Physicochem. Probl. Miner. Process. 49(1), 2013, 145−156

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received May 31, 2012; reviewed; accepted July 10, 2012

FLOTATION OF ZINC OXIDE ORE USING CATIONIC AND CATIONIC-ANIONIC MIXED COLLECTORS

Akbar MEHDILO, Mehdi IRANNAJAD, Hossein ZAREI

Department of Mining and Metallurgical Eng., Amirkabir University of Technology, Tehran, Iran
Email**:** iranajad@aut.ac.ir

Abstract: Flotation of smithsonite coming from a cerussite flotation circuit was investigated using Armac C and Armac T as cationic collectors and their mixtures with potassium amyl xanthate (KAX) as an anionic collector. Under optimum condition using Armac T with sodium hexamethaphosphate as a depressant, a smithsonite concentrate with 42% Zn and 89.6% recovery is obtained while in the presence of sodium silicate depressant Armac C produces a concentrate containing 40.8% Zn with 92.5% recovery. However, Armac T acts a little more selectively than Armac C but their mixture with KAX act inversely. The KAX-Armac C mixed collector improves the Zn grade and recovery of the flotation concentrate while KAX-Armac T does not. At the mixture ratio of KAX - Armac C 2:1, the amine collector consumption is decreased and an optimal concentrate with 94% recovery and 43% Zn grade is obtained without any gangue depressant reagents.

Keywords: *flotation, smithsonite, collector, mixed collector, zinc*

Introduction

Nowadays, new technologies to produce zinc metal from oxidized zinc ores are being developed as it is becoming more difficult to find new sphalerite mines. Oxidized ores contain zinc in various carbonate and silicates minerals, such as smithsonite ($ZnCO_3$), hydrozincite ($2ZnCO_3{\cdot}3Zn(OH)_2$), zincite (ZnO), willemite (Zn_2SiO_4) and hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) and so on (Chen et al., 2009). In practice, the commonly used method for the recovery of oxidized lead and zinc minerals from ores at present is flotation (Onal G. et al., 2005). The flotation of oxidized lead and zinc minerals, particularly zinc minerals, is much more difficult than the flotation of corresponding sulfide minerals. Hexyl and amyl xanthates are capable of collecting smithsonite. However, the process is not selective enough in practice (Gaudin, 1957; Billi and Quai, 1963; Nagano et al., 1975; Yamada et al., 1976; Yamazaki et al., 1978; Herrera Urbina et al., 1999; Hosseini and Forssberg, 2006; Hosseini and Forssberg, 2007). The fatty acids are also used

http://dx.doi.org/10.5277/ppmp130114

to recover the zinc oxide minerals such as smithsonite, hemimorphite and calamine via froth flotation method (Rey, 1953; Nagano et al., 1974; Kiersznicki et al., 1981; Hosseini and Forssberg, 2006; Irannajad et al, 2009; Ejtemaei et al, 2011). Flotation using chelating agents is another alternative for beneficiation of zinc oxide minerals (Rinelli and Marabini, 1973; Fuerstenau and Palmer, 1976; Barbery et al., 1977; Marabini et al., 2007). The most common flotation technique used commercially for the treatment of zinc oxide minerals is sulfidization with Na_2S, followed by treatment with conventional cationic collectors, namely amine (Mckenna et al., 1949; Rey, 1979; Abramov, 1961; Onal et al., 2005; Pereira and Peres, 2005; Keqing et al., 2005; Hosseini and Forssberg, 2006; Irannajad et al., 2009). The amount of sulfidizing reagent and pH of the pulp must be carefully controlled in amine flotation (Hosseini and Forssberg, 2007; Salum et al, 1992). Either sodium sulfide or sodium hydrosulfide is used as a sulfidizing agent (Onal G. et al., 2005). When the pH value decreases, there is a drop in recovery (Hosseini and Forssberg, 2007; Salum et al, 1992). A mixture of amines and xanthates can be used as a collector. A system that contains two surfactants of different charge is called a catanionic system (Herrington et al., 1993; Hosseini and Forssberg, 2006; Hosseini and Forssberg, 2007; Ejtemaei et al, 2011).

The Angooran mine, located 100 km south west of Zanjan, is one of the largest lead and zinc oxide deposit in Iran. The major zinc mineral is smithsonite with hemimorphite and hydrozincite as minor minerals while the major lead mineral is cerrusite with mimetite as a minor one. Generally, the associated minerals are mainly calcite and quartz which are accompanied with minor amount of mica, hematite, goethite, kaolonite, and montmorolinite. The exploited ore is concentrated in Dandy Processing Plant which is located 20 km far from the mine with approximately 1 Gg (gigagram or 1000 ton) daily feed. The schematic flowsheet of present concentration process is shown in Fig. 1. The tailing of cerrusite flotation is the zinc concentrate containing 20-25% Zn, which is leached by sulfuric acid to extraction the zinc metal (Irannajad 2007; Mehdilo et al, 2010; Ejtemaei and Irannajad, 2008). In recent years by decreasing the Zn content of the ore, upgrading of tailing by froth flotation before acid leaching has been attracted considerably. In this work the cationic/anionic flotation of smithsonite from the tailing of cerrusite flotation circuit is studied.

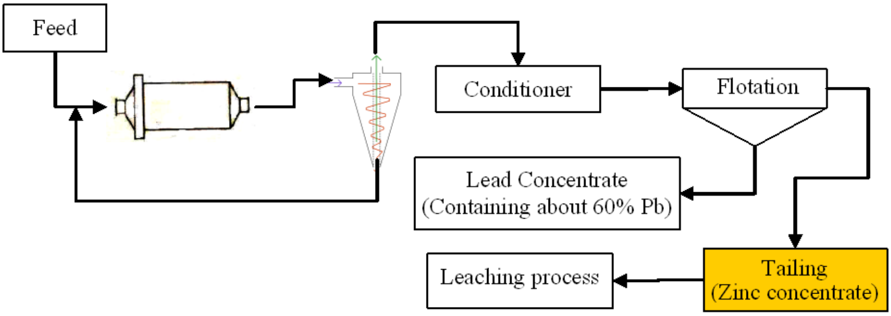

Fig. 1. Schematic flow diagram of Dandy Mineral Processing Plant

Materials and Methods

Materials

A representative sample containing 21.7% Zn was taken from tailing of the cerrusite flotation circuit. The chemical composition of the ore sample and pure smithsonite determined by XRF is presented in Table 1. The XRD (X-ray diffraction) pattern of the sample indicated that the associated minerals of smithsonite are calcite, quartz and minor amount of goethite, kaolinite, and montmorolinite. The reagents used in the study are shown in Table 2.

Table 1. Chemical composition of representative sample

Sample	Composition (wt. %)											
	ZnO	pbO	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	CdO	NiO	SO_3	L.O.I
ore sample	27.0	4.8	16.9	17.5	2.6	2.62	0.65	0.36	0.19	0.09	0.22	25.64
pure smithsonite	63.5	3.11	0.13	0.51	–	2.45	–	–	–	–	–	29.4

Table 2. Reagents used in flotation tests

Chemical	Concentration	Supplier	Role
Armac C (Cocoalkylamine) acetate)	99	Akzo Nobel	Collector
Armac T (Tallowalkylamine)	99	Akzo Nobel	Collector
Potassium amyl xanthate (KAX)	90	Cheminova	Collector
Sodium sulfide (Na_2S)	75	Merck	Sulfidizing reagent
Sodium silicate (SS)	97	Merck	Depressant
Sodium hexa methaphosphate (SH)	96	Scharlau	Depressant
NaOH	–	Merck	pH adjuster
Pine oil	99	Penn Chemical	Frother

Methods

Microflotation test

The samples were ground and then sieved to collect the –150 + 75 μm fraction for the microflotation tests. Single mineral microflotation tests were performed in a 300 cm^3 Hallimond tube at a constant air flow rate. Experiments were carried out at varying pH and reagent concentrations. Sulphuric acid and sodium hydroxide solution were used for pH adjustment. For each test, 3 g of –150 + 75 μm fractions were separately conditioned using reagents at the desired pH in a 400 cm^3 volumetric flask for a predetermined time (3 min). The collector was then added to the slurry and flotation was carried out in the Hallimond tube. After the flotation tests, the concentrate and tailings were filtered, dried and weighed.

Flotation tests

In the flotation tests carried out in 1 dm^3 Denver cell according Fig. 2, the desired amount of sodium sulfide was added to the pulp and was conditioned for 10 min by adjusting the pH at 11. A depressant was then added and conditioned for 5 min, after which the slurry was conditioned with collectors for 5 min (conditioning time for mixed collectors was 10 min). Finally, pine oil was used as a frother (120 g/Mg) with a conditioning time of 2 min. The froth collection was performed for 10 min. The flotation concentrate and tailing were filtered, dried, weighed, and analyzed by atomic absorption technique.

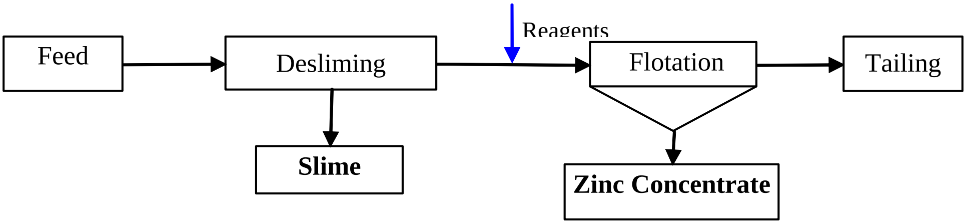

Fig. 2. Schematic diagram of flotation tests

Results and discussion

Microflotation tests

The microflotation tests were carried out in order to select the optimum amount of sulfidizer agent and pH value. The recovery of smithsonite flotation using 500 g/Mg Armac C and KAX as a function of pH value are shown in Fig. 3. The maximum recovery of smithsonite flotation occurred at pH = 9 and pH = 10.5–11 using KAX and Armac C, respectively. In the next experiments pH=11 was selected for cationic flotation by Armac C and Armac T. The effects of sodium sulfide on smithsonite flotation using 500 g/Mg Armac C, Armac T and KAX are shown in Fig. 4. The recovery of smithsonite was increased by increasing sodium sulfide concentration. The optimum dosage of sodium sulfide is 500 g/Mg which results in 82.6% and 83.7% recoveries using Armac C and Armac T, respectively, while its optimum amount is 1.25 kg/Mg for KAX with 73.4% recovery. The recovery of smithsonite decreases with the increasing sodium sulfide concentration. This is due to over-sulfidization of the pulp and a high content of HS^- ion in the flotation system (Malghan, 1986; Onal et al., 2005; Fa et al., 2005).

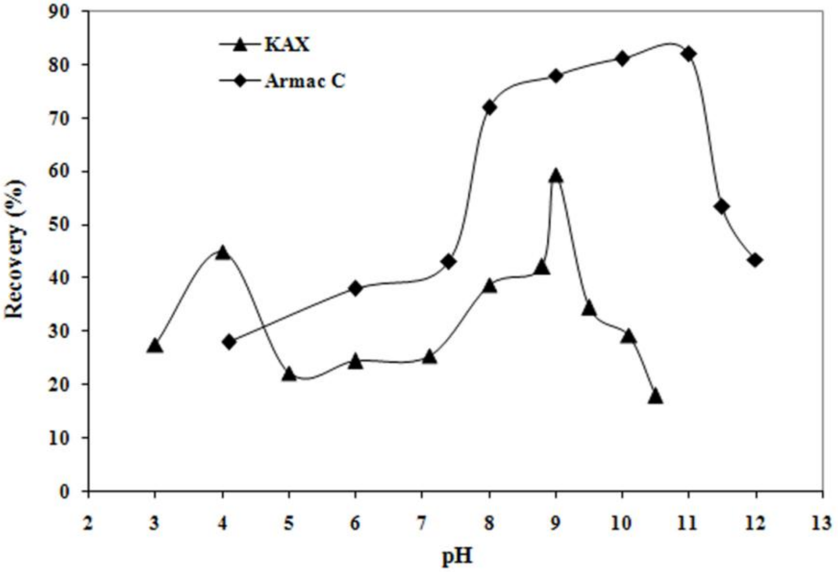

Fig. 3. Recovery of smithsonite flotation as a function of pH value
(500 g/Mg Armac C, 500 g/Mg KAX, 500 g/Mg Na_2S)

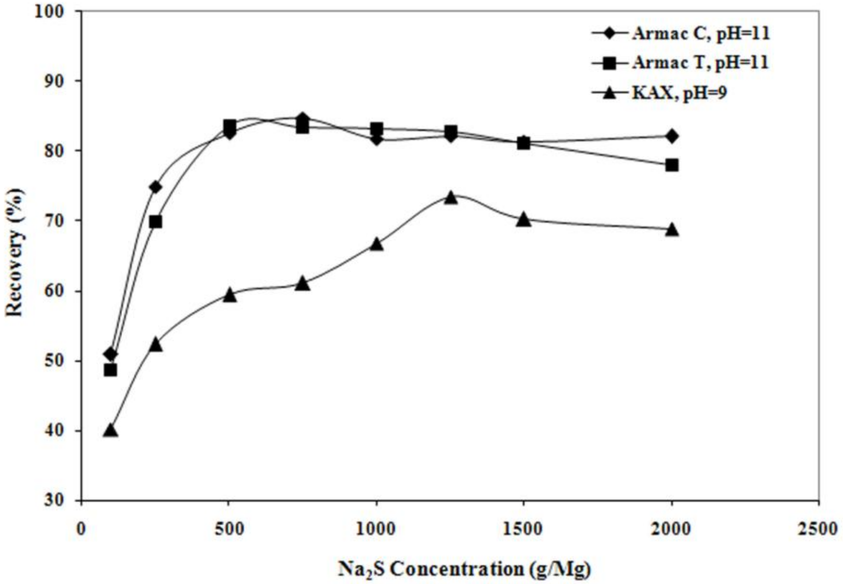

Fig. 4. Recovery of smithsonite as a function of Na_2S concentration
(500 g/Mg Armac C, 500 g/Mg Armac T, 500 g/Mg KAX)

Ore sample flotation

Cationic flotation

Figure 5 shows smithsonite flotation from the ore sample as a function of the sodium sulfide dosage using Armac C. The results revealed that the smithsonite particle surface was not sufficiently sulfidized. The optimal dosage of sodium sulfide is up to about 7500 g/Mg. At a high dosage, the adsorption of S^{2-} ions increases with the increase of sodium sulfide, and the flotation of smithsonite is hence depressed. Marabini et al., 1984, found that the smithsonite recovery is not sensitive to the Na_2S concentration when the concentration of sodium sulfide is high. The reason for this observation is that at high concentration of Na_2S, the $ZnCO_3$ component disappears totally and a dense coating of ZnS is formed on the mineral surfaces. Essentially, the full formation of ZnS on the surface of ZnO minerals results in the amine adsorption less sensitive to the effects of concentration of Na_2S. However, the Na_2S dosage is relatively high but it also has the role of a pH adjuster, and no other pH adjusting reagent is required (Marabini et al., 1984).

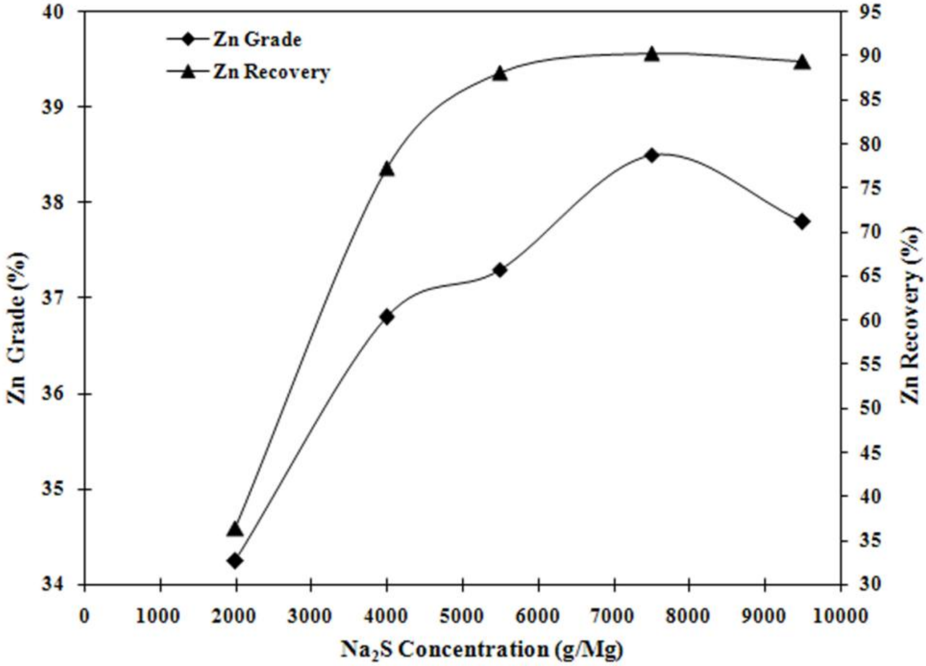

Fig. 5. Grade and recovery of zinc in smithsonite flotation concentrate as a function of sodium sulfide dosage using Armac C (Armac C 200 g/Mg, pH=11)

The flotation response of smithsonite as a function of Armac C or Armac T dosage in the presence of SS and SH as depressant reagents is shown in Figs 6 and 7. It is clear that the Zn grade of the concentrate obtained by Armac T is higher than that by

Armac C. The increase of both collectors dosage increases Zn recovery and decreases Zn grade in the smithsonite flotation concentrate. The reduction of Zn grade is attributed to the flotation of more gangue minerals due to high collector concentration.

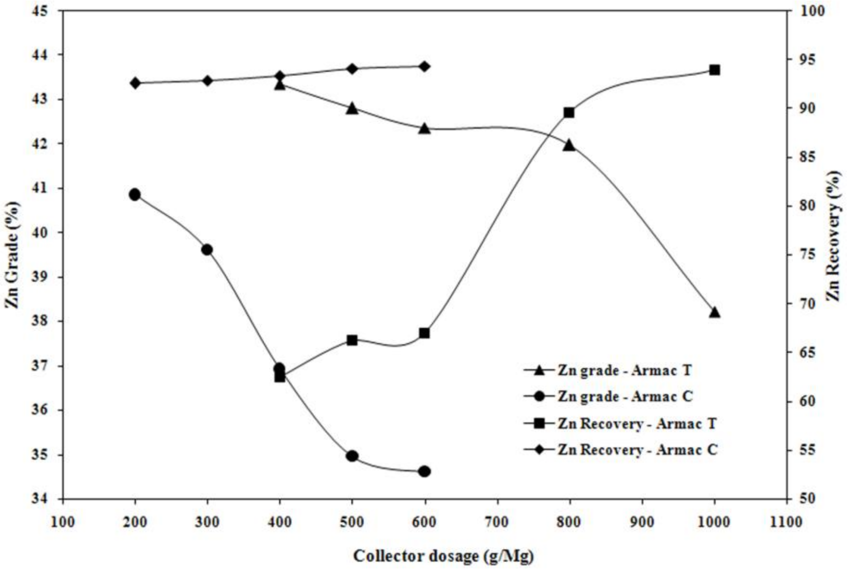

Fig. 6. Grade and recovery of zinc in smithsonite flotation concentrate as a function of collector dosage (7500 g/Mg Na_2S, 600 g/Mg SS, pH = 11)

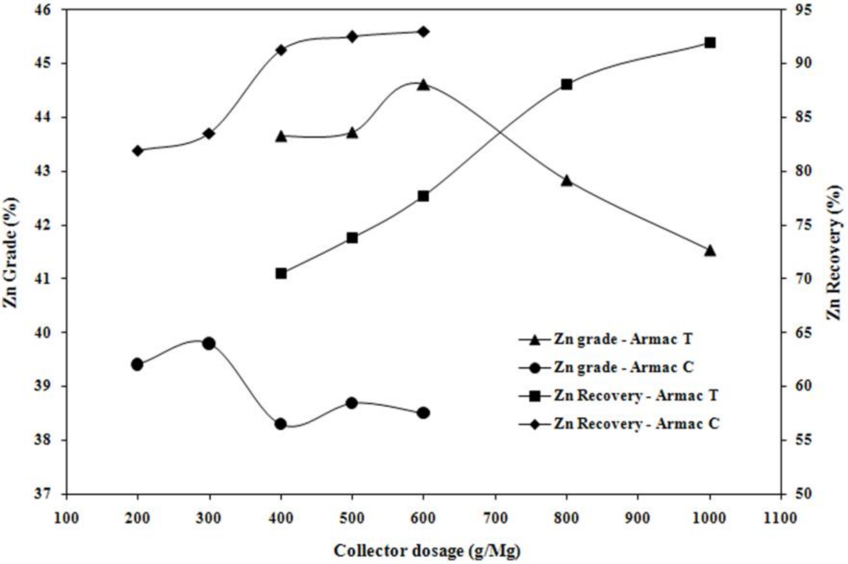

Fig. 7. Grade and recovery of zinc in smithsonite flotation concentrate as a function of collector dosage (7.5 kg/Mg Na_2S, 250 g/Mg SH, pH = 11)

In the presence of SS, the optimal dosage of Armac C is 200 g/Mg, which results in a smithsonite concentrate with 40.8% Zn and 92.5% recovery, while the optimum Zn grade and recovery in the concentrate produced by Armac T are about 42.0% and 89.6%, respectively which is obtained at dosage of 800 g/Mg. Using SH as depressant reagent increases the optimal dosage of Armac C to 300 g/Mg which results in a concentrate containing 39.8% Zn with 83.5% recovery. In the presence of SH, using 800 g/Mg as an optimal dosage of Armac T a concentrate with 42.8% Zn and 92.5% recovery is obtained.

Anionic–Cationic flotation

KAX–Armac C

The Zn grade – recovery curves of the bench flotation using mixed collectors depend on the mixture ratio and are shown in Fig. 8. At a fixed concentration of Armc C (50 g/Mg), the KAX concentration was increased from 150 to 900 g/Mg and the mixed collector ratio of KAX:Armac C was varied from 3:1, 6:1, 10:1, 14:1, to 18:1. The results (Fig. 8a) show that the increasing of KAX dosage or mixture ratio improves the Zn grade significantly but it decreases the Zn recovery from 92.5% (using Armc C only) to about 70%. The optimum mixture ratio of the mixed collector is KAX: Armac C, 6:1 (300 g/Mg KAX and 50 g/Mg Armac C) which results in a concentrate with 72.6% recovery and 47.5% Zn grade. For improving the recovery, at the optimum dosage of KAX (300 g/Mg) the dosage of Armac C was increased gradually according Fig. 8b. With increasing the concentration of Armac C, the Zn grade is decreased but the Zn recovery is improved significantly. The optimal ratio of collectors is KAX:Armac C, 2:1 (300 g/t KAX and 150 g/t Armac C) which results in a smithsonite concentrate with about 43% Zn and 94% recovery. At the optimal conditions the Zn grade and recovery of the concentrate obtained by mixed collector are 2.15% and 1.5% respectively higher than that obtained using Armac C alon. Furthermore, by using mixed collectors without any depressant reagents, the optimum consumption of amine collector is also decreased.

KAX–Armac T

The Zn grade – recovery curves of the bench flotation using the mixture of KAX and Armc T at the different mixture ratios are shown in Figure 9. At a fixed concentration of Armc T (300 g/Mg), the KAX concentration was increased from 90 to 1000 g/Mg and the mixed collector ratio of KAX:Armac T was varied from 0.3:1, 0.6:1, 1.2:1, 1.8:1, 2.3:1 to 3.3:1. As seen from Fig. 9a the increasing KAX concentration or mixture ratio improves the Zn grade and recovery and the optimum concentrate containing 43.3% Zn grade and 65.1% recovery are obtained at a mixture ratio of 1.2 : 1 (360 g/Mg KAX and 300 g/Mg Armac T). A further increase of the KAX concentration decreases the selectivity of the amine collector and Zn content of the concentrate but it does not have significant effect on the Zn recovery. At the KAX concentrations

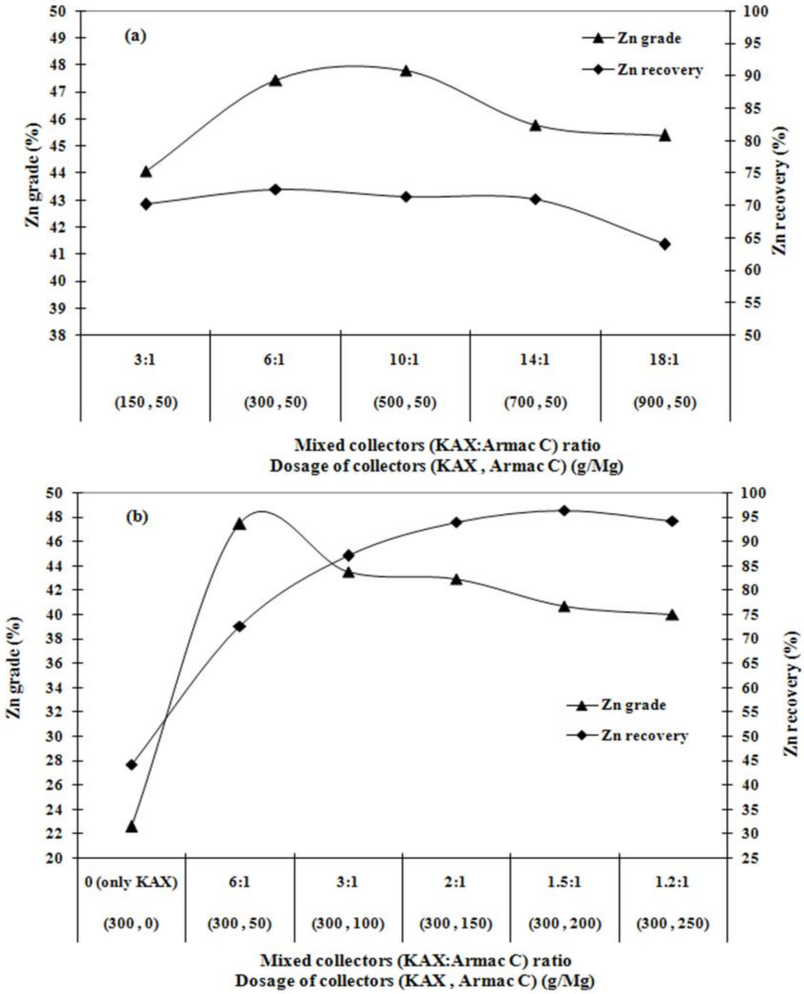

Fig. 8. Grade and recovery of Zn in smithsonite flotation concentrate as a function of mixed collectors ratio (Na_2S 7500 g/Mg, without deprassant, pH = 11): (a) variation of KAX concentration, (b) variation of Armac C concentration

higher than 700 g/Mg with decreasing the Zn grade, the recovery is increased significantly. For improving the Zn grade and recovery of the concentrate, at the optimum fixed concentration of KAX (360 g/Mg) the concentration of Armc T is increased according Fig. 9b. The results show that the increasing of Armc T consumption increases the Zn recovery of the concentrate significantly but it decreases the Zn grade of the concentrate. The optimum mixture ratio of the mixed collector is KAX:Armac T as 0.6:1 (360 g/Mg KAX and 600 g/Mg Armac T) which results in a concentrate with

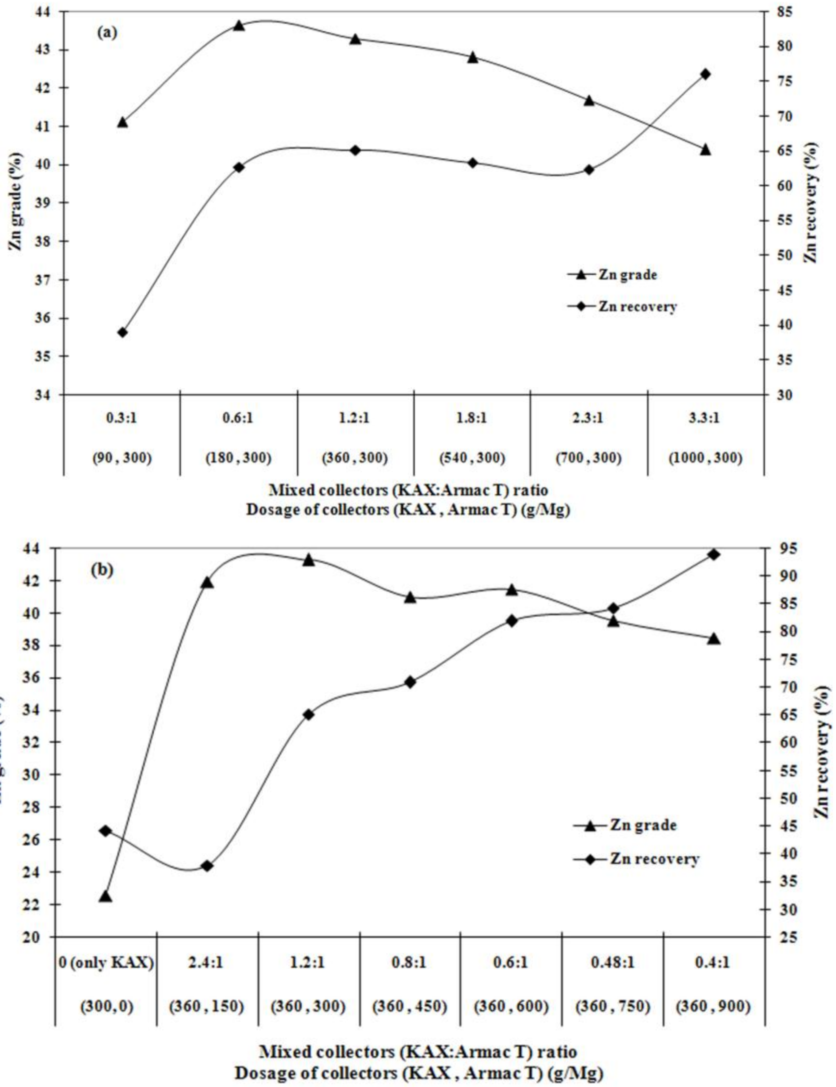

Fig. 9. Grade and recovery of Zn in smithsonite flotation concentrate as a function of mixed collectors ratio (Na_2S 7500 g/Mg, without depressant, pH = 11): (a) variation of KAX concentration, (b) variation of Armac T concentration

41.5% Zn grade and about 82% recovery. A comparison of results presented in Figs 6, 7 and 9 shows that the Zn grade and recovery of the concentrate obtained using mixed collector (KAX and Armac T) are lower than those produced by Armac T alone. However, more experiments indicated that using SH as a depressant reagent the Zn grade and recovery of the concentrate produced with mixed collector are improved a little but the results are not as good as obtained with Armac T alone.

Conclusion

From two amine collectors used in this study, Armac T acts a little more selectively than Armac C and results in smithsonite concentrate with higher Zn grade while Armac C is effective in enhancing the recovery of Zn. The KAX–Armac C mixed collector improves Zn grade and recovery of the smithsonite concentrate while the KAX-Armac T one does not. The best concentrate with 43% Zn and 94% recovery is obtained using the KAX–Armac C mixed collector at a mixture ratio of KAX:Armac C as 2:1 (300 g/Mg KAX and 150 g/Mg Armac C). The improvement of Zn grade and recovery is probably related to the co-absorption of KAX and Armac C when they are used as a mixed collector. The presence of KAX increases the Armac C adsorption due to the decrease in the electrostatic head–head repulsion between the surface and ammonium ions and increase in the lateral tail–tail hydrophobic bonds (Hosseini and Forssberg, 2007). The reason why the mixture of KAX with Armac T does not have positive effect on the smithsonite flotation concentrate should be investigated comprehensively. The decrease of collectors consumption and also no requirement of any depressant reagents are other advantages of the studied xanthate-amine (KAX-Armac C) mixed collector.

References

ABRAMOV A.A., 1961. *Use of cationic agents for oxide lead‒zinc minerals*. Chemical Abstracts 55, 26910f.

BARBERY G., CECILE J.L., PLICHON V., 1977. *The use of chelates as flotation collectors*. In: Proceeding of XII International Mineral Processing Congress, Sao Polo, pp. 19−34.

BILLI M., QUAI V., 1963. *Development and results obtained in the treatment of zinc oxide ores at AMMI mines*. In: XI International Mineral Processing Congress, Cannes, pp. 631−649.

CHEN A., ZHAO Z.W., JIA X., LONG S., HUO G., CHEN X., 2009, *Alkaline leaching Zn and its concomitant metals from refractory hemimorphite zinc oxide ore*. Hydrometallurgy (97) 228–232.

EJTEMAEI M., IRANNAJAD M., GHARABAGHI M., 2011. *Influence of important factors on flotation of zinc oxide mineral using cationic, anionic and mixed (cationic/anionic) collectors*; Minerals Engineering 24 (13), 1402–1408.

EJTEMAEI M., IRANNAJAD M., 2008. *Recovery of Zinc Oxide Minerals from Angooran Mining Tailings by Flotation*. MSc Thesis, Amirkabir University of Technology, Iran.

FUERSTENAU M.C., PALMER B.R., 1976. *Anionic flotation of oxides and silicates flotation*. In: Gaudin, A.M. (Ed.), Memorial Volume, vol. 1. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, pp. 148−196.

FUERSTENAU M.C., MILLER J.D, KUHN M.C., 1985, *Chemistry of Flotation*, SME, New York.

GAUDIN A.M., 1957. *Flotation*. McGraw Hill Inc., New York. pp. 182−189.

HERRINGTON K.L., KALER E.W., MILLER D.D., ZASADZINSKI J.A., CHIRUVOLU S., 1993. *Phase behaviour of aqueous mixtures of dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulfate (SDS)*. Journal of Physical Chemistry 97 (51), 13792−13802.

HERRERA URBINA R., SOTILLO F.J., FUERSTENAU D.W., 1999. *Effect of sodium sulfide additions on the pulp potential and amyl xanthate flotation of cerussite and galena*. International Journal of Mineral Processing 55 (3), 157−170.

HOSSEINI S.H., FORSSBERG E., 2006a. *Adsorption studies of smithsonite flotation using dodecylamine and oleic acid*, Minerals and Metallurgical Processing, Processing SME 23 (2), 87−96.

HOSSEINI S.H., FORSSBERG E., 2006b. *Flotation behaviour of oxide zinc ore from Angooran deposit, Iran in the presence of cationic/anionic and mixed (cationic/anionic) collectors*. European Journal of Mineral Processing and Environmental Protection 6 (3), 1−2.

HOSSEINI S.H., FORSSBERG E., 2007. *Physicochemical studies of smithsonite flotation using mixed cationic/anionic collector*, Minerals Engineering 20 (6), 621−624.

IRANNAJAD M., EJTEMAEI M., GHARABAGHI M., 2009. *The effect of reagents on selective flotation of smithsonite–calcite–quartz*. Minerals Engineering (20), 621–624.

IRANNAJAD M., 2007, *Recovery of zinc from low grade zones of Angouran mine (research project)*, Department of Mining and Metallurgical Engineering, Amirkabir University of Technology.

KEQING F.A., MILLER J.D., GUANG-HUI Li, 2005. *Sulfidization flotation for recovery of lead and zinc from oxide¬sulfide ores*. Transactions of Nonferrous Metals Society of China (15), 1138−1147.

KIERSZNICKI T., MAJEWSKI J.J., MZYK J., 1981. *5-Alkylsalicyladdoximes as collectors in flotation of sphalerite, smithsonite and dolomite in a Hallimond tube*. International Journal of Mineral Processing 7, 311−318.

MARABINI A.M., CIRIACHI M., PLESCIA P., BARBARO M., 2007. *Chelating reagents for flotation*. Journal of Minerals Engineering 20, 1014−1025.

MARABINI A.M., ALESSE V., GARBASSI F., 1984. *Role of sodium sulfide, xanthate and amine in flotation of lead–zinc oxidized ores*, Reagents in the mineral industry, The Institute of Mining and Metallurgy, 1984:125.

MCKENNA W.J., LESSELS V., PETERSSON E.C., 1949. *Froth flotation of oxidized zinc ores*, United States, Patent: 2482859.

MEHDILO A., ZAREI H. and IRANNAJAD M.; 2010. *Concentration of Iranian low grade zinc ore*, International Mining Congress and Exhibition. 18–21 October, Tehran, Iran.

NAGANO J., TANAKA M., SAITO K., 1975. *Flotation of zinc oxide ore*. Chemical Abstracts 83, 31384.

NAGANO J., TANAKA, M., SAITO K., 1974. *Ore flotation*. Chemical Abstracts 82, 114571.

ONAL G., BULUT G., GUL A., KANGAL O., PEREK K.T. and ARSLAN F.; 2005. *Flotation of Aladagˇ oxide lead–zinc ores*, Minerals Engineering (18) 279–282.

PEREIRA C.A., PERES A.E.C., 2005. *Reagents in calamine zinc ores flotation*, Minerals Engineering 18, 275−277.

PERES A.E.C., BORGES A.M., GALERY R., 1994. *The effect of dispersion degree on the floatability of an oxidized zinc ore*. Minerals Engineering 7 (11), 1435−1439.

REY M., 1953. *The flotation of oxidized ores of lead copper and zinc*. In: *Recent Developments in Mineral Dressing Symposium*. IMM, London, pp. 541−548.

REY M., 1979. *Memoirs of milling and process metallurgy: 1 – flotation of oxide ores*. Institution of Mining and Metallurgy, Section C 88, 245−250.

RINELLI G., MARABINI A.M., 1973. *Flotation of zinc and lead oxide-sulfide ores with chelating agents*, Inst. Min. Met. In: Proc. X International Mineral Processing Congress, London, pp. 493−521.

SALUM M.J.G., DE ARAUJO A.C. and PERES A.E.C., 1992. *The role of sodium sulfide in amine flotation of silicate zinc minerals*; Minerals Engineering, 5, 411–419.

YAMADA M., SHOJI T., ONADA T., SHIMOIIZAKA J., 1976. *Flotation of zinc carbonate*. Chemical Abstracts 84, 182894.

YAMAZAKI S., MATUSI N., OHTSUBO E., 1978. Chemical Abstracts 89, 63078.