA.

Wills, B. A.1992. *Mineral Processing Technology*, 5th edition, Pergamon Press, New York, USA.

Yin, Z., Long, X. 2003. A method of leaching sodium antimonate from antimony ores by catalytic oxidation. *Faming Zhuanli Shenqing Gongkai Shuomingshu* CN 1,462,811.

Zhang, Q., Shang, Y. 2002. Increasing the recovery of antimony ores, *Guizhou Gongye Daxue Xuebao, Ziran Kexueban* **31:** 30-32.

Zhang, S. 2004. Investigation on the ore-dressing processes for the ores of Lu'erba Gold-Antimony Mine. *Huangjin* **25:** 36-38.