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Beneficiation of a Nigerian sphalerite mineral: Solvent extraction of zinc by Cyanex®272 in hydrochloric acid

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ABSTRACT

The extraction of Zn(II) from aqueous chloride sphalerite leached liquor using bis(2,4,4-trimethylpentyl) phosphinic acid or Cyanex®272 in kerosene has been studied. The results of fundamental studies on solvent extraction of synthetic solutions of Zn(II) showed that extraction of metal ions increased with increasing pH, extractant concentration and temperature. The stoichiometry of the extracted metal species by Cyanex®272 with Zn(II) was 1:1. The apparent standard molar enthalpy ($\Delta H°$), molar entropy($\Delta S°$) and Gibb's free energy ($\Delta G°$) of 26.81 ± 0.11 kJ/mol, 107.63 ± 0.05 J mol^{-1} K^{-1} mol^{-1} and -5.48 ± 0.13 kJ/mol were calculated for the process respectively. These values showed that Zn(II) extraction by Cyanex®272 is thermodynamically favourable. The number of the theoretical stages for this process evaluated by the McCabe-Thiele diagram was six. An extraction efficiency of 95% Zn(II) was obtained with 0.047 mol/L Cyanex®272 in kerosene from an initial sphalerite leach liquor containing mainly 603.4 mg/L Zn, 121.4 mg/L Fe and 16.3 mg/L Pb. The Pb(II), Ag (I), Cu, Sn, and Al (less than 5 mg/L) were firstly separated by cementation with Zn granules and this was followed by Iron removal by precipitating with 4 mol/L ammoniacal solution to a pH of 3.5 at 25 °C ± 2 °C. A 0.1 mol/L HCl was found to be adequate for the stripping of about 95% of Zn from the organic phase. The stripped Zn(II) solution was recovered as zinc oxide (ZnO) via precipitation with sodium hydroxide followed by calcination at 600 °C during 120 min. A practicable hydrometallurgical scheme summarising the operational procedures used for the extraction of Zn(II) and Pb(II) from the sphalerite ore was presented.

1. Introduction

Zinc is mostly extracted from sphalerite (ZnS) ore. Deposits of zinc and lead ores including sphalerite which are usually found as mixture have long been known in Nigeria, but they have only been mined in the past on a very small scale. An estimated 10 million tonnes of zinc/lead veins are spread over eight states of Nigeria. Proven reserves in three prospects in the East-central areas are 5 million tonnes. (Min. and Ind., Nigeria, 2010). In the commercial flow sheet for the production of zinc metal, the sphalerite concentrate is roasted, leached in sulphuric acid and electrolyzed (Alguacil and Martinez, 2001). Zinc is used in metallic coating to improve corrosion resistance of various types of steel. The pickling of steel goods is usually carried out using 10–20% HCl (Regel et al., 2001).

Zinc is primarily produced from sulphidic ores including sphalerite, ZnS. Other sources of zinc include oxide-carbonate ores and different secondary sources such as zinc ash, zinc dross, flue dusts of electric arc furnace, leach residues, etc. Pyrometallurgical and hydrometallurgical routes or combination of the two can be employed for treating secondary materials (Turan et al., 2004). The hydrometallurgical process has been established to be more eco-friendly for treating such materials having low zinc content (Leclerc et al., 2003).

In recent years, the recovery of metals from aqueous chloride solutions has attracted much attention. This is due to the high efficiency of the chloride leaching processes, which are now recognised as a logical choice for treating complex sulphide ore concentrates which cannot be easily or economically treated by other means. Another important aspect of such leaching process is that sulphur is liberated in the elemental form rather than as sulphur dioxide (Cote and Jakubiak, 1996).

In hydrometallurgical processes, valuable metals are generally recovered by a combination of two or more of leaching, precipitation, solvent extraction and electrowinning techniques. During leaching, dissolution of metals with a suitable acid or mixture of acids is possible. The processing of leach liquor solutions containing different concentrations of acid/acids is very complex and separation of the metal ions using various techniques such as precipitation, adsorption, solvent extraction, ion-exchange, etc. can be cumbersome (Sarangi et al., 2007). Of these purification technologies, solvent extraction shows a prominent role as a separation (and concentration) operation within these processes (Alguacil and Martinez, 2001).

In this regard, the use of organophosphorus extractants in solvent extraction of metals has been steadily increasing because of their excellent selective nature in forming complexes under specific

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conditions. In particular, the introduction of diakyl phosphoric and phosphoric acids including Cyanex 272 has brought about a vast change in the separation technology (Daoud et al., 2006; Kunungo and Mohapatra, 1995). Thus, Cyanex 272 has been regarded as better reagent for the zinc extraction and very selective for the removal of other metal ions including cobalt to avoid possibility of cross contamination of reagents and has been adopted at the Murrin Murrin plant in Western Australia (Flett, 2005).

In the particular case of chloride-based zinc hydrometallurgy, a number of investigations using different extractants have been reported (Alguacil et al., 1992; Benito et al., 1996; Jia et al., 2002; Li et al., 2003; Mellah and Benachour, 2007). In most of these studies, synthetic solution containing Zn(II) was used and possible efforts in separating Zn (II) from other metal ions have been undertaken with respect to the extraction mechanism and the extracted complexes being formed. The results of some of these investigations are summarised in Table 1.

As evident from Table 1, there is a very limited work on the extraction of Zn from an aqueous leach liquor emanating from sphalerite mineral, (Baba et al., 2004).

The first part of the studies on the beneficiation of the sphalerite mineral had earlier been published (Baba and Adekola, 2010). The present investigation constitutes the second part and it is focused on the extraction and separation of zinc(II) from associated impurities such as lead, iron, Cu, Ag etc., contained in Nigerian sphalerite mineral. This is a first in-depth study on the hydrometallurgical recovery of zinc and lead from a Nigerian sphalerite origin using Cyanex 272.

2. Experimental

The experimental approach adopted for this study comprises a preliminary work aimed at establishing conditions for the optimal extraction of Zn from synthetic Zn(II) solutions by Cyanex 272 with subsequent application to the recovery of zinc from sphalerite leachate. The leachate obtained from the leaching of 10 g/L sphalerite per litre of 4 mol/L HCl solution at 80 °C for 120 min (Baba and Adekola, 2010) was used for the systematic study of the extraction of Zn(II) and Pb(II). The leachate has the following composition at pH 3.0 (Zn: 603.4 mg/L; Pb: 16.3 mg/L; Fe: 121.4 mg/L). Other metal ions such as Al, Ca, Ag, Cu, and Sn were present in traces (less than 1 mg/L).

2.1. Extraction procedure

2.1.1. Fundamental studies with Zn(II) synthetic salt

The aqueous solutions of Zn(II) with metal concentration of 1 g L^{-1} were prepared using $ZnCl_2$ by the addition of predetermined amount of 37% HCl solution into doubly distilled water. Solutions of different HCl molarities were then prepared by serial dilution. The Cyanex 272 extractant was kindly supplied by Cytec Inc. and used as received was dissolved in doubly distilled kerosene to the required concentration (Baba, 2008).

Batch experiments were carried out at ambient temperature (25 °C ± 2 °C) by equilibrating equal volumes (25 mL) of 0.047 mol/L Cyanex 272 in kerosene with zinc concentrate in aqueous solution at pH 3.0 (Daoud et al., 2006) using Gallemkamp orbital shaker (AMPS) for 25 min. After equilibration and phase separation, the concentration of metal ion in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after extraction. The influence of initial metal concentration, pH and extractant concentration on the efficiency of Zn(II) extraction was investigated.

The distribution ratio, D, was calculated as the ratio of the concentration of Zn(II) in the organic phase to that in the aqueous phase according to the relation:

$$D = \left(\frac{C_o - C}{C}\right) \cdot \left(\frac{V_{aq}}{V_{org}}\right) \quad (1)$$

where C_o is the original metal concentration before extraction; C, the final metal concentration after extraction; while V_{aq} and V_{org} are the volumes of the aqueous and organic phases respectively (Daoud et al., 2006).

2.1.2. Systematic study on the Zn(II) and Pb(II) extraction from sphalerite

The leachate from Section 2.0 was used for this study. The concentrations of Zn, Pb and Fe were all determined either spectrophotometrically (Baba, 2008; Daoud et al., 2006; Gomez et al., 1992; Yadav and Khopkar, 1971) using AQUAMATE Thermo-Electron Corporation UV–visible spectrophotometer, together with EPSON LQ 2070 recorder or by ALPHA-4 Atomic Absorption Spectrophotometer (AAS) which was used for the determination of concentration of other metals. All determinations were done in triplicate. While iron was quantitatively precipitated by adding 25 mL of 4 mol/L NH_3 solution with conc. NH_3 solution after moderate stirring (Baba, 2008), lead and other trace elements from the leach liquor were successfully separated from zinc by cementation with pure zinc metal (Baba et al., 2004; Ritcey and Ashbrook, 1984). The process was based on the electrochemical reduction of one of the metals by the other one. In this case, 1 g of zinc metal granules was added to 100 ml leached liquor. Effervescence occurs and it lasted for about 25 min. This is due to the generation of H_2 and release of heat. The solution was allowed to cool, filter and then analysed for Pb(II) and Zn (II). The stripping of zinc from the organic phase was carried out with 0.1 mol/L HCl (Baba, 2008; Daoud et al., 2006; Yadav and Khopkar, 1971).

2.2. Determination of metal extractability of Zn(II)

In the extraction experiments, the ratio of Zn(II) in the extract to its concentration in the aqueous, otherwise known as distribution ratio, Dc is given by:

$$D_c = \frac{[Zn(II)]_{org}}{[Zn(II)]_{aq}} \quad (2)$$

Table 1
Summary of literature on solvent extraction and separation of Zn(II) from other metal ions.

Author	Synthetic salt	Extractant/diluent	Aqueous media	Extractable species	Inference
Daoud, et al. (2006)	$ZnSO_4$	Cyanex 272/kerosene	HCl	Not determined	96% stripping efficiency obtained for both simulated waste and real solutions respectively.
Li, et al. (2003)	$ZnCl_2$	CA-100 and Cyanex 272/heptane	Distilled water	ZnA_2.2HA/100, ZnA_2.2HL	The synergetic system enhances extraction efficiency of Zn(II)
Jia, et al. (2002)	$ZnCl_2$	Primary amine N1923; Cyanex 272	HCl	$(RNH_3Cl)_3$.ZnClA; ZnA_2.2HA	The mixture exhibits no synergistic effects for Cd^{2+}, provides possibilities for Zn^{2+} and Zn^{2+} separations at a proper extractants ratio.
El-Dessouky, et al. (2008)	Zn(II), 25 g/L, MF 999 Plant	Cyanex 921/kerosene	HCl	$HZnCl_3$.3TBP; $HZnCl_3$.2C921	The Zn(II) extraction and stripping efficiencies are 98% and 92% respectively.
Sarangi, et al. (2007)	Metal ions supplied some by companies	TBP, MIBK, LIX 84I and Cyanex 923	HCl,	Not determined	99.1% zinc extraction achieved with 0.22 kg/m^3 zinc, free of Co and Ni
Fu, et al. (2010)	$ZnCl_2$	TOPO	NH_4Cl	ZnA_2B;	TOPO showed synergistic effect on zinc extraction and the system is exothermic driven.