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SELECTIVE SEPARATION OF LEAD FROM ALKALINE ZINC SOLUTION BY SULFIDE PRECIPITATION

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ABSTRACT

Zinc and lead are usually concomitantly present in Zn-Pb ores and solid wastes, such as electric arc furnace (EAF) dusts. One of the treatment methods is to extract zinc and lead from the ores and wastes by an alkaline leaching process if applicable. The selective and quantitative separation of lead from zinc is an important step in these processes. In this work, the separation of lead from zinc in alkaline zinc solution, in leaching solutions of EAF dusts, and in oxidized zinc ores by sodium sulfide precipitation was studied. When the weight ratio of sodium sulfide (average molecular weight 222) added to the lead present in alkaline solution was over 1.8–2.0 (molar ratio approximately 1.5–1.7), lead could be separated selectively and quantitatively, while the zinc remained in the

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solution without concomitant loss. The residues from the precipitation step were identified as mixtures of PbS and $Na_2Pb(OH)_2S$, with PbS being the predominant compound.

INTRODUCTION

Zinc and lead usually occur together in a variety of mineral zinc ores and some solid wastes, such as steel mill EAF dusts (1–5). Sulfide ores, such as sphalerite (ZnS), marmatite (ZnS and FeS), and oxidized zinc ores, such as zincite, hydrozincite, hemimorphite, smithsonite, and willemite, and their corresponding lead ores, nearly simultaneously contain both zinc and lead. Zinc is predominant in zinc ores and lead is predominant in lead ores (5).

Another important resource of zinc and lead is the dust generated in the metal melting industry, which includes iron and steel foundries and mills, as well as brass and bronze foundries. During the metal-melting process, the electric arc furnace (EAF) can reach temperatures of 1600°C or higher. Large quantities of dust will be generated under these conditions, in which many of the charged components, including zinc, cadmium, and lead, are present. The weight of dust collected in a typical carbon-steel electric furnace of a steel-making shop is about 10–15 kg per tonne of steel. Therefore, the quantity of dust produced in any one location is about 1.0×10^4–3.0×10^4 tonne/y (6–7).

Oxidized zinc ores and wastes can be treated by acidic leaching processes. However, besides leachable zinc and lead, elements such as Ca, Fe, Mg, etc. may also dissolve in the acid (6–9). As a result, a large quantity of extra acid will be consumed and a leach solution with complex components will be obtained.

Alkaline leaching in caustic soda solution is another method widely used in the extraction of zinc and lead from oxidized zinc ores and wastes (5,10). In this process, Fe, Al, Mg, Ca, etc. will not be dissolved in alkaline solution. Hence, the consumption of leaching agent will be reduced to a minimum value and a leach solution containing only Zn and Pb as predominant elements will be obtained. Zn in the alkaline leach solution can be recovered as metallic powder by electrowinning (5,10) with lower electricity consumption of 2.5–2.7 kW hour/kg, which is less than used for Zn recovery in acidic medium (3.3 kW hour/kg). Nevertheless, Pb must be removed from the alkaline solution before electrowinning.

Separation of lead from zinc in both acidic and alkaline media has been studied and applied widely. In acidic solution, Pb can be cemented quantitatively by the addition of zinc powder but not in alkaline medium. An alternative method should be developed for Pb removal from zinc in alkaline solution. In this work, several chemical methods were tested. Pb can be precipitated quantitatively without concomitant loss of zinc by sulfide precipitation using sodium sulfide as precipitant. The experimental results were reported in this paper.

EXPERIMENTAL

The Preparation of Alkaline Solution Containing Zinc and Lead

Alkaline solution containing up to 80 g/L Zn and 10 g/L Pb were prepared by dissolving zinc and lead oxides in strong NaOH solution. The solution seemed unstable after time, and powdery precipitates could form when the solution was allowed to stand for hours.

Contact EAF dust or oxidized zinc ores with 5 mol/L NaOH solution was another method of generating alkaline Zn and Pb solutions. A series of leach solutions with different concentrations of zinc and lead was obtained by changing the dusts or ores weights/NaOH solution ratios in the leaching systems. Alkaline solutions with zinc and lead concentrations of up to 60 g/L and 5 g/L, respectively, were found to be very stable and could be kept for months without forming precipitates. Hence, the zinc and lead alkaline solution was prepared by leaching the zinc and lead in EAF dusts containing 25% Zn, 1.84% Pb, 32% Fe, 4% Ca, and 1% Al (11) and ores containing 20% Zn and 2.8% Pb (weight percent) (5).

Separation of Lead from Zinc in Alkaline Leach Solution

Sodium sulfide solid or solution was mixed with leach solutions containing zinc and lead and allowed to stand for hours, under heat if necessary. Then, the supernatant was assayed by ICP and the precipitation and separation efficiencies were calculated.

RESULTS AND DISCUSSIONS

Preparation for Alkaline Leach Solution Containing Zinc and Lead

The EAF dusts or ores were contacted with 5 mol/L NaOH solution for 42 h. Typically, an alkaline leach solution contained 14.4 g/L Zn, 2.98 g/L Pb, 1 g/L Al, and 0.05 g/L Fe, which would be used as the testing solution for separation of lead from zinc.

When the EAF dusts were preliminarily treated by fusing with NaOH and then leached by NaOH solution, the zinc concentration in leach solution was increased to over 55 g/L but the lead concentration remained nearly unchanged. Over 95% of both zinc and lead was leached from the dusts. A similar leach solution was also obtained when oxidized zinc ores were contacted with 5 mol/L NaOH solution for 42 h at 95°C (5,11).

Separation of Lead from Leach Solution

Sodium sulfide is not stable and the number of hydrates in the crystal also changes gradually. The sodium sulfide used in this work was produced by Merck (Pro Analysi, Germany). The chemical formula shown on the container is Na_2S xH_2O ($x = 7-9$). The accurate concentration of sodium sulfide was determined by EPA Direct Colorimetric Analysis, and the molecular weight (M.W.) of the chemical was found to be approximately 222 ($x = 8$).

Selection of the Precipitants

The potential and available precipitants for the selective precipitation of lead from alkaline zinc solution might include sodium phosphate, sodium carbonate, sodium sulfate, and sodium sulfide. The experimental results in which these precipitants were used are shown in Table 1. The most effective separation of lead from zinc was obtained when sodium sulfide was used as precipitant. Thus, sodium sulfide was selected and used as the precipitant in the following experiments.

Precipitates could not form when the other possible precipitants were added into the alkaline solution containing Zn and Pb, indicating that lead sulfate, lead and zinc phosphates, lead and zinc carbonates, which were insoluble in neutral medium, were soluble in the strong alkaline solution.

Effect of the Weight Ratios in the Leach Solutions

When sufficient sodium sulfide was added to make the weight ratios of sodium sulfide to the lead in the solution equal to 1.7–1.9 (molar ratio approximately 1.5–1.7), the selective separation of lead from the alkaline zinc solution was always quantitative without concomitant loss of zinc (Fig. 1 and Table 2). In practical application, a weight ratio of 1.8 should be used to ensure that the lead

Table 1. Selection of the Precipitants for the Separation of Lead from Alkaline Solution of Zinc

Precipitants	Phosphates	Carbonates	Sulfates	Sulfide
Initial concentrations in leach solution (mol/L)	0.01–0.05	0.01–0.05	0.01–0.05	0.0025–0.015
Removal of zinc (wt %)	0.0	0.0	0.0	0.0
Removal of lead (wt %)	0.0	0.0	0.0	40.1–100.0

Leach solution: Zn 14.40 g/L; Pb 2.98 g/L; 12 mL

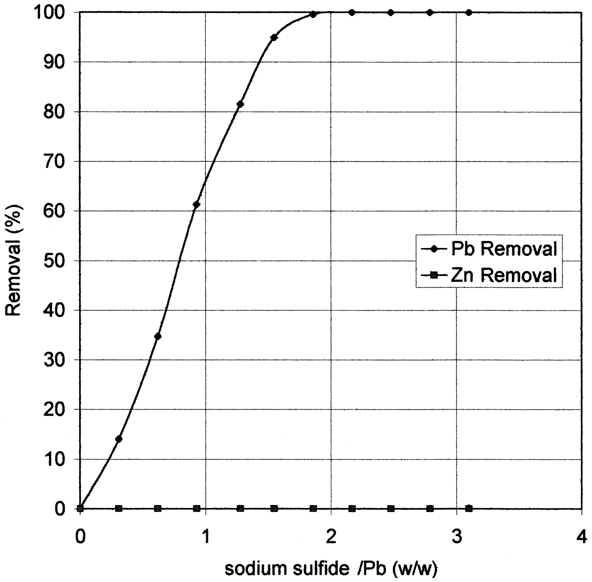

Figure 1. Removal of lead from the leaching solution of EAF dust melt by the addition of sodium sulfide (M.W. = 222). Leaching solution: Zn 45.60 g/L, Pb 3.60 g/L, Fe 0.06 g/L, Al 1.14 g/L, Cu 0.06 g/L, Cd 0.04 g/L

Table 2. Removal and Recovery of Lead from Alkaline Solution of Zinc by the Addition of Sodium Sulfide (M.W. = 204−240)

Composition of leaching solution (g/L)	Zn 26.95, Pb 6.53
Volume of leaching solution used (mL)	2700
Sodium sulfide added (g)	25.90 (M.W. 204–240, average 220)
Sodium sulfide/Pb (wt/wt)	1.47
Pb removal (wt %)	94.50
Approximate molar amounts of the sulfide added to the lead removed	1.58–1.34
Lead sulfide obtained after washing and drying at 110°C (g)	21
Content of Pb in the lead sulfide obtained (wt %)	79.58
Weight gain of the lead sulfide at 550°C (wt %)	20.74
Content of Zn in the lead sulfide (wt %)	1.05
Possible chemical formula of the lead sulfide	PbS and Na_2PbS_2

can be removed quantitatively while the zinc remains in the solutions without loss. Table 2 shows that, when a weight ratio of 1.47 was used, nearly 95% of lead was removed from the solution.

Sodium sulfide is not stable in air. It absorbs water and is oxidized considerably. Therefore, the quantity of sodium sulfide needed for quantitative and selective precipitation of lead from zinc in alkaline solution should be determined experimentally for each case.

Co-removal of Soluble Coexistent Elements

Other possible elements present in the strong alkaline solution include Cu, Al, and Cr(III). Cu can be easily removed from the alkaline solutions together with lead (Table 3). However, Al and Cr(III) could not be removed with sulfide because these 2 elements are unstable in the solutions. Hence, the separation of Al and Cr(III) from Zn in alkaline solutions should be carried out by other processes after the lead has been removed.

The Chemical Composition of Lead Sulfide Precipitates

The lead sulfide precipitate was separated from the solution, washed with hot water for 2 h, and then dried at 110°C. ICP was used to analyze the Na, Pb, and Zn content, and weight loss was determined by calcination. The precipitates contained a mixture of lead sulfide and much less sodium-lead disulfide (Table 2).

Table 3. The Co-removal of Copper with Lead from Alkaline Solutions of Zinc

Cu Added (mg/L)	Pb Removal (wt %)	Zn Removal (wt %)	Cu Removal (wt %)
0	100.0	0.0	100.0
48.0	100.0	0.0	100.0
236.0	100.0	0.0	100.0
354.0	100.0	0.0	100.0
473.0	100.0	0.0	100.0
591.0	100.0	0.0	100.0
>600	Formation of copper hydroxide precipitates		

Solution: Zn 14.4 g/L, Pb 2.89 g/L, Cu 20 mg/L
Sodium sulfide added/Pb (weight ratio): 1.8:1

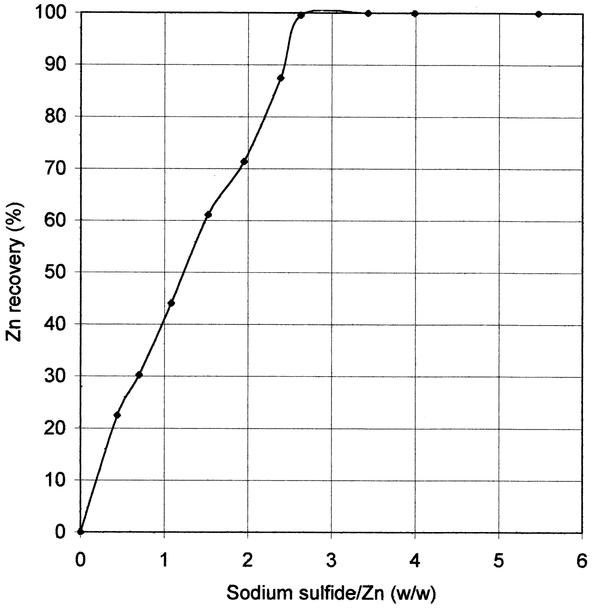

Figure 2. Recovery and precipitation of zinc from Pb-depleted alkaline leaching solution by sodium sulfide (M.W. = 222). Leaching solution: 10 mL, Zn 45.63 g/L

Sodium Sulfide Precipitation of Zinc from Lead-Free Solution

After the lead was separated from the solution, the zinc was precipitated quantitatively if the weight ratios of sodium sulfide to the zinc were higher than 2.6–2.7 (molar ratios approximately 0.7–0.8) as shown in Fig. 2 and Table 4. The zinc sulfide precipitates were separated and treated the same way as was the lead sulfide (Table 4) and may have consisted of ZnS, ZnO, $Zn(OH)_2$, and $Na_2Zn(OH)_2S$.

The particles of freshly precipitated lead and zinc sulfides are very fine and very difficult to separate from the liquid. The precipitates should be washed or hydrolyzed in water for hours under heat to release the entrained NaOH. After the sulfides of lead and zinc were hydrolyzed thoroughly, the composition of the resultant sulfides were of the simplest forms: PbS and ZnS.

Free Sulfide Concentration in the Alkaline Solution

The concentration of sulfide ion was determined after lead or zinc was precipitated quantitatively. The sulfide concentrations present in the solutions were

Table 4. Recovery of Zinc from the Pb-Free Leaching Solution by the Addition of Sodium Sulfide (M.W. = 204−240)

	Sample No.		
	1	2	3
Pb-free leaching solution (mL)	1250	300	600
Zn content in leaching solutions (g/L)	26.95	45.00	50.85
Sodium sulfide added (g)	84.00	33.21	80.00
Sodium sulfide/Zn (wt/wt)	2.49	2.46	2.62
Zinc sulfide obtained after washing and drying at 110°C (g)	43.93	18.11	38.02
Zinc content in the zinc sulfide (wt %)	72.18	71.45	74.52
Zinc recovery based on the zinc sulfide collected (wt %)	94.12	95.85	99.86
Zinc content in the aqueous solution after recovery of zinc as zinc sulfide (g/L)	1.06	2.32	0.12
Approximate molar ratios of the sulfide added and the zinc precipitated	0.85–0.72	0.82–0.70	0.84–0.71
Weight loss at 550°C (wt %)	4.22	6.09	3.73
Possible chemical formulas of zinc sulfides	Complex mixtures of ZnS, ZnO, $Zn(OH)_2$, and $Na_2Zn(OH)_2S$	Complex mixtures of ZnS, ZnO, $Zn(OH)_2$, and $Na_2Zn(OH)_2S$	Complex mixtures of ZnS, ZnO, $Zn(OH)_2$, and $Na_2Zn(OH)_2S$

approximately 1 mg/L for lead and 32 mg/L for zinc after precipitation. The added sulfide is consumed almost completely during the formation of lead or zinc sulfide precipitates.

DISCUSSION

Sulfide in aqueous solution may be present as S^{2-}, H_2S^{2-}, and H_2S at different pH values. In the strong alkaline solution, S^{2-} will be predominant. The solubility of ZnS and PbS is 2×10^{-23} and 1×10^{-28}, respectively; PbS is much more insoluble than ZnS. This relative insolubility accounts for one reason why lead can be preferably precipitated prior to zinc. However, little selectivity was observed for zinc and lead separation in neutral medium by sulfide precipitation. Both zinc and lead precipitated in the neutral and weakly alkaline solution (< 2.5 mol/L NaOH) after the addition of sodium sulfide. The selective separation of lead from zinc was possible when the initial NaOH concentration was kept from 2.5 to 11 mol/L if proper weight ratios of sodium sulfide to lead were used.

The precipitates of zinc and lead sulfides were colloidal and quite difficult to filter. Filtration operation improved by heating the solution or allowing it to stand for 1 to 2 days to allow settlement through gravity.

The chemical forms of zinc and lead may change dramatically in different media. The simplest forms, Zn^{2+} and Pb^{2+}, were present in acidic media, and hydrates of the ions were found in neutral media. In weakly and strong alkaline solutions, precipitates of zinc and lead hydroxides formed. Lead can only be selectively and quantitatively precipitated from zinc in strongly alkaline solution by sulfide precipitation.

We initially thought that lead could be precipitated as the simplest form of PbS and that zinc would precipitate as ZnS in alkaline solution. In fact, the experimental results show that the simplest forms of lead and zinc in strongly alkaline NaOH solution may be $Na_2Pb(OH)_4$ and $Na_2Zn(OH)_4$. When sodium sulfide was added, 2 OH groups in $Na_2Pb(OH)_4$ were substituted by S^{2+} to form $Na_2Pb(OH)_2S$, which has less solubility than the corresponding zinc complex. When the sodium-lead-hydroxide sulfide and its zinc analogues were hydrolyzed in water after having been heated for hours, lead species were nearly completely transformed into PbS, but only some zinc species were transformed into ZnS.

The lead sulfide obtained was quite pure if little or no copper is present. After the metal hydroxides were hydrolyzed, PbS accounted for over 95% to 98% of the precipitates. Such a high grade of lead sulfide can be used as raw material for lead smelting and production of metallic lead. The sale of PbS may partly offset the prices for the consumption of the sodium sulfide used for lead separation.

Zinc can be readily electrowon in metallic form from the lead-depleted alkaline solution even in the presence of the Al that dissolves together with Zn and Pb from ores or dusts. This is a cost-effective method for the recovery of zinc from the solution with little loss of NaOH in the whole process of PbS precipitation and electrowinning (11).

CONCLUSIONS

Lead can be removed selectively and quantitatively as mixtures of lead sulfide and sodium-lead sulfide from alkaline zinc solutions when the weight ratios of added sodium sulfide to lead were kept at 1.8–2.0 (molar ratio approximately 1.5–1.7), while the zinc remains in the solution. The content of PbS in the sulfide precipitates may be over 95–98% and may be used directly in lead smelters for the production of metallic lead and other purposes.

REFERENCES

1. Gill, C.B. *Nonferrous Extractive Metallurgy*; John Willey & Sons: New York, Chichester, Brisbane, Toronto, 1981; 18–279.
2. Morgan, S.W.K. *Zinc and Its Alloys*; Industrial Metal Series; Macdonald & Evans Ltd: Estover, Plymouth, UK, 1977; 88–112.
3. Brooks, C.S. *Metals Recovery from Industrial Waste*; Lewis Publishers, Inc: Mich, 1991; 33–14.
4. Collie, M.J., Ed. *Extractive Metallurgy, Development Since 1980*; Noyes Deta Cooperation: Park Ridge, NJ, 1984; 118–153.
5. Youcai, Z.; Stanforth, R. Production of Zn Powder by Alkaline Treatment of Smithsonite Zn-Pb Ores. Hydrometallurgy **2000,** *56,* 237–249.
6. Tippin, R.B.; Tate, R.L. Metal Reclamation and Detoxification of Brass Foundry Waste Sand. In *American Foundrymen's Society Transactions*, Vol. 97, Proceedings of the 93th Annual Meeting, USA, May 7–11, 1989; 513–520.
7. Barrett, E.C.; Nenniger, E.H.; Dziewinski, J. A Hydrometallurgical Process to Treat Carbon Steel Electric Arc Furnace Dust. Hydrometallurgy **1992,** *30,* 59–68.
8. Swarnkar, S.R.; Gupta, B.L.; Sekharan, R.D. Iron Control in Zinc Plant Residue Leach Solution. Hydrometallurgy **1996,** *42,* 21–26.
9. Peters, E. Hydrometallurgical Process Innovation. Hydrometallurgy **1992,** *29,* 431–459.
10. Frenay, J.; Ferlay, S.; Hissel, J. Zinc and Lead Recovery from EAF Dusts by Caustic Soda Process. In *Electric Furnace Proc., Treatment Options for Carbon Steel Electric Arc Furnace Dust*; Iron Steel Soc., 1986; 43,171–175.
11. Youcai, Z.; Stanforth, R. Integrated Hydrometallurgical Process for Production of Zinc from Electric Arc Furnace Dust in Alkaline Medium. J. Haz. Mat. **2000,** *122* (3–4), 281–297.

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