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Thiosulfate leaching of silver, gold and bismuth from a complex sulfide concentrates

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Abstract

The intensification of the thiosulfate leaching of silver, gold and bismuth from sulfide concentrates using mechanical activation and mechanochemical pretreatment step was investigated. The physico-chemical changes in a complex sulfide concentrate (Casapalca, Peru) as a consequence of mechanochemical pretreatment had a pronounced influence on the subsequent silver extraction. The optimum results from mechanochemical pretreatment and subsequent leaching of the concentrate with ammonium thiosulfate were achieved with 99% recovery of Ag after only 3 min of leaching. The leaching of gold from a mechanically activated complex sulfide concentrate (Banská Hodruša, Slovakia) using ammonium thiosulfate was studied as follows. Physico-chemical transformations in the concentrate due to mechanical activation have an influence on the rate of extraction and the recovery of gold. It was possible to achieve 99% Au recovery within 45 min for a sample mechanically activated. Mechanical activation proved to be an appropriate pretreatment for this concentrate before extraction of gold into thiosulfate leaching solution. The selective leaching of a bismuth from the lead concentrate (Atacocha, Peru) by using of sodium thiosulfate and mechanical activation as the pretreatment step was examined as the last example. It is possible to achieve more than 90% recovery of a bismuth in leachate even in three minutes for mechanically activated samples.

Keywords: Silver; Gold; Bismuth; Sulfide concentrate; Mechanochemistry; Leaching

1. Introduction

The key stage for silver, gold and bismuth leaching from sulfide concentrates is the way of pretreatment of the concentrates and selection of leaching reagents. Chemical, biological and physical pretreatments are applied to the sulfide concentrates, with the aim of changing the chemical composition and/or particle size of the sulfides, thus facilitating the subsequent leaching (La Brooy et al., 1994; Baláž et al., 1998). The relatively new process of mechanochemical pretreatment is being successfully applied in both fundamental research and plant operations (Baláž,

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2000). In this process, the minerals are subjected to high-intensity milling either alone (mechanical activation) or in combination with chemical agent (mechanochemical leaching). This milling results in particle size reduction and causes chemical or physico-chemical transformations, which significantly affect on subsequent hydrometallurgical processing (Tkáčová, 1989; Welham, 1997; Baláž, 2000).

Thiosulfate leaching represents an alternative for the non-cyanide leaching of gold, silver as well as for selective leaching of bismuth from complex sulfide concentrates (Hiskey and Atluri, 1988; Marsden and House, 1994; Wan and Brierley, 1997; Ficeriová et al., 2002).

The mechanical activation and mechanochemical pretreatment proved to be a very effective method of pretreatment of complex sulfide concentrates before extraction of examined metals into leach liquors. The process of thiosulfate leaching is bringing the kinetic advantage and moreover good selectivity in the cases of silver, gold and bismuth extraction.

It is the aim of this paper to verify the possibilities of mechanical activation and mechanochemical leaching for three different sulfide concentrates with the application of thiosulfate salts in order to obtain good recovery and selectivity for Ag, Au and Bi extraction.

2. Experimental

2.1. Materials

1. A silver-bearing complex sulfide concentrate (Casapalca, Peru) was used to test the effect of mechanochemical pretreatment and subsequent thiosulfate leaching of silver. The X-ray data indicated the presence of tetrahedrite ($Cu_{12}Sb_4S_{13}$), galena (PbS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), quartz (SiO_2), bournonite ($CuPbSbS_3$), chalcocite (Cu_2S) and seligmanite ($CuPbAsS_3$) in the concentrate.
2. A gold-bearing complex sulfide concentrate (Banská Hodruša, Slovakia) was selected as a model material for testing the effect of mechanical activation on the subsequent thiosulfate leaching of gold. Chalcopyrite ($CuFeS_2$), galena (PbS), sphalerite (ZnS), tetrahedrite ($Cu_{12}Sb_4S_{13}$), pyrite (FeS_2) and quartz (SiO_2) are the main phases indicated by XRD in the concentrate.
3. Lead sulfide concentrate (Atacocha, Peru) was used to test the effect of mechanical activation and subsequent leaching of bismuth. XRD analysis indicates the presence of galena (PbS), sphalerite (ZnS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and quartz (SiO_2).

The chemical composition of the concentrates is given in Table 1.

2.2. Physico-chemical characterization

The specific surface area (S_A) was determined by the BET technique using low-temperature nitrogen adsorption in a Gemini 2360 sorption apparatus (Micromeritics, USA).

X-ray diffractometry (XRD) was accomplished by using a DRON 2.0 diffractometer with a GUR-5 goniometer (Techsnabexport, Russia) equipped with an FeK_α source operating at 25 kV and 10 mA. Data were collected every 2 s and the detector was moved at a rate of 2° min^{-1}.

2.3. Mechanical activation and mechanochemical pretreatment

The mechanochemical pretreatment of concentrate from Casapalca and mechanical activation of concentrates from Banská Hodruša and Atacocha was

Table 1
Chemical composition of the concentrates under study

Concentrates	Components (%)										
	Ag (g t^{-1})	Au (g t^{-1})	Bi	Cu	Pb	Zn	Fe	Sb	As	S	SiO_2
Casapalca (Peru)	15 500	0.9	–	19.5	16.5	8.8	3.4	8.3	3.2	29	0.7
B. Hodruša (Slovakia)	353	170	0.02	0.9	4.1	3.6	20	0.2	0.12	44	5.5
Atacocha (Peru)	2210	–	1.3	1.5	51.3	8.4	3.9	–	–	19	–

Table 2
Parameters of mechanical activation and mechanochemical pretreatment of the concentrates

Parameters	Concentrates		
	Casapalca (Peru)	Banská Hodruša (Slovakia)	Atacocha (Peru)
Volume of milling chamber (mL)	500	500	500
Milling medium	H_2O+ (Na_2S+ NaOH)	H_2O	H_2O
Volume of milling medium (mL)	200+ (80 g L^{-1}+50 g L^{-1})	200	200
Weight of sample (g)	50	50	50
Weight of milling balls (g)	2000	2000	2000
Diameter of milling balls (mm)	2	2	2
Material of milling balls	Steel	Steel	Steel
Milling time (min)	30	30	30
Revolutions of milling shaft (min^{-1})	1000	1000	1000
Temperature (°C)	90	25	25

performed in a stirring ball mill (Attritor, Molinex PE-075, Netzsch-Germany) using of conditions listed in Table 2.

2.4. Thiosulfate leaching

The leaching of concentrates Casapalca (Peru), Banská Hodruša (Slovakia) and Atacocha (Peru) was investigated at conditions presented in Table 3.

3. Results and discussion

3.1. Mechanochemical pretreatment and mechanical activation

The mechanochemical pretreatment of concentrate Casapalca in alkaline solution (Na_2S+NaOH) comprise milling and leaching which act in a combined effect. The milling leads to destruction of a silver-bearing tetrahedrite, which decomposes because of simultaneous leaching to set antimony free in the leach. The content of Sb has decreased from the original value of 8.3% to value of 1.02% which indicate the destruction of tetrahedrite. This is in agreement with previous papers on mechanochemical alkaline leaching of tetrahedrite (Baláž et al., 1994; Baláž and Kammel, 1996).

The typical change due to mechanochemical pretreatment and/or mechanical activation of all concentrates in an attritor was an increase in the specific surface area, S_A (Table 4). This change has influence on both the rate of extraction and the recovery of silver, gold and bismuth from used concentrates.

3.2. The effect of mechanochemical pretreatment and mechanical activation on thiosulfate leaching of Ag, Au and Bi

The mechanochemical pretreatment and mechanical activation proved to be a very effective method of pretreatment of the complex sulfide concentrates

Table 3
Parameters for leaching of the concentrates

Parameters	Concentrates		
	Casapalca (Peru)	Banská Hodruša (Slovakia)	Atacocha (Peru)
Volume of glass reactor (mL)	1000	1000	500
Leaching agents	$(NH_4)_2S_2O_3$+$CuSO_4$. 5 H_2O	$(NH_4)_2S_2O_3$+$CuSO_4$. 5 H_2O	$Na_2S_2O_3$. 5 H_2O
Concentration of leaching reagent	74 g L^{-1}+10 g L^{-1}	74 g L^{-1}+10 g L^{-1}	124 g L^{-1}
Volume of leaching solution (mL)	500	500	400
pH	6	6	7
Weight of sample (g)	2	1	1
Time of leaching (min)	15	60	60
Stirring rates (s^{-1})	8.33	8.33	8.33
Temperature (°C)	70	70	25

Table 4
Specific surface area, S_A of "as-received" samples and samples after mechanochemical pretreatment and mechanical activation

Concentrates	Samples	S_A (m^2 g^{-1})
Casapalca (Peru)	"As-received"	0.26
	Mechanochemically pretreated	15.7
Banská Hodruša (Slovakia)	"As-received"	0.18
	Mechanically activated	8.19
Atacocha (Peru)	"As-received"	0.69
	Mechanically activated	11.95

before extraction of silver, gold and bismuth into leach liquor.

The dependence of silver recovery on the leaching time for concentrate from Casapalca is shown in Fig. 1. The leaching of "as-received" sample of the concentrate with the ammonium thiosulfate afforded only 6% Ag into leach. The results for the same but the mechanochemically pretreated concentrate shows that the physico-chemical changes in the silver-bearing tetrahedrite have accelerated the process of thiosulfate leaching. Mechanochemical pretreatment enables to achieve more than 90% recovery of silver in leachate even in 3 min. Recoveries of accompanying metals 27% Cu, 19% Pb, 5% Zn, 2.5% Fe, 0.15% Sb and 1.1% As were obtained under 15 min of leaching.

Fig. 2 shows the effect of leaching time on gold recovery for mechanically activated concentrate from Banská Hodruša. In the "as-received" sample only 54% of gold and 52% of silver were recovered after 60 min leaching in ammonium thiosulfate. The results for the mechanically pretreated concentrate indicated that the physico-chemical changes of the gold-bearing minerals brought about an acceleration of the leaching process. It was possible to achieve gold and silver recoveries of 99% and 65% within 45 min for pretreated sample. 27% Cu, 17% Pb, 2.5% Zn and 1.3% Fe presented recoveries of accompanying metals in this case.

The dependance of bismuth recovery together with the recoveries of accompanying metals is represented in Fig. 3 for mechanically activated concentrate Atacocha and with the application of sodium thiosulfate as the leaching agent. It is possible to achieve

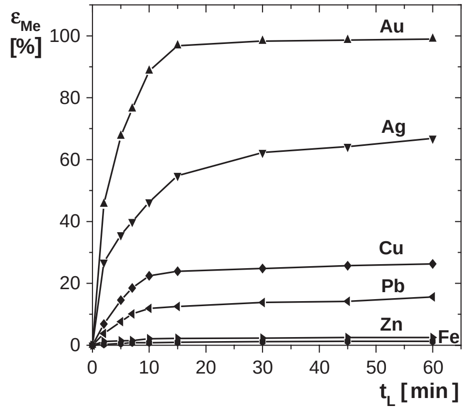

Fig. 2. Recovery of Au, Ag, Cu, Pb, Zn and Fe, ε_{Me} vs. leaching time, t_L for mechanically activated concentrate Banská Hodruša. Leaching agent: $(NH_4)_2S_2O_3$+$CuSO_4$. $5H_2O$.

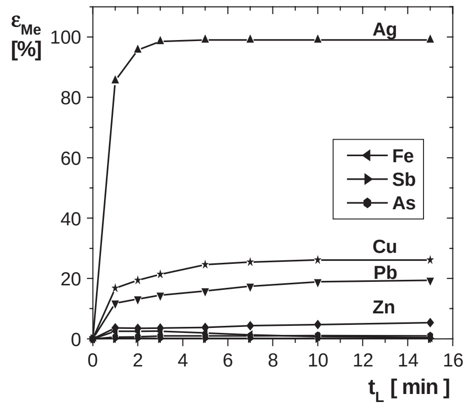

Fig. 1. Recovery of Ag, Cu, Pb, Zn, Fe, Sb and As, ε_{Me} vs. leaching time, t_L for mechanochemically pretreated concentrate Casapalca. Leaching agent: $(NH_4)_2S_2O_3$+$CuSO_4$. $5H_2O$.

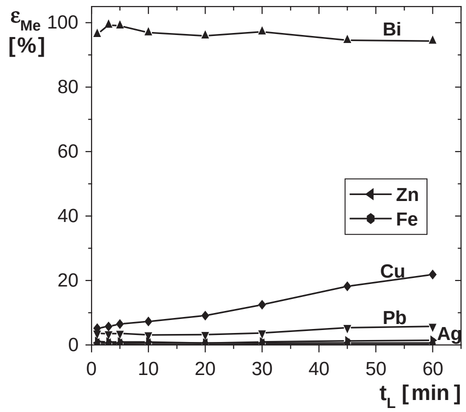

Fig. 3. Recovery of Bi, Cu, Pb, Zn, Fe and Ag, ε_{Me} vs. leaching time, t_L for mechanically activated concentrate Atacocha. Leaching agent: $Na_2S_2O_3$. $5H_2O$.

the 99% recovery of bismuth in leach even in 3 min with recoveries of 22% Cu, 5% Pb, 1% Zn, 0.5% Fe, 1% Ag during 60 min. The recovery of only 38% Bi was obtained in 60 min for “as-received“ sample.

The results demonstrated that mechanochemical pretreatment as well as mechanical activation of this sulfide concentrates leads to improved leaching selectivity.

4. Conclusions

Mechanochemical pretreatment and mechanical activation of the complex sulfide concentrates from deposits Casapalca (Peru), Banská Hodruša (Slovakia) and Atacocha (Peru) in a stirring ball mill (attritor) influence the increase of their specific surface area as well as bring about the structural changes in the concentrates and this result in the following thiosulfate leaching. This type of leaching is more advantageous for selective and rapid extraction of silver, gold and bismuth from the concentrates. It is possible to achieve more as the 90% recovery of an examined metals. The process of thiosulfate leaching is nontoxic and moreover brings kinetic advantage over classical cyanide leaching.

Acknowledgements

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References

Baláž, P., 2000. Extractive Metallurgy of Activated Minerals. Elsevier, Amsterdam. 290 pp.

Baláž, P., Kammel, R., 1996. Application of attritors in hydrometallurgy of complex sulphide ores. Metall 50, 345–347.

Baláž, P., Kammel, R., Achimovičová, M., 1994. Mechanochemical treatment of tetrahedrite as a new ecologically non-polluting way of metals recovery. Metall 48, 217–220.

Baláž, P., Achimovičová, M., Ficeriová, J., Kammel, R., Šepelák, V., 1998. Leaching of antimony and mercury from mechanically activated tetrahedrite $Cu_{12}Sb_4S_{13}$. Hydrometallurgy 47, 297–307.

Ficeriová, J., Baláž, P., Boldižárová, E., Jeleň, S., 2002. Thiosulphate leaching of gold from a mechanically activated CuPbZn concentrate. Hydrometallurgy 67, 37–43.

Hiskey, J.B., Atluri, V.P., 1988. Dissolution chemistry of gold and silver in different lixiviants. Mineral Processing and Extractive Metallurgy Review 4, 95–134.

La Brooy, S.R., Linge, H.G., Walker, G.S., 1994. Review of gold extraction from ores. Minerals Engineering 7, 1213–1241.

Marsden, J., House, I., 1994. The Chemistry of Gold Extraction. Ellis Horwood, New York. 569 pp.

Tkáčová, K., 1989. Mechanical Activation of Minerals. Elsevier, Amsterdam. 155 pp.

Wan, R.Y., Brierley, J.A., 1997. Thiosulfate leaching following biooxidation pretreatment for gold recovery from refractory carbonaceous-sulfidic ore. Mining Engineering 15, 76–80.

Welham, N.J., 1997. The effect of extended milling on minerals. Bulletin of Canadian Institute of Metallurgy 90, 64–68.