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HYDROMETALLURGICAL TREATMENT OF ZINC WASTE DUSTS

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ABSTRACT

Hydrometallurgical separation processes offer attractive potential for recovery of marketable zinc from industrial wastes. In view of the importance of having a supply of zinc from a diversity of sources to supplement zinc imports, it is useful to assess the applicability of available separation technology. A brief review is presented of applications of several separation processes which have been applied to a variety of zinc waste dusts. In addition the results of bench scale tests are presented for a technically feasible scheme applied to a high zinc content fly ash from a waste to energy power plant which show a potential of providing a marketable zinc recovery product.

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INTRODUCTION

Zinc is the fourth most commonly used metal after steel, aluminum and copper. United States industrial demand in 1992 was 964,000 tons (1). Imports provided about 34% of this annual demand and 360,000 tons originated with secondary sources such as scrap, waste dusts, fly ash, oxides and various chemicals. Primary United States demand is expected to attain 1,650,000 tons by the year 2000 with substantially less than one half provided by United States mine production, so the importance of secondary sources is expected to have increasing significance (2).

Zinc is used primarily in metallic form but about one third of the annual United States production, 230,000 tons, finds application in nonmetallic forms such as rubber, chemicals and paint products (1).

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Hydrometallurgical separation technology has particular relevance for the secondary recovery of zinc from industrial wastes. Consideration must be given to both the chemical and physical condition of the zinc waste systems in order to devise successful metallurgical separation processes appropriate for the specifics of industrial cases. Some published results are cited below that have been used on an industrial scale or experimentally for zinc waste dusts.

One particular scheme is described that has been devised for zinc recovery from a fly ash generated by a waste to energy plant. Results are presented of bench scale experimentation conducted to evaluate technical feasibility and to demonstrate the potential for producing a marketable zinc product.

Hydrometallurgical metal separation processes provide a number of advantages for application to nonferrous metal recovery from industrial wastes (3). These advantages include a low energy requirement relative to pyrometallurgical processing, flexibility in processing complete metal mixtures, applicability to small processing plants, convenience in handling of aqueous systems and minimal environmental problems such as toxic gas and dust emissions.

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There are some disadvantages associated with hydrometallurgical processing such as relatively slow reaction rates due to low reaction temperatures, which leads to a requirement of larger reaction vessels and in some cases additional handling precautions when processing fine dusts, more highly instrumented process control, and in some instances more attention is required to minimize toxic secondary waste effluents.

SOLUBILIZATION

Solubilization of solid zinc wastes is the first step in preparation for hydrometallurgical processing. Both acids and alkalies have been used in solubilization. And, in some instances, pyrometallurgical roasting, in addition, has been conducted for generation of more water soluble compounds such as chlorides or sulfates in combination with various hydrometallurgical separation processes for zinc recovery. Some published results for several kinds of waste dusts have been cited below.

Ammonium carbonate has been used for zinc recovery from steel dust (4,5), automobile scrap (6) and incinerator fly ash (7), in the latter case with a 400°C roasting step included. Chlorine leaching has been used for steel dust (10,11,12). Combination treatments have also been used such as sulfuric acid and chloride leaching with electrogalvanizing dust (13); waste acid and alkali for fly ash (14); sulfuric acid and sodium bisulfide/carbonate for flue dust (15); and a combination of acid/oxygen/ $H_2O_2/K_4S_2O_8$ with blast furnace dust (16). Sulfuric acid leaching has been used for steel dusts (17,18) and is the most commonly used approach for the solubilization of solid zinc waste solids.

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SEPARATION PROCESSES

Separation processes that are commonly used to make metal separations from industrial waste solutions and that are likely to be appropriate for zinc waste dusts consist of electrowinning, solvent extraction, precipitation, adsorption/ion exchange and cementation. Some examples for applications to zinc wastes are cited below.

Electrowinning

Several examples for zinc recovery from mixed metal electrolyte solutions by electrowinning can be cited for waste systems such as ore concentrates, mixed metal sludges, zinc processing wastes and copper and lead smelter flue dusts (19-26).

Solvent Extraction

An alternative to electrowinning for zinc separation from mixed metal electrolyte solutions is solvent extraction. A number of organic complexing agents have been used successfully for solvent extraction separations. To name a few of these there is bis 2-ethylhexyl phosphoric acid (27,28,31,32), trioctylphosphine oxide (28), Versatic 10 and 911 (carboxylic acid) (29), oleic acid plus cyclohexanoneoxime (31,33,34) and chelating agents like acetylacetone, thenoylthflouracetone, sodium diethyldithiocarbonate and 8 hydrooxyquinoline (35) and alamine 336(36). Solvent extraction separations offer several disadvantages, however, such as often less than desired selectivity for mixed metal solutions, the necessity of handling a two phase system and the necessity of being able to realize efficient regeneration of the organic solvent extraction phase for reuse.

Precipitation

Metal separation as hydroxides, carbonates, sulfides, phosphates and certain organic compounds have been used to advantage. Precipitation of metal hydroxides with alkalies (NaOH, Na_2CO_3,$NaHCO_3$) is commonly used (37,38,39,40) but coprecipitation for mixed metal solutions and the creation of amorphous sludges that are difficult to filter and dewater are common problems. There are advantages in minimizing solids separation and recovery problems by using carbonate (41,42,43,44,45) or a combination of hydroxide/ carbonate precipitation (46,47,48). Metal separation by sulfide precipitation has been used also and can be very efficient but the persistence of colloidally dispersed metal sulfides is often encountered (49-53).

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Improvements in the separation of metal impurities such as iron in the presence of divalent metals like zinc in electrolyte solution have been achieved by using low concentrations of anionic surfactants like acetic acid or EDTA to sequester or competitively adsorb on the ferric hydroxide precipitate in a moderate pH range of 3 to 5. This minimizes coprecipitation of the iron impurity (54).

An alternative to hydroxide precipitation for removal of iron, aluminum or chromium (III) impurities from mixed metal solutions with divalent metals like zinc is the use of phosphate precipitation in a moderate pH range to separate these metals in the trivalent state (55).

Organic precipitants such as oxalic acid have been also demonstrated to efficiently separate divalent metals in a moderate pH range from multimetal solutions to obtain a zinc salt of high purity (56). Zinc oxalate can be readily thermally decomposed to yield zinc oxide if that was the desired product.

Adsorption

Removal of metals at low concentration from aqueous solution by adsorption has been used extensively. Adsorbents reported for metals like Cd, Pb and Zn include carbon (57,58); chelating exchange resins (59); portland cement/chlorides (60);

hydrotalcite (61); cellulose xanthate (62); MgO (63) and sodium dimethyldithiocarbamate/limestone (64). The adsorbents most commonly reduced to commercial practice are carbon, alumina and xanathate fibers.

Removal efficiency can be high but regeneration with metal recovery is not commonly achieved at least for mixed metal systems. Metal recovery from carbon adsorbents can be obtained by oxidation destruction of the adsorbent.

Ion Exchange

Metal separation from aqueous solution by ion exchange with anionic, cationic and chelate type exchange resins has been used extensively. Exchange systems reported for Cd, Pb and Zn include microporous resins, AV-17-10P (65); anionic resins for Donnan dialysis (66); cationic resins (67,68,69,70,71); and chelate type resins (72,73,74). Although high efficiency in separation and frequently high selectively in separation can be achieved, the synthetic resins are relatively high cost materials compared with the previously cited adsorbents so that the economics of metal separation and potential recovery on the synthetic exchange resins must be evaluated against nonrecoverable removal on adsorbents like carbon, alumina or xanthate fibers. Clean up of low concentrations of residual metals in aqueous effluents is probably the most appropriate application of either adsorbents or ion exchange resins.

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Cementation

The electrode potentials of magnesium, aluminum, zinc and iron are such that cadmium and lead should undergo cementation displacement from an electrolyte solution like zinc sulfate. Zinc has been used extensively and iron to a lesser extent for such cementation displacements and there are a number of literature citations for removal of cadmium and lead as impurities in zinc electrolyte solutions (75-90).

It is also theoretically possible for electrochemical displacements to occur with aluminum making possible cementation removal of cadmium, iron, lead and zinc from electrolyte solutions. There are several citations for such applications in the literature (95-98). There are at least three literature citations for the cementation purification of electrolyte solutions using magnesium for removal of cadmium, copper, iron and zinc (99-101).

In the case of the present system, sulfuric acid solubilized fly ash with high zinc and iron content, cementation removal of iron, cadmium and lead would be an attractive purification scheme. Although there are numerous examples of zinc cementation separation of cadmium and lead from zinc electrolytes and a few examples of purification using aluminum for cementation, there is limited published experience where iron was an impurity to be removed. An assessment of the potential for using either aluminum or zinc for cadmium and lead removal, as well as reducing the iron content, was considered a worthwhile objective for the present investigation.

DEMONSTRATION OF ZINC RECOVERY

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The diversity in compositions for zinc waste dusts is extensive so that successful separation schemes need to be tailored to the specifics of a given waste. To illustrate how available separation technology can be effectively adapted, a scheme has been devised for a waste to energy fly ash derived from tire combustion which requires separation from carbon, iron and possibly cadmium and lead to find market acceptability. Separation alternatives selected consisted of solubilization in sulfuric acid, iron separation by precipitation or cementation, cadmium and lead separation by cementation and ultimate zinc recovery as zinc sulfate or zinc oxalate. Bench scale experimentation has been conducted to establish the technical feasibility of these alternatives and to assess what kind of a zinc recovery product can be obtained.

Experimental Procedures

The fly ash material used consisted of bag house ash from a waste to energy plant with tires as the fuel. The bench tests were conducted with fly ash collected in a bag house for the flue gas cleanup with one sample consisting of a sample calcined at 1600°F for carbon burnoff.

The fly ash, 10-20 g, was solubilized in 100 mL of 20 wt % H_2SO_4 for 24 hours at 70-90°F and for one hour at 350°F. For one test the heating at 350°F was omitted. Upon completion of solubilization the insolubles were separated by filtration. Iron was separated by precipitation as the hydroxide by addition of NaOH or as the phosphate by addition of Na_3PO_4.

The cementation tests were conducted over the pH range from 1.5 to 5.0 over aluminum foil (Reynolds household foil) or 10 mesh zinc pellets (Aldrich reagent grade 24, 346-9) following the acid solubilization and, in some instances, following iron precipitation. Cementation separations of Fe, Cd, Pb and Zn were measured. Cementations were conducted with 5±.5 g of Al and 10±.5 g of Zn for each 100 mL of pH adjusted solution.

Several tests were conducted with zinc separated as the oxalate salt by addition of sodium oxalate at a pH of about 4 following the cementation tests.

The solid fly ash analyses were conducted by the Environmental Research Institute, University of Connecticut at Storrs, CT. All metal in solution analyses were conducted by the Phoenix Environmental Laboratories, Inc. in Manchester, CT.

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RESULTS OF BENCH SCALE TESTS

Solubilization

Solubilization of the fly ash with sulfuric acid was selected because there is an extensive experience of demonstrated technical feasibility and the prospects are promising for obtaining products that are marketable. The results for several small scale bench tests are given in Table 1. A typical composition for the fly ash as collected in a bag house consists of a 0.282 weight fraction Zn, 0.111 weight fraction Fe, 0.0012 weight fraction Pb, 0.00021 weight fraction Cd, 0.101 weight fraction carbon, 0.016 weight fraction Al, 0.008 weight fraction Ca, 0.0056 weight fraction K, 0.0014 weight fraction Mg, 0.0079 weight fraction Na, 0.063 weight fraction SiO_2, 0.015 weight fraction S, 0.008 weight fraction chloride.

The results reported in Table 1 show that for uncalcined fly ash, Tests 5A and 6A, a high order of zinc solubilization of 0.95 and 0.99 weight fraction can be obtained with relatively mild extraction conditions with 20 wt % H_2SO_4 accompanied by a distinctly preferential removal of the zinc compared to the iron. An omission of the one hour heating to 350°F and limiting the extraction temperature to about 90°F provides a somewhat less efficient zinc extraction of 95 percent but with a greater preferential removal of zinc over iron. It is suggested that these observed differences are due to more extensive formation of insoluble iron/zinc jarosites in the latter cast, Test 6A.

TABLE 1

Ash Solubilization

Test	Ash	Composition Metal Wt.Fraction	Solubilization Process pH$<$1	Metal in Soln. ppm	Metal Fraction in Soln.
1A	Calcined ash	.146 Fe	24 hr at 75-90F +1hr at 350F 10g of Ash in 100 ml 20 wt% H_2SO_4	3810	0.60
		.279 Zn		10095	0.83
5A	uncalcined ash	.0168 Al	"	340	0.24
		.111 Fe		2510	0.27
		.282 Zn		23875	0.99
		.00021 Cd		< .1	
		.0012 Pb		< .1	
5C	uncalcined ash	Al	Leached with 36% acetic acid after above sulfuric acid leach	31.	.019
		Fe		200.	.016
		Zn		1830.	.077
		Cd		< .1	-
		Pb		< .1	-
6A	uncalcined ash	.0168 Al	24 hr at 75-90F 20g of ash in 100 ml 20 wt% H_2SO_4	220.	0.20
		.111 Fe		490.	0.067
		.282 Zn		23120.	0.95
		.00021 Cd		2.7	0.24
		.0012 Pb		7.2	0.11

The weight fractions reported in the last columns for Table 1 as metal weight fraction in solution, for Table 2 as weight fraction metal separated, for Table 3 as fraction of metal cemented and for Table 4 as weight fraction of metal separated were calculated based on the total metal contents of the analyzed leachate solutions referred to the initial metal content of the air dry fly ash (10 g) in Table 1 or to the initial solutions of the leachate in Tables 2, 3 and 4. Data not shown in the tables are the final leachate solution volumes which consists of the residual sulfuric acid solutions combined with water added during washing of the insoluble residues.

A leach of the residue from the initial extraction in Test 5A, with acetic acid in Test 5C shows that using more than one extraction stage will yield only negligibly more extraction of Cd or Pb; the initial one-stage extraction has provided a residue that should be able to pass a TCLP (Toxicity Characterization Leaching Procedure) extraction test.

The results of the 1A extraction with sulfuric acid for a fly ash sample calcined at 1600°F to 1800°F to burn off the carbon shows a distinctly lower zinc separation efficiency. This is possibly due to the creation of more extensive amounts of zinc ferrite

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TABLE 2

Iron Separation by Precipitation as Hydroxide or Phosphate

Test No.	Metal	Initial Metal Conc.PPM	Separation Process	pH	Residual Metal Conc.PPM	Weight Fraction of Metal Separated
5B	Fe	2510	Precipitation with NaOH	4.0	620	0.75
	Zn	23875			9370	0.61
6B	Fe	490	Precipitation with NaOH +200 PPM EDTA (54)	4.5	58	0.86
	Zn	23650			9910	0.49
7B	Fe	597	Precipitation with $NaPO_4$ (55)	2.5	6.0	0.99
	Zn	22590			10450	0.30

TABLE 3

Cd and Pb Cementation on Aluminum Foil

Test	Initial Metal Conc. H_2SO_4 Soln.	pH	Metal Conc. ppm after Cement.	Fraction of Metal Cemented
3B 2nd stage after iron precip.	170 Fe	5	94	0.41
	7900 Zn		5120	0.31
	10 Cd		9.8	0.02
	38 Pb		28	0.26
4	390 Al	3	800	-
	3970 Fe		2200	0.45
	27000 Zn		20000	0.17
	4.4 Cd		1.0	0.75
	6.3 Pb		$<.1$	0.92
4-OA	390 Al	2	1600	-
	3970 Fe		3850	0.028
	27000 Zn		17000	0.12
	4.4 Cd		2.0	0.22
	6.3 Pb		$<.1$	0.97

TABLE 4

Zinc Separation by Precipitation as Oxalate (56)

Test No.	Metal	Initial Metal Conc.ppm	Separation by Precipitation with Sodium Oxalate	pH	Residual Metal Conc.ppm	Weight Fraction of Metal Separated
6C	Fe	58	After iron separattion by hydroxide precipitation	4.5	83	0.43
	Zn	9910			111	0.995
	Cd	1.6			0.31	0.72
	Pb	4.2			0.14	0.952
7C	Fe	6.0	After iron separation by phosphate precipitation	2.5	1.3	0.68
	Zn	10450			127	0.983
	Cd	6.4			0.19	0.957
	Pb	0.1			0.1	-

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resulting from the more extended high temperature exposure. A direct sulfuric acid solubilization of the fly ash with the 10 wt % carbon present appears to provide an advantageous alternative to calcining for producing an improved zinc recovery product.

Iron Separation

Recovery of a zinc product such as zinc sulfate with a lower iron content for either electrowinning zinc recovery or preparation of superior zinc chemicals which as $ZnSO_4$ or ZnO, led to conduct of several precipitation separations of iron, Test 5B, 6B and 7B reported in Table 2. The initial solutions in all cases are the acid zinc sulfate solutions produced as described above under solubilization.

A direct precipitation in Test 5B with NaOH limiting the pH to 4 separated a 0.75 weight fraction of the iron as hydroxide but at the expense of precipitation a 0.39 weight fraction of the zinc present. By using a NaOH precipitation modified by the presence of a low concentration, 200 PPM, or EDTA (ethylene diamine tetra-acetic acid) to inhibit zinc coprecipitation (54) an improved separation of iron of a 0.86 weight fraction was obtained but still at the expense of losing a 0.49 weight fraction of the zinc to the hydroxide coprecipitate. The use of Na_3PO_4 as the precipitant (55) and limiting the pH to 2.5 provides an efficient iron separation of a 0.99 weight fraction but still at the expense of coprecipitating a 0.3 weight fraction of the zinc.

It is necessary to limit the upper range of the pH in these precipitations, either with hydroxide or phosphate to minimize solubilization of the Cd and Pb.

Cementation

Several tests were conducted to evaluate the prospects for using cementation to remove Cd and Pb from the zinc sulfate solutions produced by sulfuric acid solubilization. These results are reported in Table 3. The results from Test 3 on a solution adjusted to pH 5 to precipitate the iron with NaOH demonstrates high iron and zinc cementation on aluminum foil accompanied by production of unacceptably high Cd and Pb in solution. The Tests 4 and 4-OA, conducted at pH 3 and 2 with solutions containing both high zinc and iron from direct sulfuric acid solubilization of uncalcined fly ash, demonstrate that for room temperature exposures for times of about 24 hours that quite low concentrations of Cd of the order of 1-2 PPM and of less than 0.1 PPM Pb can

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be obtained, accompanied by some loss of zinc in the range of 0.17 to 0.12 weight fraction.

An evaluation of cementation separations of Cd and Pb with Zn was also conducted but with unsatisfactory results. At pH below 3 where the cementation removal of Cd and Pb is most favorable the dissolution of zinc with copious hydrogen evolution was the dominant reaction. At pH of 5 and above there is extensive loss of zinc by hydroxide precipitation and inefficient cementation of Cd and Pb. There is extensive publication of examples of Cd and Pb cementation from zinc sulfate solutions, however, there are few instances where iron is present in major amounts.

Zinc Recovery by Oxalate Precipitation

Another option that has attractive possibilities is to initially conduct sulfuric acid solubilization of the fly ash, separate the bulk of the iron by phosphate precipitation at low pH (2.5) and precipitate the zinc as the oxalate by addition of sodium oxalate (56). In this manner a high purity zinc oxalate can be separated by filtration leaving a residual solution with low enough Cd and Pb concentrations to provide a nontoxic effluent for disposal. Results are given for two bench scale tests using acid solubilized zinc sulfate solution with the bulk of the iron removed by hydroxide precipitation, Test 6C, or by phosphate precipitation, Test 7C, (Table 4). The resultant zinc oxalate has potential as a high grade chemical or the zinc oxalate can be resolubilized in sulfuric acid to be used for zinc recovery by electrowinning or concentrated for recrystallization of high grade zinc sulfate.

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CONCLUSIONS

The results of the bench-scale tests indicate several alternatives that have potential for producing marketable zinc recycle products, namely:

1. The direct solubilization with sulfuric acid of uncalcined fly ash, avoiding high temperature calcining to burn off carbon, can provide a zinc sulfate solution that has potential for blending with the zinc sulfate recycle solutions currently used by zinc refiners using the jarosite process. The acceptability of the amounts of iron, cadmium and lead present would require evaluation.

2. Another option might be solubilization of the uncalcined fly ash with sulfuric acid combined with iron separation by phosphate precipitation with possible further reductions of Cd and Pb by either cementation on aluminum or zinc separation by oxalate precipitation. The objectives for this option would be to
   a. Produce a refined zinc sulfate solution for ultimate recovery of metallic zinc.
   b. Produce refined chemical products such as $ZnSO_4$, ZnO, or zinc oxalate.

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