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Short Communication

Solvent Extraction of Zinc with Triphenylphosphite (TPP) from a Nigerian Sphalerite in Hydrochloric

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Abstract

A hydrmetallurgical study based on the extraction of Zn and Pb from a Nigerian sphalerite mineral leached with 4 M hydrochloric acid has been undertaken. Triphenylphosphite (TPP) has proved to be very effective for the extraction of zinc. With 2 M TPP and at ambient temperature of 25±2°C; 35.71% and 66.7% of Pb and Zn were extracted, respectively, into the organic phase within 60 min. The recovery rates of 93.27% and 91.16% from the organic phase were obtained after de-extraction with 6 M HCl for Pb and Zn, respectively. Finally lead has been successfully separated from zinc by the cementation of the former with zinc metal. The mechanism of extraction appeared to be chelate formation and ion exchange.

Keywords: Solvent extraction; Zinc; Triphenylphosphite; Sphalerite; 8-hydroxyquinoline

Introduction

Sphalerite (ZnS) is a common and widely distributed mineral association with galena (PbS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), quartz (SiO_2), greenockite (CdS) and barite ($BaSO_4$). It occurs both in veins and in replacement deposits in linestones [1]. Pure sphalerite contains 67% zinc and 33% sulphur. Other elements such as lead, iron, manganese, cadmium, silver, antimony and tin may however be present as impurities [2].

Deposits of lead and zinc ores which are usually found as mixtures have long been known in Nigeria, but they have only been mined in the past on a very small scale. The Nigerian lead-zinc field extends for about 560km in a narrow belt from Ishiagu in Ebonyi State, Nigeria [3].

Solvent extraction is a technique, which enables isolation of substances originally present in a solution by selective transfer from one solution, say aqueous to another say organic. Liquid-liquid extraction is not commonly used in zinc hydrometallurgy. The only metallurgical company that uses this technique for zinc processing is Bilbao Metallurgical Company in Spain [4]. The process, known as Espandes process is based on extraction of zinc in chloride media from a pyrite leaching solution. This technique is carried out in four stages [5] namely:

- Extraction of zinc chloride ($ZnCl_4^{2-}$) by a secondary amine (R_2NH_2Cl)
- De-extraction of zinc chloride into aqueous medium
- Extraction of only zinc by di(2-ethyl hexy1) phosphoric acid (D_2EHPA).
- De-extraction of only zinc (II) by sulphuric acid.

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A lot of works have been reported in the literature regarding the use of extractants of diverse nature and in various media. A major review has been carried out by Kossir [6].

Extractants such as dithizone and cyclohexanones have limited solubility in organic solvents, and so not recommended when zinc concentration is greater than 10^{-3}mol/L. Carboxylic acids, amines, organophosphorus compounds, and chelex-100 have been cited as good candidates for the extraction of Zn. At times, the investigators are more or less confronted with problem of separation of associated metals such as Pb and Cd.

Kossir [6] also carried out a detailed study on the extraction of Zn(II) in cyanide medium using 4-ethyl-l-methyl-7-octyl-8-hydroxyquinoline, a commercial reagent known as chelex 100. He also reported Sb and Pb as the only metals which accompany Zn during the extraction. Ag, Cu and other metals are not extracted. There is however a lot of environmental problems associated with the handling of cyanide solutions due to its high toxicity.

In the present work, a comparative study was carried out on the effectiveness of 8-hydroxyquinoline (HQ) and triphenylphosphite (TPP) as extractants for zinc(II) from aqueous solution. 8-hydroxyquinoline belongs to the group of compounds with general formula $C_aH_bN_eO_d$. 8-hydroxyquinoline has been reported to be effective for the extraction of palladium in acid medium. The extraction is based on complex formation [7], while triphenylphosphite with formula $(C_6H_5O)_3P$ is effective for the extraction of Zn, Cu, Pb, and precious metals in HCI with concentrations greater than 3 mol\L. The mechanism of extraction is mainly by either ion exchange plus solvation and formation of ion pairs according to the following equations, respectively [6]:

$$(1)\ MCl_p^{(p-n)} + {}_mTPP \rightarrow MCl_n\,(TPP)_m + (p-n)Cl^-$$

$$(2)\ MCl_k + (p-n)\,(TPP,H^+,CI)_{org}\ \square\ \ MCl_p^{(p-n)},$$

$$(TPPH^+)^{p-n}{}_{org} + (k-n)Cl^-.$$

Other extractants such as D_2EHPA (Di-2-ethyl hexyl phosphoric acid), TBP (tributylphosphite) have also been cited to be good candidates for the extraction of zinc (II) in acid media.

Selecting HQ and TPP was based on availability of these extractants. There is practically little or no information on the ability of TPP to extract Pb or Zn, except a report on its use for extraction of palladium [8].

Experimental

With the use of a 600 ml beaker, covered with a glass lid, about 0.5 g of sphalerite ore was weighed and introduced into the beaker. A magnetic stirring bar was inserted and the solution was covered with glass lid. Then, the ore was left to be in contact with the lixiviant for 2 h. At the end of the contact time, the solution obtained was then filtered and the insoluble residue left on the filter paper was washed thoroughly with distilled water. The filtrate was then carefully transferred into a 100 ml standard flask. The solution was made to mark with distilled water. The filtrate in the standard flask was then analyzed using SP_9 atomic absorption spectrometer with PM 8251 single-pen recorder with appropriate cathode filters for Pb, Zn, Fe and Mn. This solution constituted leachate used for the solvent extraction study in this work, and it has the following composition in 4 M HCl: Pb: 33.4 ppm; Zn 1325.7 ppm; Mn: 1.4 ppm; Ag, Cu, Sn, Fe were present in traces [9].

The two extractants used were HQ and TPP. Fifty milliliters of the leachate (aqueous phase) and 100 ml of organic phase were shaken vigorously in separation funnels on a shaker (Burrel Wrist Action shaker-model 75) at room temperature (25±2°C) until equilibrium was reached (about 1 h). Phase separation required up to one minute.

When the two phases were clearly separated, metal concentrations in the aqueous phase were determined by SP_9 atomic absorption spectrometer (A.A.S.) with PM 8251 single-pen recorder. The difference between the initial and final aqueous metal concentrations was assumed to be equal to the metal concentration in the organic phase (the volume changes were below 5%).

The pH of the aqueous solution was measured with a pH meter. All standard solutions used for spectrometric measurements were prepared with double distilled water. All reagents used were of analytical grade except the TPP and HQ that were of synthetic grade. Commercial kerosine was used as a diluent for the two extractants.

Results and Discussion

The results of preliminary study on the performance of 8-hydroxyquinoline and triphenylphosphite for the extraction of zinc from aqueous solution were summarized in Table 1. The time of contact was 2 min.

The percentage of metals extracted with 8-hydroxyquinoline were higher with kerosene as diluent. This is due to higher solubility in kerosene than in chloroform. The above results clearly indicate that TPP is a better extraction agent than HQ.TPP was then retained for further investigation in this study.

The effect of time of agitation on the extraction of Zn and Pb was studied. The results obtained were

Table 1. Search for the best extractant

Extractant	% Extracted into the organic phase		
	Pb	Zn	Mn
0.1 M HQ in kerosene	11.20	17.24	6.67
0.5 M HQ in chloroform	6.50	12.00	11.11
0.5 M TPP in kerosene	20.61	44.84	2.96

Table 2. Variation of pH of aqueous phase with concentration of TPP

[TPP] M	pH
0	0.9
0.1	0.5
0.2	0.4
0.5	0.35
1	0.3
2	0.2

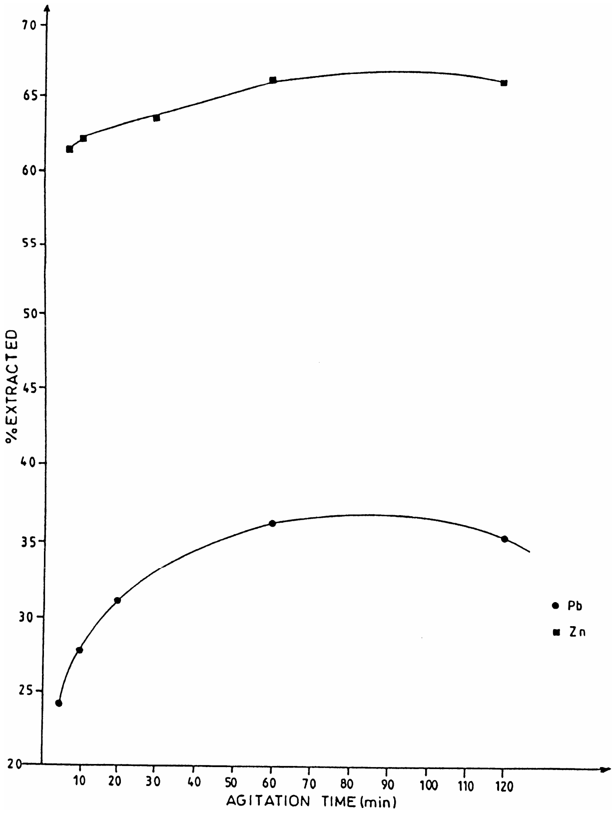

Figure 1. Amount of Lead and Zinc extracted with 0.5 M TPP in kerosene at various time.

illustrated in Figure 1. The figure shows that the optimum time of agitation is 60 min. At this time, the percentage of Pb and Zn extracted are 36.07% and 66.45%, respectively. The level of extraction of other metals including Mn and Fe are very low (less than 2%). At t > 60 min, there is no significant gain in the percentage of Pb and Zn extracted with 0.5 M TPP in kerosene. The percentage of Pb and Zn extracted with 0.5 M TPP in kerosene were 35.71% and 66.07%, respectively.

The effect of concentration of TPP on the extraction Pb and Zn was also investigated in order to determine the optimum concentration of the extracting agent. The effect of TPP concentration on Zn and Pb extraction is shown in Figure 2. It is evident that as the concentration of TPP increases from 0.1 to 2 M, the percentage of Zn extracted also increases. For instance, at 2 M TPP, the percentage of Zn extracted was 77.05%. The percentage of Pb extracted was however on the decline as TPP concentration increases. The optimum concentration of TPP was then fixed at 2 M. Two distinct organic phases were observed in addition to the aqueous phase. At TPP concentration > 0.5 M, using a modifier was however avoided in this work since adding a modifier usually leads to a decrease in the extractive properties of the extractant [10].

The results of the analysis indicate that the concentration of zinc is higher in the lower organic layer than in the upper organic layer. The ratio is 9 to 2. The intense yellow colour of the lower organic phase compared to the almost colourless appearance of the upper organic phase again provides evidence for the higher concentration of zinc-extractant complex in the former. The presence of these two organic phases suggests that the extraction of zinc by TPP occurs via two different mechanisms. In order to confirm this, a graph of log D of Zn *vs.* log of the concentration of TPP is shown in Figure 3. Two slopes appear in this figure. The first being 0.161, when [TPP] < 0.5 M, while the second is 0.67 when [TPP] > 0.5 M.

This lends support again to the proposition made earlier that two different complexes of zinc appeared to be participating in the extraction. At higher concentration of TPP, the slope is 0.67, which is close to 1. This suggests a ratio of 1:1 for zinc and TPP in the extracted complex.

The variation in pH of aqueous phase of the extraction system was also monitored at different concentrations of TPP. The variations in pH are summarized in Table 2.

This table shows that increase in the amount of Zn extracted into the organic phase is accompanied with a decrease in the pH value. This could be attributed to the

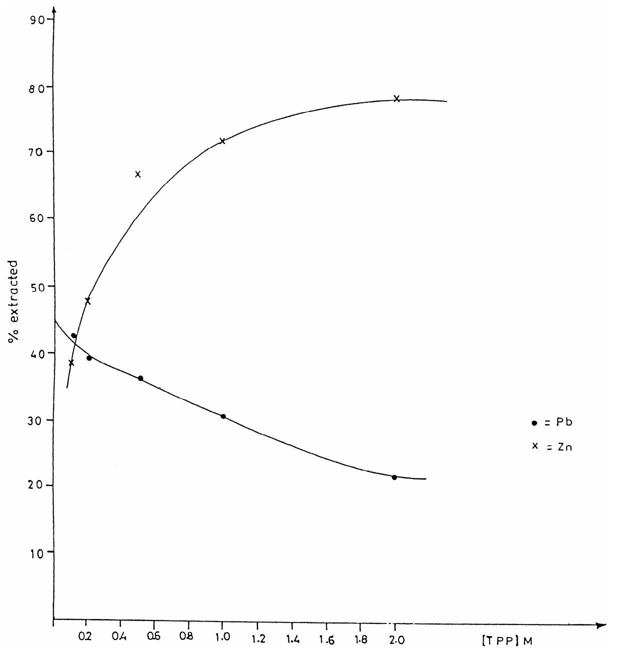

Figure 2. Percent of Lead and Zinc extracted at various concentrations of TPP.

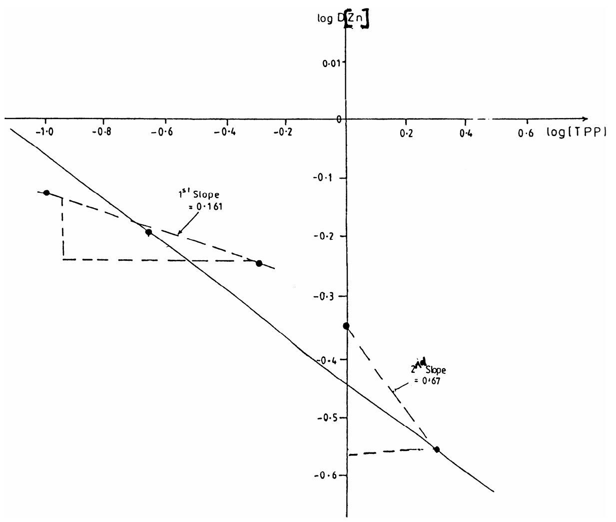

Figure 3. Log of distribution coefficient of zinc against log of concentration of TPP.

increasing replacement of Cl^- by TPP. The release of Cl^- into aqueous solution might lead to increase in the ionic strength of the solution, resulting in a pH decrease [12]

From a previous study by Sato *et al.* [11], it was revealed that when HCl concentration is less than 6 M and in the presence $SnCl_2$, certain platinum metals can be extracted with TPP by ion exchange reaction and by the formation of coordinating compounds. Since one molecule of TPP appeared to be involved with respect to zinc in the extraction system (Fig. 3), the following mechanism can therefore be proposed for the extraction of zinc with TPP in hydrochloric acid media:

$$ZnCl_4^{2-} + (TPP)_{org} \rightleftharpoons (ZnTPP)^{2+}_{org} + 4Cl^-$$

Further studies will however be required to confirm the above mechanism.

Both Pb and Zn earlier extracted into the organic phase have been quantitatively de-extracted with 6 M HCl. The average recovery percentage of lead and zinc from the organic phase were 93.25% and 91.86%, respectively.

A preliminary study on the possible use of cementation for the separation of Pb from Zn in the de-extracted (aqueous) solution has been carried out [13]. The process is based on the electrochemical reduction of one of the metals by the other one. In this case, zinc metal granules were added to each de-extracted solutions (with 6 M HCl) previously obtained from the different concentrations of TPP. Effervescence occurred and it lasted for about 30 min. This is due to generation of H_2 and release of heat. The solution was allowed to cool, filtered and then analysed for Pb and Zn with the aid of atomic absorption spectrometer. The results of some trials were summarized in Table 3.

The cementation appears to be very effective as Pb^{2+} was quantitatively cemented. The efficiency of the cementation process was 100%. The process can be described by the equation below.

$$nZn_{(s)} + Pb^{2+}_{(aq)} + Zn^{2+}_{(aq)} \rightarrow Pb_{(s)} + (n+1)Zn^{2+}_{(aq)}\ ,$$

where n is the number of moles of Zn metal granules introduced.

Conclusion

Triphenylphosphite (TPP) appeared to be very effective for the extraction of zinc and lead from hydrochloric acid leached sphalerite mineral. With 2 M TPP and at ambient temperature, 35.71% and 66.07% of Pb and Zn were extracted into the organic phase within 60 min. The recovery rates of 93.27% and 91.16% from the organic phase were obtained for Pb and Zn, respectively, after de-extraction of the organic phase with 6 M HCl. Lead has been separated from zinc by cementation process. However, studies are currently going on to find out the influence of some cations and anions on the extraction system.

Table 3. Results of cementation process

Extraction with TPP at various concentrations		**Pb**		**Zn**	
		Lower organic layer	Upper organic layer	Lower organic layer	Upper organic layer
0.5 M	Initial quantity (mg) of Pb^{2+} or Zn^{2+} in the de-extracted aqueous solution	0.44	0.13	32.64	9.21
	Final quantity (mg) of Pb^{2+} or Zn^{2+} after cementation	0.0	0.0	32.31	8.91
	Efficiency of cementation (%)	100	100	–	–
1 M	Initial quantity (mg) of Pb^{2+} or Zn^{2+} in the de-extracted aqueous solution	0.38	0.11	35.22	9.26
	Final quantity (mg) of Pb^{2+} or Zn^{2+} after cementation	0.0	0.0	32.70	8.99
	Efficiency of cementation (%)	100	100	–	–
2 M	Initial quantity (mg) of Pb^{2+} or Zn^{2+} in the de-extracted aqueous solution	0.26	0.07	37.25	9.31
	Final quantity (mg) of Pb^{2+} or Zn^{2+} after cementation	0.0	0.0	37.21	9.06
	Efficiency of cementation (%)	100	100	–	–

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