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Alkaline leaching of metal melting industry wastes and separation of zinc and lead in the leach solution

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Abstract: In this work, a thorough examinations on the extractability of zinc and lead present in the steelmaking dusts using alkaline leaching process and the effectiveness of the zinc and lead separation in the resultant leaching solutions using sulfide precipitation method were made. It was found that only about 53% of zinc and over 70% of the lead could be leached out of the dusts, while the other 47% of zinc and 30% of lead were left in the leaching residues. The zinc and lead in the resultant leaching solution can be effectively and selectively separated. When the weight ratio of sodium sulfide (M.W. = 222—240) to Pb was kept at 1.8, the lead in the solution could be precipitated out quantitatively while all the zinc was remained in the solution. The zinc left in the solution can be further recovered by the addition of extra sodium sulfide with a weight ratio of sodium sulfide to the zinc over 2.6. The resultant filtrate can be recycled to the leaching of dust in the next leaching process.

Key words: alkaline leach; leaching solutins; zinc; lead

Introduction

The metal melting industry is one of the larger industries world-wide, including iron and steel foundries and mills, as well as brass and bronze foundries (Morgan, 1977; Gill, 1981; Brooks, 1991; Collie, 1984; Swarnkar, 1996; Peters, 1992; Elgersma, 1992). During the metal melting process, the electric arc furnace (EAF) can reach temperatures of 1600℃ or higher. Under these conditions, many of the components of the charge, including zinc, cadmium, and lead, are volatilized and enter the vapor phase. In addition, due to the inherent turbulence of the melt, some fine particular matter is also captured by the baghouse. As the fume is cooled, the vapore tends to oxidize and condense on the fugitive matter and this results in a chemically and physically complex dust. This dust contains up to 32% mass percent zinc. However, the average zinc content is approximately 19% mass percent with somewhat smaller content of lead and trace levels of cadmium and other heavy metals. The bulk waste is generally iron oxide. The fumes from a brass melting furnace can have up to 65% or higher zinc. Zinc ferrite spinel accounts for 20 to 50 mass percent of the zinc in the dusts. The quantity of such dusts are enormous. About 600000 t/a of EAF dusts are generated in North America alone. The weight of dust collected in a typical carbon steel electric furnace is about 10—15 kg per tone of steel. Therefore, the quantity of dust produced in any one location is comparatively small, about 10000—30000 t/a (Swarnkar, 1996; Peters, 1992; Elgersma, 1992; Barrett, 1992; Tippin, 1989). Because of their metal leaching potential, the wastes are frequently classified as hazardous wastes under the US EPA classification. Classification as hazardous wastes greatly increase the cost of disposal, due to the need for treatment to render the wastes nonhazardous, as well as greater transportation and disposal costs and increases the paperwork requirements.

A number of treatment process are in operation, particularly high-temperature reduction processes which reduces and fume off the volatile metals. Most of these installations are based on rotary kiln technology, which is sensitive to economies of scale and therefore the dust must be collected from numerous sources and transported to the relatively large processing plant. Plasma-based treatment processes are currently being developed, which are custom-designed for the capacity of a special steel-making location. All pyrometallurgical operations have high thermal energy requirements, elaborate dust collecting systems and require additional processing to separate the lead, zinc and halides as intermediate products. Moreover, the quantity of dusts treated by this process is also very limited (Elgersma, 1992; Barrett, 1992; Tippin, 1989; Peek, 1995; Donald, 1995).

The hydrometallurgical approach is aimed at eliminating the above problems and is being

considered to be important alternatives for the current treatment methods. Currently, however, no hydrometallurgical processes are known to be operating on EAF dust (Barrett, 1992; Tippin, 1989; Peek, 1995; Donald, 1995).

So far most of these wastes are disposed of in the industrial landfills, with the exception of steel mill electric are furnace (EAF) dust. Although the landfills are still the most important places for the wastes to go, it is necessary that an economically viable processes is developed to treat these wastes.

This paper presents only partial experimental results of our integrated research process on the recovery and cost-effective treatment of the dusts. In this work, firstly, we made a thorough examinations on the conventional alkaline leaching process, followed by the selective separation between zinc and lead in the leaching solution.

1 Experimental

1.1 Chemicals

All the chemicals used were of analytical grade, unless indicated otherwise. All the metallic elements were analyzed with ICP.

1.2 Characterization of the dusts studied

A given weight of dusts, which was kindly supplied by a steelmaking plant, was digested in concentrated nitric acid, and then analyzed by ICP. The results are shown in Table 1. The particles of dusts are very fine. No pretreatment was conducted in the study.

Table 1 Composition of the dust (weight %)

Elements	Zn	Fe	Pb	Mn	Ca	Al	Cd	Cu	Water
Content, %	24.80	32.00	1.84	3.31	4.08	1.03	0.01	0.02	0.01

1.3 Direct leaching of dusts

A given weight of dust was added into a glass bottle containing NaOH solution, leached the dusts by rotating with an orbital shaker for 42 hours (15 r/min), filtered, and then analyzed the filtrate and the residue if necessary.

1.4 Separation of zinc and lead in the leaching solution by sodium sulfide

To a given volume of leaching solutions sodium sulfide solid was added, and the suspension was mixed, stood by for hours. The Zn and Pb in the supernatant was analyzed and the amount of metals precipitated and the separation efficiencies were calculated.

2 Results and discussions

2.1 Effect of leaching parameters

2.1.1 Contacting time

It took about 72 hours for the leaching process to reach equilibrium of the dissolution of zinc and lead from the dusts used. Nevertheless, when the dusts were contacted for 42 hours, the extraction of zinc and lead increased slightly. Therefore, a 42-hour contacting time was used in the following experiments.

2.1.2 Phase ratios of liquid to dusts

It was found that a phase ratio (L/S) of 3 seems enough to reach a maximum leaching and extraction of zinc, i.e., around 35%, from the dust. Nevertheless, the leaching of lead increased as the phase ratios increased. When phase ratio was kept at 3, it was found to be about 55%—60%.

2.1.3 Concentration of NaOH in leaching agent

When the concentration of NaOH solution was higher than 5 mol/L, the maximum leaching rate of zinc and lead will be obtained. In the most tests, 5 mol/L NaOH solution were used as the leaching agent.

2.1.4 Leaching temperature

The temperature increase for the leaching systems hardly enhances the leaching process. It was suggested that all the experiments should be carried out at room temperature (25℃)

2.2 Sequential and multi-stage leaching of dusts

One-stage leaching rate of zinc was quite low (<40% for zinc). In order to improve the leaching efficiencies, multi-stage leaching process was conducted as follows: 50g of dust was contacted with 180 ml of 5 mol/L NaOH solution for 42 hours, filtered, and 160 ml of filtrate was obtained; the residue was contacted again with another 180 ml of fresh NaOH solution for 42 hours, and so on. A filtrate of 180 ml for the second and third contact was obtained. The results are shown in Table 2.

Table 2 Sequential extraction of zinc and lead from dust

Mixing sequences	Zn in leach solution, g/L	Pb in leach solution, g/L	Fe in leach solution, g/L
Paralleling test I			
First extraction	20.13	2.80	0.10
Second extraction	9.82	0.82	0.09
Third extraction	3.85	0.15	0.08
Fourth extraction	0.49	0.00	0.08
Total extraction	53.67%	73.66%	0.13%
Paralleling test II			
First extraction	21.11	2.88	0.11
Second extraction	9.80	0.85	0.08
Third extraction	2.63	0.14	0.08
Fourth extraction	0.23	0.00	0.08
Total extraction	52.86%	75.72%	0.13%
Paralleling test III			
First extraction	22.31	2.89	0.10
Second extraction	8.75	0.72	0.09
Third extraction	2.73	0.21	0.09
Fourth extraction	0.00	0.00	0.08
Total extraction	52.86%	74.74%	0.13%
Average extraction	53.13%	74.71%	0.13%

It can be seen that the maximum extraction for zinc was around 53%, and two-stage leaching was found to be practically enough to get such leaching recovery. It may consider that the portion of leachable zinc in the dusts is around 53%, and the remaining 47% of zinc may exist as zinc ferrites, which can not be attacked further by alkaline solution.

When the leach solution was contacted with the fresh dusts multiply, the elemental concentrations would be increased (Table 3). It can be seen that the highest concentration of zinc and lead in leach solution are around 33 g/L and 9 g/L, respectively.

Table 3 Multi-contact of fresh dust with leach solutions

No.	Leaching agent	Fresh dust, g	Volume of the leach solution, ml	Zn in leach solution, g/L	Pb in leach solution, g/L	Fe in leach solution, g/L
1	180 ml of 5 mol/L NaOH solution	50	160	21.13	2.89	0.10
2	160 ml of leach solution of No.1	50	140	25.58	6.40	0.11
3	130 ml of leach solution of No.2 and 30 ml of 5 mol/L NaOH solution	50	140	28.63	8.20	0.10
4	130 ml of leach solution of No.3 and 30 ml of 5 mol/L NaOH solution	50	140	33.08	9.01	0.12

Note: For each extraction, dust 50g, volume of filtrate 180 ml, mixing time 48 hours

2.3 Tests on the enhancement for the leaching of leaching residues

After three-stage leaching of dusts, the zinc content in the residues decreased to around 12% (Table 4). Fe powder, NaCl, NaAc, NH_4Ac and Citric acid were added to the leaching system of such residues, and the results are shown in Table 5. It can be seen that the zinc in the residues can not be extracted further in the presence of the chemicals used.

Table 4 Typical composition of the leaching residues after three-stage leaching (referred to Table 2)

Elements	Zn	Fe	Pb	Mn	Ca	Al	Cd	Cu
Content, %	12.15	39.24	0.32	3.31	3.97	0.01	0.01	0.09

Table 5 Effect of the addition of chemicals on the leaching of residues

Chemicals added, g	0.32 Fe powder	1.16 Fe powder	2.48 Fe powder	2.00 NaCl	1.90 NaAc	2.67 NH_4Ac	2.70 Citric acid
Zn extraction, %	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Note: Residue 2.5g, 5 mol/L NaOH 9 ml, leaching time 42 hours

2.4 Respective recovery of lead and zinc as sulfides from the leach solutions

2.4.1 Removal of lead by the addition of zinc dust

The experimental results showed that lead can not be removed at all from the alkaline leaching solution by the addition of zinc metal, as usually practiced in hydrometallurgy of zinc in which the leaching solution is acidic and lead can be cemented out by metallic zinc.

2.4.2 Removal of lead by the addition of sodium sulfide solid

It was found that the lead in leach solutions can be precipitated selectively and quantitatively by sodium sulfide, when the weight ratios of sodium sulfide to the lead present is 1.8 or higher to up to 3.2, while the co-precipitation of zinc is negligible.

2.4.3 Recovery of zinc from the lead-free leach solution by sodium sulfide

The zinc left in the leach solutions can be recovered quantitatively from the lead-free leach solution by adding sodium sulfide solid to the solution, when the weight ratio of sodium sulfide to the zinc present is kept at around 2.6—2.8.

2.4.4 Batch tests

(1) Removal of lead from leach solution by the addition of solid sodium sulfide

The results are shown in Table 6. It should be pointed out that less sodium sulfide, i.e., a weight ratio of sodium sulfide to the lead with 1.47 other than 1.8, was added to the leach solution. In this case, about 95% of lead was removed.

In addition, the possible chemical formula of lead precipitate of sulfide was proposed to be the mixture of lead sulfide and sodium hydro-lead sulfide, as there was certain content of sodium was detected in the precipitate.

Table 6 Removal and recovery of the lead from the direct leaching solution of the dust by the addition of sodium sulfide (M.W. = 222—240)

Composition of leaching solution, g/L	Zn 26.95 Pb 6.53
Leaching solution volume used, ml	2700
Sodium sulfide added, g	25.90 (M.W. = 222—240)
Sodium sulfide/Pb, w/w	1.47
Pb removal, %	94.50
Approximate molar ratio of the sulfide added to the lead removed	1.58—1.34
Lead sulfide obtained after washing and drying at 110℃, g	21
Content of Pb in the lead sulfide sample, %	79.58
Weight gain of the lead sulfide sample at 550℃, %	20.74
Content of Zn in the lead sulfide sample, %	1.05
Proposed chemical formula of the sample	PbS and $Na_2Pb(OH)_2S$

(2) Recover of zinc from lead-free leach solution by the addition of solid sodium sulfide

After the lead was removed, more sodium sulfide solid was added to such an extent that the weight ratio of sodium sulfide to the zinc present was from 2.46 to 2.62. It can be seen that the higher the ratios were used, the higher the precipitation percentages would be obtained (Table 7). The remaining zinc in the filtrate can be recycled to the next leaching step. The corresponding chemical formula of zinc precipitate was proposed to be the mixtures of ZnS, $Na_2Zn(OH)_2S$, and so on.

Table 7 Recovery of zinc from the Pb-free leaching solution by the addition of sodium sulfide (M.W. = 222—240)

Sample No.	1	2	3
Pb-free leaching solution, ml	1250 (from the direct leaching of dust)	300 (leaching solution of the melts)	600 (leaching solution of the melts)
Zn content in the leaching solutions, g/L	26.95	45.00	50.85
Sodium sulfide added, g	84.00	33.21	80.00
Sodium sulfide/Zn, w/w	2.49	2.46	2.62
Zinc sulfide obtained after washing and drying at 110℃, g	43.93	18.11	38.02
Zinc content in the zinc sulfide sample, %	72.18	71.45	74.52
Zinc recovery based on the zinc sulfide sample collected, %	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 gain, %	-4.22	-6.09	-3.73
Proposed chemical formula	ZnS $Na_2Zn(OH)_2S$	ZnS $Na_2Zn(OH)_2S$	ZnS $Na_2Zn(OH)_2S$

2.5 Discussions

It is well known that zinc ferrites are very difficult to be attacked by conventional alkaline and acidic leaching processes (Barrett, 1992). In this work, it may be proposed the proportion of zinc as zinc ferrites in the total zinc may be around 47%. Those zinc in zinc ferrites should be treated with other processes in order to recover the remaining zinc in the alkaline-treated residues. Such a process is being developed in our lab.

Most of the lead in dusts can be recovered in the alkaline leaching process. After lead and zinc is removed from the dusts, the resultant residues become non-toxic and non-harmful wastes, and can be filled into the common industrial landfills or dumped into the sea for the making of new land.

3 Conclusions

The zinc as zinc oxides and lead as lead oxide in the foundries dusts can be leached out with alkaline solutions. Lead can be removed selectively and quantitatively as the mixtures of lead sulfide and sodium lead sulfide from the leach solution when the weight ratios of sodium sulfide added to the lead present were kept at around 1.8. The content of lead in the sulfides is as high as about 80%, and may be possible to be used directly in the lead smelters for the production of metallic lead. The zinc in the lead-free solution can be further precipitated out and recovered quantitatively as mixtures of zinc sulfides and zinc hydroxide.

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