

Recovery of Zinc from Metallurgic Waste Sludges

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Abstract

Zinc-bearing sludge deposits resulting from metallurgical zinc production have been investigated. They were found to contain 11.0-13.0% of zinc, 1.4-1.5% of copper, 1.1-1.3% of arsenic, and *ca* 1% of lead, plus small amounts of cadmium and nickel (0.5 and 0.1%, respectively). The results of the leaching of these deposits with hydrochloric, sulfuric, and lactic acids, as well as with ammonia and NaOH, are presented. The composition of the leachates was dependent on the leaching reagent used. The effectiveness of leaching decreased in the following order of the reagents used: ammonia (10.5%), HNO₃ and NaOH (10.0% each), H₂SO₄ (9.5%), HCl (9.0%), and lactic acid (8.0%). Due to the poor selectivity of the strong mineral acids used, the most effective leaching reagents were concentrated ammonia, NaOH, and lactic acid. The recovery of zinc using electrolysis and solvent extraction also was evaluated. As much as 92.0-99.0% of zinc was deposited on the cathode for a sulfuric acid solution having a pH in the range 1-2. The extractants used in the extraction process were a 60% TBP solution in toluene for acidic solutions and 1-decyl-2-methylimidazole for weakly acidic and weakly alkaline solutions. From a solution having a pH of around 2.7, Zn(II) ions were most effectively extracted (99.0%), whereas from those of a pH > 4, also Cu(II) and Cd(II) (98.5 and 96.0%, respectively) ions were co-extracted along with Zn(II). The Ni(II) ions were most effectively extracted at a pH around 5.5 (74.0%). From solutions left after leaching with NaOH, 1-decyl-2-methylimidazole extracted mostly Zn(II) and Cu(II), whereas from those left after leaching with ammonia, Cd(II) could be extracted in addition to Zn(II) and Cu(II). An optimum pH for zinc recovery was 7.5-8.0.

Keywords: zinc-bearing sludges, separation of metal ions, heavy metals, zinc recovery

Introduction

The domestic mining industry of zinc and lead and their metallurgy have a long history. However, nowadays their dwindling resources indicate that in order to continue its existence, this industrial branch will be forced to be based either on imported ores or on recovery of zinc from zinc-bearing waste. It is also worth emphasizing that zinc has been categorized as a strategic metal [1, 2]. An irregular increase in demand for metals has been observed since 2004 and, occasionally, the demand surpasses the supply, resulting in soaring prices on the markets. For instance, in

2005 the price of 1 Mg of zinc was 1,450 USD, in 2006 it increased up to 4,500 USD, while in 2014 it oscillated around 2,300 USD [3]. There is also an increased demand for zinc in various sectors of the economy, including production of anticorrosive coatings in the building and automotive industries.

Nowadays in zinc metallurgy, materials with elevated zinc contents, including copper metallurgy waste, are recycled. However, zinc mills call for materials with zinc contents above 20% [4]. Consequently, there is a need for the development and search for effective methods of extraction of this costly metal from poorer raw materials.

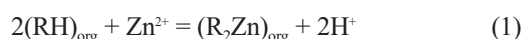
The literature includes many reports concerning procedures for extraction of zinc and other metals from industri-

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al wastes. The process of zinc recovery depends on the form in which it occurs, on its concentration and degree of contamination [5]. In many reports, solvent extraction has been proposed to selectively recover heavy metals (zinc, copper, cadmium, and nickel) using extractants such as TBP (tributyl phosphate), crown ethers, β -diketones, carboxylic acids and their derivatives, and imidazole derivatives [6, 7]. With many zinc-bearing wastes, leaching is a potential method of choice for their processing [5, 8, 9]. Zinc from the leachates can be recovered using various methods, e.g., electrolysis, crystallization, and precipitation of the metal [10].

Zinc can also be separated by selective solvent extraction using an industrial extractant (RH). For extraction from acidic solutions, the extractants used were tributyl phosphate (TBP) [11-13], di(2-ethylhexyl)phosphoric acid (D2EHPA) [12, 14], and a phosphonium ionic liquid [15, 16], for neutral ones containing chlorides – trioctyl amine (TOA) [17] or LIX63 (5,8-diethyl-7-hydroxydodecan-6-oxime) [18], while imidazole derivatives were used for solutions left after leaching with ammonia or NaOH of a pH of 7-8 [6]. Either extraction naphtha or toluene were used as water-immiscible solvents.

An (RH) extractant transports Zn(II) ions to the organic phase according to the equation:



In the next step, during re-extraction with sulfuric acid or ammonia, the extractant can be recovered and zinc extracted into the water phase according to the reaction:



The objective of our investigations was zinc-bearing sludge deposits originating from hydrometallurgical zinc production after purification of the electrolyte supplied to electrolytic tanks. So far, the wastes have not been utilized, hence our interest in those sludges. In this work, the results of leaching such sludges with acids and bases are presented. The composition of the leachates was dependent on the leaching agent used. Also, the possibility of zinc deposition from the leachates by electrolysis and elimination of extraneous metals by grouting with zinc metal, as well as the extraction of the metal in the liquid-liquid system, were studied.

The extractant used for acidic solutions was TBP (Fig. 1a), whose effectiveness and utility have been reported in the literature, whereas 1-decyl-2-methylimidazole (Fig. 1b) was used for neutral solutions after neutralization to a pH of 6-8.

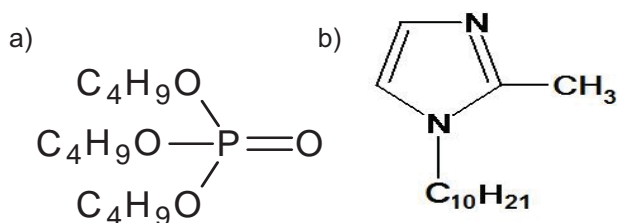


Fig. 1. Structural diagrams of the a) tributyl phosphate, and b) 1-decyl-2-methylimidazole extractants.

Substitution of the methyl group in position 2 of the imidazole ring (Fig. 1b) increases the basicity of a molecule by one order of magnitude ($\text{pK}_a = 8.44$), compared with that of 1-alkylimidazoles [19]. At the same time, the 2-methyl group provides steric hindrance during complexation with metals and decreases their stability [20]. This weakening of stability due to steric hindrance depends on the type of central ion. The most remarkable decrease in stability has been noticed with octahedral complexes of Co(II) and Ni(II) [20]. However, the steric effect caused by the substituent in position 2 does not affect the formation of the Cu(II) [21] and Zn(II) complexes [22], because these ions form tetrahedral species that are less prone to steric hindrance. This has been utilized in the separation of ionic mixtures.

1-Decyl-2-methylimidazole was used as the carrier of non-ferrous ions across polymeric inclusion membranes [23].

Experimental

The sludges to be analyzed are brown clayey solids.

The sludge samples formed a compact (though heterogeneous) mass, which was homogenized. The dry mass content was monitored every three hours using a RAD-WAG gravimetric drier. The dry weight was determined every three seconds at 105°C.

Procedures

Drying of Precipitates

Before leaching, the sludge was dried. Thus a sample of the sludge was placed in a laboratory drier (WTC Binder 78532 Tuttlingen/Germany) at 105°C to a constant weight. The sludge contained approx. 35% water.

The dry material was then processed as described below.

Mineralization

Two samples of the sludge were divided into three subsamples each, which were mineralized with a concentrated nitric acid in a MARS 5 (CEM) microwave oven. After mineralization, the solutions were diluted to a defined volume (50 cm³) in which the metal concentrations were determined using the ICP-OES VISTA-MPX (Varian) emission spectrometer.

Leaching

The following leaching agents were used: NH₃ (a 25% solution, p.a., PChO, Lublin), NaOH (PPCh STANLAB Sp.J: p.a., Lublin), HCl (a 36% solution, PPCh, STANLAB, p.a.), HNO₃ (a 65% solution, PPCh STANLAB, p.a.), and lactic acid (POCh, Gliwice, p.a.).

To ca 0.5-g samples of the materials, 50 cm³ volumes of each of the following solutions were added: concen-

Table 1. Metal contents (average values) in the mineralized sludge from hydrometallurgy of zinc.

Sample No.	Elements [%]							
	Zn	Fe	As	Pb	Cd	Cu	Cr	Ni
1	11.43±0.11	13.23±0.15	1.2±0.02	1.01±0.02	0.36±0.01	1.41±0.02	0.32±0.01	0.11±0.01
2	13.1±0.20	15.4±0.12	1.32±0.01	1.14±0.02	0.39±0.01	1.55±0.02	0.35±0.01	0.12±0.01

Table 2. Percentage of metals in solutions left after leaching the sludge.

Leaching reagent	Elements [%]							
	Zn	Fe	Cu	Pb	As	Cd	Cr	Ni
Concentrated NH ₃	10.5	0.4	1.1	0.2	0.2	0.2	0.2	-
30% NaOH	10.0	-	0.5	0.6	0.3	-	0.25	-
2M HCl	9.0	12.0	0.6	0.1	0.1	0.3	0.3	0.1
2M HNO ₃	10.0	13.0	1.0	1.0	1.0	0.4	0.3	0.1
2M H ₂ SO ₄	9.5	11.0	1.2	-	0.05	0.3	0.3	0.1
80% Lactic acid	8.0	1.5	1.0	0.1	-	0.1	0.3	0.1

trated NH₃, 30% NaOH, 2M HCl, 2M H₂SO₄, and 80% lactic acid. The mixtures were shaken for *ca* 1 hr and left to stand for 24 hrs. Then they were filtered into measuring flasks.

Determination of Metals Concentration

The metal concentrations in the leachates were determined on the ICP-OES VISTA-MPX (Varian) emission spectrometer in a WASTE LAB Instrumental Analysis Laboratory in Poznan, Poland.

Cementation

Zinc metal was added to the solutions left after leaching and the samples were placed in a thermostatted water bath shaker (ELPAN type 357) until equilibrium was attained (no longer than 10 hrs). In the water bath, the temperature was held at 25°C.

Solvent Extraction

The extractants used were: a 60% TBP (tributyl phosphate) (Fluka) solution in toluene (POCh, Gliwice; p.a.) for solutions left after leaching with acids, and 1-decyl-2-methylimidazole (synthesized according to a method reported in the literature [24]) in toluene for basic solutions.

Test tubes with two immiscible liquids were shaken on a thermostatted shaker at 25°C until equilibrium was attained (no longer than 30 min). Then the phases were separated, the pH of the water phase was measured, and the metal concentrations were determined.

Electrolysis

The purified electrolyte was acidified with sulfuric acid and electrolyzed in a Chemical Analysis Apparatus EP-4 (Nysa, Poland), at 32-37°C, at a current density of 3-7 A/dm². Aluminum was used as the cathode, and lead as the anode.

Discussion of Results

Mineralization of Sludges

Preliminary data on the composition of the sludge obtained after mineralization are shown in Table 1. Table 1 contains the average values and standard deviations.

The sludge contained 11-13% of zinc, *ca* 1.4-1.5% of copper, 1.1-1.3% of arsenic, *ca* 1% of lead, and small amounts of cadmium and chromium (*ca* 0.5% each), and nickel (*ca* 0.1%).

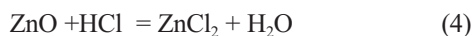
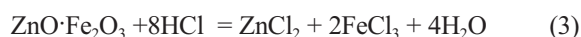
Leaching of Sludges from the Hydrometallurgy of Zinc

The percentages of metals determined after leaching with various solvents are shown in Table 2.

Apart from zinc, the sludge contained also As, Cd, Cr, Cu, Fe, Ni, and Pb. The metal contents varied depending on the leaching reagent used, due to different mechanisms of the process (see below). However, in each case zinc was leached, its content ranging from 8 to 10.5%. The greatest amounts of the metal were leached with solutions of ammonia and NaOH.

Leaching with Acids

During the sludge leaching with hydrochloric acid, the following reactions took place:



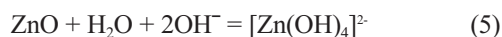
Apart from zinc, during the leaching with acids the following ions also can be leached: Cd(II), As(III), Cr(III), Cu(II), Fe(III), Ni(II), and Pb(II) (although the last-named ion forms a sparingly soluble chloride PbCl_2 , hence its amount in the filtrate was negligible).

Similar processes occurred when HNO_3 , H_2SO_4 , and lactic acid were used. However, during the leaching with sulfuric acid, Pb(II) could not be detected in the filtrate because it forms a sparingly soluble PbSO_4 .

During the leaching with lactic acid, first of all Zn(II) was present in the filtrate, together with small amounts of Fe(III) and Cu(II), while As(III) was not present at all.

Leaching with NaOH

In basic solutions, zinc compounds readily form hydroxocomplexes according to the reaction:



...which are solubilized together with As(III), Cu(II), Cr(III), and Pb(II), which were detected by spectrophotometry.

Leaching with Ammonia

Leaching with ammonia occurs according to the reaction:



Summary of the Leaching Process

Trace amounts (0.1%) of Ni were found in solutions left after leaching with 0.03% HCl and 0.02% HNO_3 solutions. Also, small amounts of Cr and Cd (0.1-0.4%) were found, the highest of them (0.4 and 0.3%, respectively) were detected in the samples leached with nitric acid. The highest amounts of the Pb(II) ions (1%) were extracted with HNO_3 , whereas in the remaining leachates its content was negligible (0-0.6%). With the exception of the 10% NaOH, Fe was found in all leaching solutions. Its content was higher than 10% in leachates containing strong acids. Most of the leachates contained *ca* 1% of Cu(II). With the exception of the 1% HNO_3 solution, the content of arsenic in the remaining solutions was low, ranging from 0% in lactic acid to 0.3% in 30% NaOH.

Concentrated ammonia leached mostly zinc and copper, the amounts of the former being 10-fold higher than those of copper. Lactic acid turned out to be quite interesting. Zn (8%), Fe (1.5%), and Cu (1%) prevailed in its solutions.

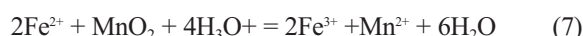
As far as the effectiveness of zinc extraction is concerned, the leaching solutions can be arranged in the following order: NH_3 (10.5%), 2M HNO_3 and 30% NaOH (10% each), 2M H_2SO_4 (9.5%), 2M HCl (9%), and lactic acid (6%). However, due to the poor selectivity of the strong acids, 2M HCl, 2M HNO_3 and 2M H_2SO_4 , concentrated NH_3 , 30% NaOH, and 80% lactic acid were the most effective extractants.

Recovery of Zinc from the Leachates

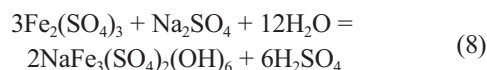
Electrolysis

Before electrolytic deposition of zinc from the leachates, the following ions were removed:

a) Fe(II), which was oxidized by the following reaction:



Then Fe(III) was precipitated in the form of basic ferric and sodium sulfate (jarosite):



b) Ions of more positive metals, Cu(II), Pb(II), Ni(II), and Cd(II) were removed by cementation with zinc powder. The rate of chemical digestion is slow and does not compete with the progress of cementation:



The deposited metals, along with any unreacted zinc, were filtered off. During electrolysis of the solutions acidified with sulfuric acid to a pH in the range 1-2, 92-99% of zinc was deposited on the cathode.

Solvent Extraction

A percentage extraction (%E) of each metal was calculated from the following equation:

$$\% E = \frac{C_M}{C_M^0} * 100\% \quad (10)$$

...where C_M and C_M^0 denote metal concentration at an equilibrium in the water phase and an initial metal concentration in that phase, respectively.

The extractant binds metal ions and transfers them to the organic phase according to the equation:



It is observed that zinc(II) ions (99.0%) were effectively extracted from acidic solutions (Table 3) of a pH around 2.7; Cu(II) (98.5%) and Cd(II) (96.0%) ions were effectively extracted from solutions of $\text{pH} > 4$ along with Zn(II); whereas Ni(II) were most effectively extracted at a pH around 5.5 (74.0%).

Iron(III) ions, of which the concentration in solutions after leaching with acids is considerable, are complexed

Table 3. Percentage recovery of the metals during extraction with an 80% TBP solution in toluene from solutions after leaching with acids.

pH	%Zn	%Cu	%Cd	%Cr	%Ni	%Pb
Leaching with hydrochloric acid						
0.86	45.0	40.0	37.0	20.0	35.0	-
1.95	91.0	72.0	58.0	38.5	53.0	-
2.92	98.2	88.0	81.0	50.0	69.0	-
Leaching with sulfuric acid						
0.56	40.0	35.0	30.0	15.0	22.0	-
1.72	89.5	66.0	58.0	36.0	43.0	-
2.78	99.0	87.0	82.0	60.0	48.0	-
Leaching with lactic acid						
4.43	90.0	95.0	91.1	63.0	70.0	75.0
5.52	94.5	97.0	94.0	60.0	74.0	60.0
6.37	95.2	98.5	96.0	54.0	67.0	51.5

Table 4. Percentage recoveries of the metals during extraction with 1-decyl-2-methylimidazole solution in toluene from solutions after leaching with NaOH or ammonia.

pH	%Zn	%Cu	%Cd	%Cr	%Pb
Leaching with NaOH					
6.85	76.0	84.0	-	42.0	48.0
7.23	85.9	90.0	-	45.0	53.0
7.59	97.7	93.0	-	50.0	57.5
7.96	98.3	95.0	-	54.0	63.0
8.35	96.3	95.0	-	56.0	67.0
Leaching with ammonia					
6.20	69.0	72.0	63.0	35.0	45.0
6.67	75.0	80.0	67.0	38.0	48.0
7.12	90.5	88.0	74.0	40.0	52.0
7.58	98.0	94.0	76.0	42.0	60.0
7.91	99.0	96.0	78.0	47.0	64.0

with TBP (extractant) and undergo extraction together with other metals into the organic phase. On the other hand, Fe(II) cannot be complexed with TBP. To prevent its transfer by dibutylphosphoric acid (a product of partial hydrolysis of TBP), the hydrolysis products must be removed, for instance, by washing the organic phase with a dilute NaOH solution or ammonia.

Fe(III) ions could also be eliminated by reduction, for instance by passing the solution through a steel-wool-packed column. However, the operation provides an addi-

tional step, hence it seems more desirable to use extraction with 1-decyl-2-methylimidazole of the solution after leaching with NaOH or ammonia (Table 4).

After leaching with NaOH, 1-decyl-2-methylimidazole extracts mainly Zn(II) and Cu(II) ions, whereas after leaching with ammonia, large amounts of Cd(II) were found in addition to Zn(II). The recovered amount of copper increases with an increase in the pH of the water phase. An optimum pH for the recovery of zinc is in the range 7.3-8.0.

Conclusions

The content of zinc in the sludge is high enough (10-13%) to justify its recovery by hydrometallurgical techniques.

As far as the efficiency of leaching zinc is concerned, the solutions used can be arranged in the following order: NH₃ (10.5%), 2M HNO₃ and 30% NaOH (10% each), 2M H₂SO₄ (9.5%), 2M HCl (9%), and lactic acid (8%). However, due to the poor selectivity of strong acids (2M HCl, 2M HNO₃, and 2M H₂SO₄), the most effective leaching solutions were: the concentrated ammonia, 30% NaOH, and 80% lactic acid.

Zinc from the leachates can be recovered using:

- Electrolysis (92-99% of the metal is deposited on the cathode)
- Solvent extraction (by using either TBP as the extractant for solutions of a pH around 2.7-efficiency being 99%-, or by using 1-decyl-2-methylimidazole at a pH of 7.5-8.0 with an efficiency of 96-99%.

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