Influence of mechanochemical pretreatment on leaching of silver in cyanide and non-cyanide medium

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The leaching of silver from a mechanochemically pretreated silver-bearing complex sulphide concentrate of Peruvian origin (Casapalca) has been studied. The results with as-received concentrate have shown very low extraction of silver (up to 5.7%) in all cases of leaching. The mechanochemical pretreatment has caused 85% amorphization of tetrahedrite as silver-bearing mineral and an increase in the specific surface area of the concentrate from 0.3 m² g⁻¹ to a maximum value of 15.7 m² g⁻¹. This fact manifested itself in the subsequent process of silver extraction. By application of thiosulphate and thiourea leaching 99% recovery of Ag was reached already after 3–5 min of leaching. -^C *2004 Kluwer Academic Publishers*

1. Introduction

The mechanochemical leaching belongs among the innovation processes which intensify the hydrometallurgical processes by creation the new surface area and bulk defects in sulphides [1]. Alkaline leaching using Na₂S and NaOH with the application of mechanochemical pretreatment has been shown to be effective for the decomposition of silver-bearing antimony and arsenide sulphosalts [2, 3].

The aim of this paper is to study the combined process of mechanochemical alkaline pretreatment and following non-cyanide and cyanide leaching of silver from a complex sulphide concentrate with tetrahedrite as the main silver-bearing component.

The leaching of silver in thiourea, thiosulphate and cyanide solutions can be described after [4] by equations:

$$
Ag + Fe3+ + 3CS(NH2)2
$$

= Ag[CS(NH₂)₂]⁺₃ + Fe²⁺ (1)

$$
2Ag + 4S_2O_3^{2-} + H_2O + 1/2O_2
$$

$$
= 2Ag(S_2O_3)_2^{3-} + 2OH^-
$$
 (2)

$$
2Ag + 4CN^- + H_2O + 1/2O_2
$$

$$
2A \circ (CN^- + 2OII^-)
$$
 (2)

$$
= 2\text{Ag(CN)}_2^- + 2\text{OH}^- \tag{3}
$$

2. Experimental

Silver-bearing complex sulphide concentrate from Peru (deposit Casapalca) was used to test the effect of mechanochemical pretreatment and subsequent noncyanide and cyanide leaching of silver. The chemical composition of the concentrate was as follows: 15 500 gt^{-1} Ag, 0.9 gt⁻¹ Au, 19.49% Cu, 16.52% Pb, 8.8% Zn, 3.35% Fe, 8.25% Sb, 3.23% As, 29% S, 0.02% Na, 0.73% SiO₂.

The XRD analysis of the sulphidic concentrate confirms the presence of tetrahedrite $(Cu_{12}Sb_4S_{13})$, galena (PbS), pyrite (FeS_2) , chalcopyrite (CuFeS₂), quartz $(SiO₂)$, bournonite (CuPbSbS₃), chalcocite (Cu₂S), seligmanite $(CuPbAsS₃)$ and iron (Fe), see Fig. 1.

Mechanochemical pretreatment of the concentrate has been performed using an attritor Molinex PE 075 (Netzsch, Germany). The 500 ml milling chamber was filled with 24, 30, 45, 60 and 66 g of the sample, respectively, 2000 g of steel balls (2 mm in diameter) and 200 ml of solution (80 gl⁻¹ Na₂S, 50 gl⁻¹ NaOH). The mill was run at 1000 min^{-1} for different milling times (24, 30, 45, 60, 66 min) and was operated at 90° C. The specific milling energy, E_M , can be defined by the following equation [5]:

$$
E_{\rm M} = \frac{m_{\rm B}}{m_{\rm S}} \cdot n \cdot t_{\rm M} \cdot g \cdot \pi \cdot d \cdot \mu(v) \tag{4}
$$

where m_B –weight of balls [kg], m_S –weight of sample [kg], *n*–revolutions of the mill $[s^{-1}]$, *t*_M–milling time [s], *g*–gravitational acceleration, *d*–diameter of milling chamber ($d = 0.075$ m), $\mu(v)$ –coefficient of friction $(\mu(v) = 0.9).$

The subsequent chemical leaching was performed in a 1000 ml glass reactor into which 500 ml of leaching

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Figure 1 The XRD pattern showing the mineralogical composition of the concentrate.

solution and 2 g of the concentrate after mechanochemical pretreatment were added. The leaching in noncyanide solutions was performed for up to 15 min and in the case of cyanide leaching up to 180 min at a stirring rate of 8.33 s⁻¹. The leaching of the mechanochemical pretreated concentrate was performed in three solutions under the conditions determined in our previous works [6, 7]:

1. Thiourea - $10 \text{ gl}^{-1} \text{ CS}(\text{NH}_2)_2 + 5 \text{ gl}^{-1} \text{Fe}_2(\text{SO}_4)_3$. $9H_2O + 10 \text{ gl}^{-1} H_2SO_4$; 293 K; pH = 1. 2. Ammonium thiosulphate - 74 gl⁻¹ (NH₄)₂S₂O₃ +

 10 g l⁻¹ CuSO₄·5H₂O; 343 K; pH = 6.

3. Sodium cyanide - 0.5 gl⁻¹ NaCN + 1 gl⁻¹ $Ca(OH)_2$; bubbling of air; 293 K; pH = 12.

3. Results and discussion

Fig. 2 shows the effect of the leaching time on silver recovery for various leaching medium for as-received sample. The leaching for 180 min of the as-received sample in an cyanide solution resulted in 3.5% Ag dissolution (Fig. 2, curve 1). In solutions of thiourea and ammonium thiosulphate, 5 and 5.7% Ag was dissolved

 $\begin{smallmatrix} \epsilon_{_{\mathsf{A}\mathsf{g}}} \\ \mathsf{I} \mathsf{w} \end{smallmatrix}$ ϵ 5 1 3 \overline{c} 1 $\mathbf C$ 30 60 90 120 150 180 12 15 Ω э 6 9 t_{L} [min]

Figure 2 Recovery of silver into leach, εAg versus leaching time, *t*^L for the as-received sample. Medium: $1 - \text{NaCN}, 2 - \text{CS(NH}_2)_2, 3 (NH_4)_2S_2O_3.$

from the as-received sample during the leaching for 15 min (Fig. 2, curves 2, 3).

The results of the XRD study and of the measurements of the specific surface area (Fig. 3) revealed that the mechanochemical pretreatment of the concentrate in alkaline medium has caused 85% amorphization of

Figure 3 The specific surface area (*S*A) as a function of specific milling energy (E_M) for the mechanochemically activated samples.

Figure 4 Recovery of silver into leach, ε_{Ag} versus leaching time, t_{L} for mechanochemically pretreated (60 min) sample. Medium: 1 - NaCN, 2 $-CS(NH₂)₂$, 3 - $(NH₄)₂S₂O₃$.

tetrahedrite as silver-bearing mineral and an increase in the specific surface area of the concentrate from 0.3 m² g⁻¹ to a maximum value of 15.7 m² g⁻¹.

Fig. 4 indicates that the mechanically incuced physicochemical changes of silver-bearing minerals brought about an acceleration of the process of the susequent leaching. By application of thiosulphate and thiourea leaching, 99% recovery of Ag was reached already after 3–5 min. of leaching (Fig. 4, curves 2, 3). In cyanide medium, recovery of Ag was only 40% during 180 min of leaching (Fig. 4, curve 1).

4. Conclusions

Mechanochemical pretreatment of the complex sulphide concentrate in alkaline medium has a positive influence on recovery of silver, when using thiourea, thiosulphate and cyanide solutions. The non-cyanide as well as cyanide leaching of silver from complex sulphide concentrate has shown dependence on the mechanically induced defects (the increase of specific surface area of the concentrate and the amorphization of silver-bearing tetrahedrite). The process of thiourea and thiosulphate leaching is less toxic and brings kinetic advantage over classical cyanide leaching.

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