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Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium

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Abstract

In this study, a novel and integrated hydrometallurgical process for the production of zinc powder from electric arc furnace (EAF) dust in alkaline medium is reported. The dust is firstly hydrolysed in water, and then fused in caustic soda at 350°C for 1 h, followed by leaching in alkaline solution in which both zinc and lead are effectively extracted. Zinc powder is then produced by electrowinning from the leach solution after the lead is selectively removed by precipitation using sodium sulphide as precipitant. The EAF dust tested contained 25% Zn, 1.8% Pb and 33% Fe. It was found that 38% of zinc and 68% of lead could be extracted from the dust when leached directly in caustic soda solution. Leaching of zinc increased to 80% when dust was directly fused with caustic soda followed by alkaline leaching. However, the leaching further increased to 95% when the dust was hydrolysed first with water before fusion. Zinc powder with a purity of 99.95% was then produced by electrowinning from the lead by electrowinning from the lead solution. Stainless electrodes were used as both anode and cathode. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: EAF dust; Zinc; Lead; Solid wastes; Leaching; Fusion

1. Introduction

The metal industry is one of the large size industries of world-wide, including iron and steel foundries and mills, as well as brass and bronze foundries [1–5]. During the metal fusing process, the electric arc furnace (EAF) can reach temperatures of 1600°C

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or even higher, and many components of the charge, including iron, zinc, cadmium, and lead, are volatilised and entered the vapour phase. A large quantity of dust will be generated when the vapour is cooled and collected. The bulk waste generally is iron oxide. The fumes from a brass fusing furnace can have up to 65% or higher zinc. Zinc ferrite spinel accounts for 20–50 mass% of zinc in the dusts. The weight of dust collected in a typical EAF with carbon steel as charge for steel refining is about 10–15 kg for production of 1 ton of steel. Because of their metal leaching potential, these wastes are frequently classification [6]. Classification as hazardous wastes greatly increases the cost of disposal of dusts, due to the need for the treatment to render the wastes non-hazardous, as well as higher transportation and disposal costs and even increases the paperwork requirements.

So far most of these wastes are disposed in the industrial landfills. Since dusts and fumes have been classified as hazardous, conventional landfills should be modified in order to meet the need of environmental constraints required for hazardous materials.

Another treatment method for dusts is by dissolution in mineral acids. However, the composition of the dusts is very complex, which may include oxides of Zn, Pb, Al, Fe, Cu, Si, Cd, Mn, Mg, etc. When the wastes are digested in strong mineral acids such as hot hydrochloric acid, nitric acid and sulphuric acid, most of Zn, Pb, Al, Cu, and also Fe, etc. will be dissolved. In general, sulphuric acid is used, if zinc is recovered as electrolytic metal zinc in the later part of process [7–12]. This process has not been used widely in industries, mainly because the bulk materials in the dusts are the oxides of iron and the solubility of zinc ferrite is quite limited. Digestion of iron oxides in dusts also consumes a lot of acid and thus increases the treatment costs.

Considering that only oxides of Zn, Pb, and Al, and limited cases, Cr and Cu can be dissolved effectively in strong NaOH solution (the solubility of Cu and Cr oxides in alkaline solution are much lower than those of Zn, Pb and Al, especially when these oxides co-exist in wastes), it should be of great significance to use the alkaline processes to leach Zn, Pb selectively from the wastes and zinc oxides ores. In the 1970s, Amax Co. operated a pilot plant in New Jersey, USA, based on caustic leaching and purification of alkaline solutions by depletion of lead with zinc dust followed by electrowinning. This development was eventually abandoned due to a combination of technical and economic problems. A similar plant, based on direct caustic leaching was later built in France, but this also has been abandoned [12].

The objective of this study is to explore the technical and economic possibilities of increasing the leaching efficiencies of both zinc and lead from dusts in alkaline medium by using two-stage process, i.e. fusing with caustic soda and then leaching. The experimental results on laboratory-scale studies were reported in this paper.

2. Experimental

2.1. Chemicals used

All the chemicals used were of analytical grade, unless indicated otherwise.

Composition of the dust studied									
Elements	Zn	Fe	Pb	Mn	Ca	Al	Cd	Cu	Water
Wt.%	24.80	32.00	1.84	3.31	4.08	1.03	0.03	0.02	0.01

2.2. Characterisation of samples

Table 1

The sample of 5 g (dust or leaching residue) was digested in 30 ml of concentrated nitric acid, heated nearly to the boiling point (90°C) for 20 min, and then water added to dilute the acidity and continued the heating for another 60 min. A small portion of samples cannot be dissolved. The supernatant was analysed by ICP. The composition was shown in Table 1. The particles of dusts are very fine (<0.2 mm in diameter as determined), and no pre-treatment was conducted in the study.

2.3. Direct leaching of dusts

5 g of dust was added into a glass bottle containing 18 ml of 5 M NaOH solution, and then leached by rotating with an orbital shaker for 42 h (15 rpm). Filtered, analysed the filtrate and the residue by ICP if necessary.

2.4. Hydrolysis of dusts

A given ratio of dusts and water was stored in glass bottles, and mixed by an orbital shaker for a given time (15 rpm). Filtered, washed the cake by half amount of water using for the hydrolysis. Dried the hydrolysed dusts for the coming studies. It was found that the composition of dusts was kept unchanged after hydrolysis.

2.5. Fusion of dust and hydrolysed dust with caustic soda and leaching

To an alumina crucible added 1.5 g of dust or hydrolysed dust and a given quantity of NaOH pellets to make a designed dust/NaOH weight ratio, added 10–15 ml of water to make the mixture mix as thoroughly as possible, dried at 290°C for 20 min, and then fused at 350°C for 1 h, unless otherwise indicated. Leached the fused product with sufficient volume of 5 M NaOH solution by rotating for 42 h with an orbital shaker. The phase separation between leaching solution and residue may be realised by vacuum filtration or centrifugation, or just standing by for 1 day.

2.6. Separation of zinc and lead in the leach solution

To a given volume of leach solutions containing zinc and lead and other metal ions added a given quantity of sodium sulphide crystal or solution, mixed, stood by for hours, analysed the supernatant by ICP, calculated the precipitation and separation efficiencies.

2.7. Electrowinning

Stainless steel electrodes were used as both anode and cathode. The obtained zinc metal powder could easily be removed from the electrode by scrapping with simple tools and was washed thoroughly with water and then with ethanol. Finally, it was dried at 50° C, weighed and analysed.

2.8. Toxicity leaching test for leaching residue and titration of NaOH concentration

The toxicity leaching test was conducted according to the USEPA standard [6]. NaOH concentrations in aqueous solutions in each step were chemically titrated attempting to qualify the NaOH consumption. In most cases the data obtained are just for rough estimation because of the presence of silicates, hydroxides of iron, aluminium, and lead which interfere the end point of titration.

3. Results and discussions

Table 2

3.1. Direct alkaline leaching of dusts by NaOH solution

Leaching of zinc and lead from dusts in alkaline solutions is a function of leaching time, concentrations of alkaline solutions, phase ratios, and leaching temperature. The experimental results are shown in Figs. 1 and 2 and Table 2. It may take about 72 h for the leaching process to reach equilibrium. Nevertheless, after the dusts have contacted for over 42 h, the extraction of zinc and lead increases only slightly (Fig. 1). Therefore, a 42 h contacting time was used in the following experiments.

Leaching of zinc and lead increases with the increase of initial NaOH concentration up to 5 M in the leaching solution. Further increase of NaOH concentration has little effect on the leaching when it is higher than 5 M (Fig. 2). Hence, a 5 M NaOH solution was always used for the alkaline leaching of dust and hydrolysed dust in this study. Additionally, higher NaOH concentration in the leach solution will also increase the solution viscosity considerably, leading to rather difficult for phase separation and filtration between solid and liquid.

Sufficient volume of 5 M NaOH should be used for optimum extraction of zinc and lead from dust. Higher phase weight ratios of NaOH/dust (v/w) are favourable to the leaching. For zinc, a phase ratio (L/S) of 3 is enough to reach a maximum leaching and extraction, and for lead, an increase of phase ratio always improves the leaching, though only slightly when it is higher than 3 (Table 2). In practical application, a phase ratio of 3 to 4 may be used.

and lead from EAF dusts										
Phase ratios	1	2	3	4	5	6	8			
Zn extraction (%)	17.85	26.50	33.25	34.70	34.85	35.10	36.01			
Pb extraction (%)	37.55	44.21	57.30	58.92	60.85	64.25	65.23			

Relationship between the phase ratio (volume of NaOH (ml) to weight of dust (g)) and percent leaching of zinc and lead from EAF dusts

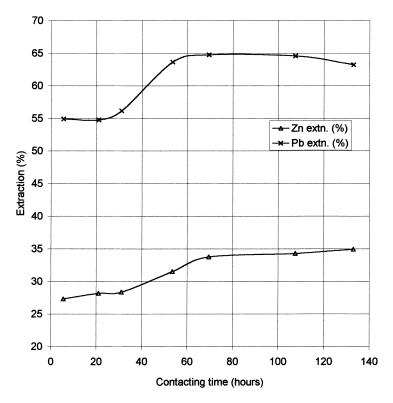


Fig. 1. Effect of leaching time on the extraction of Zn and Pb from dust by direct leaching process (dust 5 g, 5 M NaOH, 18 ml).

There was little improvement to be observed when the leaching of dust was conducted at higher temperature. All the experiments in this study were carried out at room temperature $(25^{\circ}C)$. Obviously, around 36% of zinc and 65% of lead can be leached from dust by direct leaching in NaOH solution at the optimum conditions.

3.2. Extraction of zinc from the dust by direct fusing with solid NaOH

Poor extraction of zinc from dust by direct alkaline leaching could be originated from the presence of zinc ferrites in the dust [8]. Hence, the leaching of zinc could be improved when zinc ferrites can be decomposed by special methods, e.g. by fusing with caustic soda, as explored in this study.

Destruction of zinc ferrites structure in a medium of NaOH depends on fusing temperature, weight ratios of NaOH/dust, and structure of ferrites. The experimental results are shown in Figs. 3 and 5. As shown in Fig. 3, leaching of zinc from dust increases with the increase of fusing temperature. Nevertheless, the curve of leaching and extraction of zinc from dust against temperature can be separated into three phases. The first phase ranges from room temperature to 200° C, and the third phase from 400° C and above. In the second phase with a temperature of $290-400^{\circ}$ C range, a temperature range around the fusing point

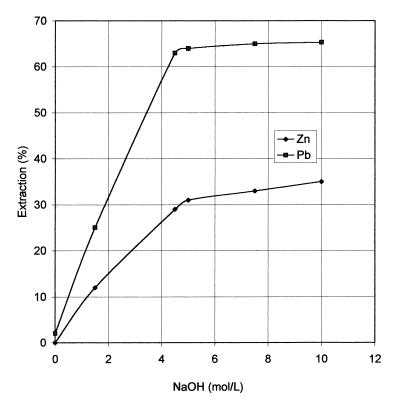


Fig. 2. Effect of NaOH concentration on the extraction of Zn and Pb from dust by direct leaching process (dust 5 g, L/S (v/w) 3.6, leaching time 42 h).

of NaOH (318°C), slight improvement of leaching is observed. Balancing the leaching efficiency and fusing temperature, a fusing temperature of 318°C or slightly higher was selected, as used in the following experiments.

Effect of fusing time on the extraction of zinc from dust is shown in Fig. 4. The extraction increases rapidly as fusing time extends for up to 1 h. Longer fusing time improves the extraction only slightly. Hence, 1 h of fusion is sufficient for a maximum extraction of zinc.

In addition, at least 24 h leaching is needed for a maximum extraction from the fused products (Fig. 5). In general, a leaching time of 42 h was used. Leaching efficiencies can be improved only slightly with increase of leaching temperature. Also, it should be pointed out that leaching efficiencies of lead decreases to around 30% when dusts are fused with NaOH, in comparison to about 65% when leached directly with NaOH solution (Fig. 5).

Weight ratios of dust to solid NaOH in the fused product also influences the leaching efficiency (Table 3). A weight ratio of 1.27 was used in this experiment. High weight ratios seem unreasonable for practical application in industry.

Hence, the leaching efficiencies of zinc increase to around 65% while those of lead decrease to around 30%, when the dusts are fused with solid NaOH at the fusing point of NaOH (318°C) for 1 h before alkaline leaching, in comparison to the facts that around 38% of zinc and 65% of lead can be extracted when leached directly with NaOH solution without fusion.

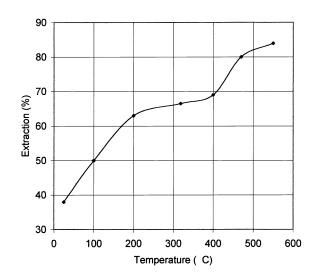


Fig. 3. Dependency of extraction of zinc from dust on fusing temperature by fusing with NaOH (dust 1.5 g, NaOH/dust (w/w) 1.27, fusing time 1 h).

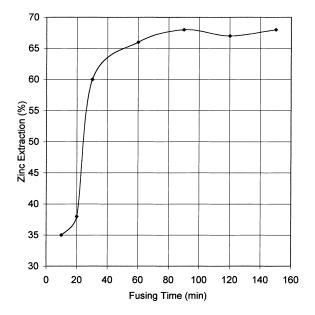


Fig. 4. Effect of fusing time on the extraction of zinc from dust by fusing at 318° C (dust 1.5 g, NaOH/dust (w/w) 1.27).

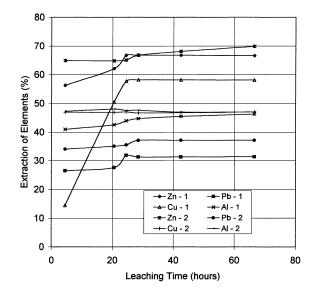


Fig. 5. Effect of leaching time on the extraction of elements from the fused product of dust (NaOH/dust 1.27, leaching temperature 1-25 and $2-70^{\circ}$ C).

Table 3 Effect of dust/NaOH weight ratios

Number	Dust/NaOH weight ratios	Zinc extraction (%)		
1	0.00	38.19		
2	0.38	43.98		
3	1.14	65.89		
4	1.27	67.88		
5	1.67	70.98		

3.3. Extraction of zinc from dust via hydrolysis-fusion-leaching process

In order to improve the leaching rate of zinc, several methods for preliminary treatment of dust were tested. It was found that the leaching of zinc increased greatly when the dust was contacted with water or dilute alkaline solution before fusing with caustic soda, as shown in Tables 4 and 6 and Figs. 6 and 8.

Table 4

Effect of water to dust ratios (v/w) leaching from the fused product of hydrolysed dust (dust 1.5 g, hydrolysis time 24 h) $\,$

Number	1	2	3	4	5
Water/dust ratios (v/w)	0.0	0.5	1.0	2.0	3.3
Zn extraction from the fused product of hydrolysed dust (%)	68.91	95.19	96.02	95.62	94.56

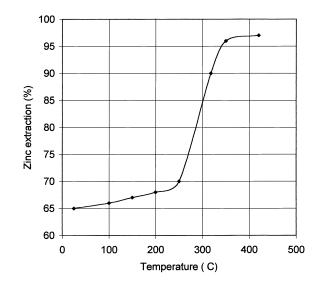


Fig. 6. Effect of fusing temperature on the extraction from hydrolysed dust (NaOH/dust (w/w) 1.1:1).

Table 5	
Effect of hydrolysis time on leaching from the fused product of hydrolysed dust (dust 6 g, water/dust 1:1)	

Number	1	2	3	4	5
Hydrolysis time for the dust (h)		9	23	28	48
Zn extraction from the fused product of hydrolysed dust (%)		93.09	95.23	94.33	94.89

3.3.1. Hydrolysis of dust

A water/dust weight ratio of 1:1with a hydrolysis time of at least 4 h should be utilised to obtain a maximum extraction effect (Tables 4 and 5). In addition, it was found that filter cake must be washed by fresh water after the hydrolysed dust was filtered (Table 6), in order to get a higher zinc extraction from the melts.

Most important steps affecting the extraction of zinc from dust are hydrolysis and fusion. Dust is formed in high temperature and its morphology may change when it is contacted with water. Such structure change facilitates the attack of NaOH to zinc ferrites and release of zinc. Fusion of zinc ferrites with NaOH further destroys the structure and makes the zinc in zinc ferrites extractable.

Table 6

A comparison of washing or non-washing of the cake resulting from the filtration of No. 1 in Table 5

Treatment ways for the cake	Washing with 3 ml fresh water	Non-washing
Zn extraction from the melts of hydrolysed dust (%)	95.01	83.98

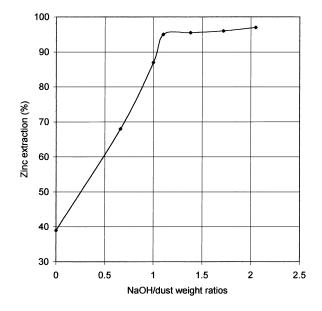


Fig. 7. Effect of NaOH/dust weight ratios on the extraction of zinc from hydrolysed dust by fusing at 350°C.

3.3.2. Fusion of hydrolysed dust with NaOH

From Fig. 6 it can be seen that the fraction of extraction of zinc increases slowly from ambient temperature to 250° C, and then increases rapidly from 250 to 350° C and then follows a platform from 350° C and above, quite different to those shown in Fig. 3. A fusing temperature of 350° C was used in which a maximum extraction can be obtained.

A NaOH/dust weight ratio of at least 1:1 (Fig. 7) and a leaching time of 42 h (Fig. 8) should be used in order to achieve the maximum extraction from the dust.

3.3.3. Effect of additives

NaF and Na₂HPO₄ were added to hydrolysed dust and then fused and leached. It was thought that the addition of these two chemicals may be favourable to the destruction of ferrites structure and reduction of fusion temperature required as the fusing point of Na₂HPO₄ is rather low. The results are shown in Table 7. It can be seen that the presence

Table 7 Effect of the addition of chemicals on the fusion and leaching of hydrolysed dust

Chemicals added	NaOH used (g)	Fusing temperature (°C)	Fusing time (h)	Zn extraction (%)
1.0 g NaF	1.0	350	1	72.71
2.0 g NaF	2.0	350	1	97.10
0.5 g Na ₂ HPO ₄	0	110	2	41.84
1.0 g Na ₂ HPO ₄	0	110	2	46.40
1.5 g Na ₂ HPO ₄	0	110	2	46.98
2.0 g Na ₂ HPO ₄	0	110	2	46.40
2.0 g Na ₂ HPO ₄	0.8	110	2	46.32
2.0 g Na ₂ HPO ₄	1.4	110	2	46.32

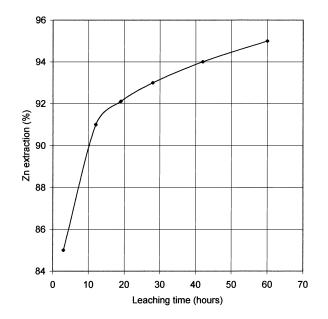


Fig. 8. Effect of leaching time on the extraction of zinc from hydrolysed dust by fusing at 350° C (NaOH/dust 1:1.1).

of both NaF and Na_2HPO_4 do not improve the extraction. In addition, NaOH cannot be substituted by the chemicals with lower fusing point such as Na_2HPO_4 .

3.3.4. Scale-up experiments

When 400 g rather than 1.5-5 g of dust samples as in the above laboratory experiments was used, similar extraction and leaching efficiencies were also obtained, concent as given in Table 8. It can be seen that the concentration of zinc in the filtrate can reach around 50 g/l.

Table 8

Scale-up experiment and counter-contact leaching of the melts (dust 400 g, NaOH 440 g, fusing at 350° C for 1 h, leaching for 42 h)

Leaching times	First leaching	Second leaching
Leaching agent	Fresh 5 M NaOH solution	Fresh 5 M NaOH solution
NaOH solution used (ml)	1120	950
Volume of the filtrate after leaching (ml)	1120	950
Volume of the cake after filtration (ml)	400	400
Filterability	Very difficult	Very difficult
Composition of the filtrate (g/l)	Zn 49.60, Pb 2.89, Fe 0.071,	Zn 14.01, Pb 0.49, Fe 0.028,
	Al 1.23, Cu 0.010, Mn 0.02,	Cu 0.010, Al 0.17, Mn 0.03,
	Cd 0.011	Cd 0.001
Total zinc extraction based on the composition of residue (%)	80.08	95.23
Total lead extraction based on the composition of residue (%)	66.67	74.44

After two sequential leaching, 94% of the zinc can be extracted from the fused product of dust with about 1% of zinc remained in the leaching residue.

Moreover, together with Zn and Pb, Al, Cu and Cr(III) may also be dissolved in strong alkaline solution, while Fe, Cd, Ca, Mg, remain in the leaching residue (Table 8). The experiments show that the solubility of these amphoteric elements in strong alkaline solution decreases in the following sequences.

Zn > Pb > Al > Cr(III) > Cu

The solubility of Cr(III) and Cu are found to be negligible in the presence of zinc and lead. Meanwhile, the solubility of lead in alkaline solution is also depressed greatly in the presence of zinc, especially when the content of zinc is relatively high. As a result, the extraction percentages and concentration in leach solution of lead become relatively low, as the zinc content in dust is much higher than that of lead, and the concentration of zinc in the leaching solution is thus much higher than that of lead.

In addition, the extraction of lead is also somewhat related to the treatment approaches by which the metals are leached. Lead (70–75%) in the dust can be extracted when the direct leaching process is used (Figs. 1 and 2). Nevertheless, slightly higher lead extraction (about 70–80%) is obtained when the dust is hydrolysed and fused at 350°C (Table 8). However, the leaching of lead decreases to 30–40% when the dust is directly fused with NaOH (Fig. 5).

From Table 8 it can be seen that the concentration of lead in leach solution is less than 3 g/l with a zinc concentration of 50 g/l. However, it may increase to over 9 g/l with a lower zinc concentration of 30 g/l (Figs. 1 and 3) when using direct leaching process. Obviously, under the conditions of Table 8, the saturation concentration of lead in leach solution seems to be around 3 g/l.

The extraction of Al from dust is about 65-75% regardless of the extraction approaches used. The typical concentration of Al in leach solution is around 1-1.5 g/l. Al is not a harmful element in the subsequent treatment of leach solutions (purification and electrolysis). Because Al cannot be removed together with lead when sodium sulphide is added to leach solution, it may be accumulated when the leach solutions are recycled after zinc is electrowon as zinc metal. In this case, part of Al should be removed in certain stage of recycling. The concentrations of other elements (Fe, Ca, Cu, Cd, Mn) in leach solutions are all lower than 0.5 g/l and can be reduced further to lower than 0.1 g/l after sodium sulphide is added to selectively remove lead.

In hydrometallurgy of zinc with sulphuric acid as leaching agent, the presence of Cd always exerts a lot of problems in the subsequent purification and electrolysis steps for leach solutions. However, the Cd concentration in alkaline leach solution is found to be negligible (<0.01 g/l).

3.3.5. Typical composition of leaching residue

After zinc was extracted as completely as possible, the leaching residue was washed with 5% NaOH solution and then with water, followed by drying the cake at 110°C. Table 9 shows the analysis results of the resultant cake (residue). It can be seen that zinc and lead contents have been reduced from the original around 25 and 1.8% to lower than 1 and

Table 9
Typical composition of the leaching residue of the fused product of hydrolysed dust (nitric acid digestion method)

Elements	Zn	Pb	Fe	Cu	Al	Mn	Cd
Contents (%)	0.59–1.00	0.20-0.50	34.30-37.01	0.15-0.28	0.21-0.28	1.23–1.94	0.054-0.088

0.5%, respectively. The other heavy metals such as Cd and Cu also exist at a very low level in the residues. Such residue may be used to make bricks, or to use as materials for road construction or as stock feed for steel making plants, or just to be placed in landfill if available, depending on the heavy metals contents and economic and technical feasibility study case by case.

3.4. Selective separation of lead from leach solution

Lead should be removed from leaching solution before zinc is electrowon. Several methods can be used for lead removal from acidic solution. However, the methods available for selective separation of lead from zinc in alkaline solution are limited. Our previous experiments show that addition of zinc powder leads only to partial removal of lead (20%) in alkaline solution. In this study, sodium sulphide was used as precipitant and the experimental results are shown in Fig. 9. It can be seen that lead can be removed quantitatively when the weight ratio of sodium sulphide/Pb in leach solution is slightly higher than 1.9.

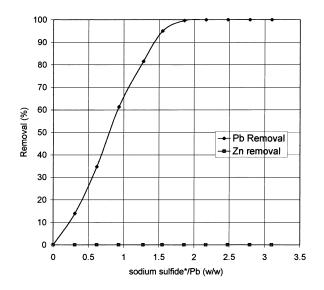


Fig. 9. Removal of lead from the leaching solution of hydrolysed dust melt by the addition of sodium sulphide (MW = 204-240) (leaching solution: Zn 45.60 g/l, Pb 3.60 g/l, Fe 0.06 g/l, Al 1.14 g/l, Cu 0.06 g/l, Cd 0.04 g/l).

Zn (g/l)	NaOH (M)	Electrode	Voltage (V)	Current density (A/m ²)	Specific energy consumption (kWh/kg Zn)	Zinc metal purity (%)
24–30	5	Stainless steel	2.4–2.7	700–1100	2.5-2.6	99.0–99.9

Typical electrowinning conditions for production of zinc from lead-free leach solution

3.5. Eletrowinning of zinc powder from depleted leach solution

Much work has been done on the electrolysis of zinc from alkaline solution. It has been shown that electrolysis of zinc from alkaline media is cost-effective [13–15]. In this study, the electrolysis process was tested, as the leach solution used was more complex than that obtained by the dissolution of zinc oxide in NaOH solution as reported in literature [14]. Experimental results are shown in Table 10. The electricity consumed for production of 1 kg of metallic zinc from the alkaline leach solution is 2.4-2.7 kWh, while that from acidic solution is 3.3-3.4 kWh. Hence around 20% of energy can be saved for electrowinning from alkaline medium.

The zinc metal deposited on the cathode was grey with a slightly bright metallic lustre. It can be removed easily from the cathode by scraping the metal by simple tools such as glass rod and small stainless knife.

4. Discussion

Table 10

The wetting of fused product by both water and alkaline solution was found to be very slow. In order to accelerate the wetting and dispersing of fused products in NaOH solution, the hot fused matter can be inserted into NaOH solution after it was taken out of the furnace. It cannot be pulped completely in a quench, and should be heated for a while or just stood by for hours to days depending on the scale of the fused matter.

In another test, the original and hydrolysed dust were directly leached at 121°C in a pressurised steam cylinder. The extraction of zinc was found to be very low, with an extraction of 38% from dust and 36% from the hydrolysed dust. Hence it is impossible to decompose the stable ferrite structure by pressure leaching.

Electrowinning of zinc from alkaline and acidic solutions was compared and found that the quality of zinc powder from alkaline solution is much more stable than that from acidic solution. Perhaps heavier corrosion of containers in alkaline medium might occur. According to our research, however, it is not a problem. Cheap and commercial availability of Cr steel is an excellent material for both containers and electrodes used in alkaline medium.

The content of Si in dust was estimated to be in 1–5% range. Part of silica may fuse with caustic soda and dissolve in solution, which will consume some NaOH. Sodium silicate cannot be removed in the whole process and may accumulate. Hence, sodium silicate should be separated during alkaline solution is recycled.

The Cd in the leaching residues is a major heavy metal that considerably increases the treatment costs. Cd content in the original dust is very low, and may be disposed of more easily when the dust is treated by alkaline fusion and leaching.

Table 11	
Comparison of alkaline treatment of dust and acidic treatment of zinc sulphide ores	

Items	Alkaline treatment of dust to produce zinc powder	Acidic treatment of sulphide ores to produce zinc powder		
Energy required	Fusing and electrowinning	Roasting and electrowinning		
Energy for eletrowinning (kWh/kg Zn)	2.5	3.3		
Purification of leaching solution	Simple	Complex		
Accumulation of silicate	Yes	No		
Chemical consumption	Caustic soda	Mineral acids (sulphuric acid)		

One concern is the cost-effectiveness of this process. This depends on the zinc price in world market. It may be reasonable to compare the process developed in this study with hydrometallurgical process of zinc using sulphide ores (Table 11). Energy needed includes fusing and electrownning for dust treatment, and roasting and electrowinning for sulphides. Around 20% of energy for electrownning in alkaline solution is reduced in comparison to acidic solution. From the viewpoints of environmental protection, dust is a hazardous waste that should be treated properly. Extra payment may be received from dust generators. After treatment by alkaline process, the resultant residues may be less hazardous and can be further treated at a much lower cost. Nevertheless, heavy pollution arises when sulphide is roasted in kiln. Bulky components in the roasted product are oxides of Fe, Al, Si, Cd, Pd, etc. which will dissolve in acidic solution together with zinc and a large quantity of extra acid will be consumed. Subsequent complex purification process should be used for the leaching solution to remove impurities.

The dust tested contained 25% zinc and 1.8% lead, and 90 and 80% of zinc and lead can be extracted from dust by using hydrolysis-fusing-leaching process. Hence, 200 kg of metallic zinc and 15 kg of lead (as lead sulphide) can be produced from 1000 kg of dust. The cost balance for NaOH is given in Table 12. Most NaOH loss occurs in the fusion step. NaOH concentration in leach solutions before and after lead separation, electrowinning, etc. were determined based on laboratory bench scale tests. Around 10% of NaOH will be lost in the steps of fusion and leaching of the fused product.

The cost used for fusion depends on the form of energy. It may be quite high by using electricity, and relatively low by coal. In addition, the NaOH used for fusion is dissolved in leaching solution, and should be recovered as solid state after lead separation and electrowinning. A lot of energy will be consumed for evaporation in this step. The exact data

Table 12

NaOH mass	balances	in l	nvdrol	vsis-	fusing-	leaching	process
1 tuon muoo	oundiecos		i j ui oi	<i>y</i> 010	rability	reacting	process

Dusts treated	1000 kg
Extractable zinc	250 kg (3827.3 mol)
Extractable lead	18 kg (86.9 mol)
NaOH required for the fusion of hydrolysed dust	1100 kg
NaOH required for leaching of the fused products	26661, 5 M (533 kg)
NaOH loss in the fusion and first leaching	$10\% \times (533 + 1100) = 163 \mathrm{kg}$
Cost of NaOH loss	$163 \text{ kg} \times 310 \text{ US}/\text{ton} = 50 \text{ US}$

may be estimated from a pilot test. It is roughly estimated that around 500–600 US\$ will be needed for production of 1 ton of metallic zinc with a purity of 99.9% from dust, including NaOH loss, energy consumption for fusion and NaOH recovery, electrowinning, capital investment, etc.

Chemical reactions in the fusion and leaching processes may be summarised as follows. It is proposed according to the following data based on 1000 kg of dusts are treated. Zinc (53%) exists as ZnO and 47% of zinc as Zn(FeO₂)₂ (as determined), in which 100% of ZnO (132.5 kg Zn as ZnO) and 95% of zinc ferrites (105 kg Zn as Zn(FeO₂)₂, i.e. 1607 mol) are extractable.

The consumption (loss) of NaOH in the fusion and leaching processes is 163 kg (4075 mol), in which the loss in leaching step is negligible. Thus the molar ratios of NaOH consumed to the zinc ferrites extracted in the fusing step is 4075/1607 = 2.5. Therefore, the following reactions may be proposed in the fusion and leaching processes.

• Leaching of ZnO

 $ZnO(s, in dust) + 2NaOH(aq.) + H_2O(l) = Na_2Zn(OH)_4(aq.)$

• Leaching of PbO

$$PbO(s, in dust) + 2NaOH(aq.) + H_2O(l) = Na_2Pb(OH)_4(aq.)$$

This reaction will be taken place at ambient temperature.

Fusion

$$\begin{split} &Zn(FeO_2)_2 \ (s, \ in \ dust) + 8NaOH \ (s) = Na_2ZnO_2 \ (s) + 2Na_3FeO_3 \ (s) + 4H_2O \\ &ZnO \ (s, \ in \ dust) + 2NaOH \ (s) = Na_2ZnO_2 \ (s) + H_2O \\ &PbO \ (s, \ in \ dust) + 2NaOH \ (s) = Na_2PbO_2 \ (s) + H_2O \\ &SiO_2 \ (s, \ in \ dust) + 2NaOH \ (s) = Na_2SiO_3 \ (s) + H_2O \end{split}$$

• Leaching of fused products

$$Na_2ZnO_2 (s) + 2Na_3FeO_3 (s) + 5H_2O = Na_2Zn(OH)_4 (aq.)$$

+2Fe(OH)₃ (s) + 6NaOH

 $Na_2PbO_2(s) + 2H_2O = Na_2Pb(OH)_4(aq.)$

$$Na_2SiO_3 (s) + H_2O = Na_2SiO_3 (aq.) + H_2O$$

• Overall reactions in the fusion and leaching processes

$$ZnO (s, in dust) + Zn(FeO_2)_2 (s, in dust) + PbO (s) + 6NaOH (s) + 6H_2O$$
$$= 2Na_2Zn(OH)_4 (aq.) + 2Fe(OH)_3 + Na_2Pb(OH)_4 (aq.)$$

• For zinc ferrites alone

$$Zn(FeO_2)_2 (s, in dust) + 2NaOH (s) + 4H_2O = Na_2Zn(OH)_4 (aq.) + 2Fe(OH)_3$$

That is the molar ratio of NaOH needed to the zinc ferrites reacted should be 2:1. Nevertheless, the estimated value is 2.5 as mentioned above. Some NaOH may be consumed in the formation of sodium silicates and iron hydroxides. It is sure that 163 kg of NaOH will be lost as long as the dust is treated by fusion followed by leaching.

Chemical reactions taking place in the sulphide precipitation processes are also proposed. The molar ratios of Pb/S in the lead sulphides is around 1.5. Therefore the components of the sulphides may be very complex. The following reactions may be proposed.

$$x \operatorname{Na_2Pb}(OH)_4 (aq.) + y \operatorname{Na_2S} (s)$$

$$\rightarrow n \operatorname{PbS}_y (s) + b \operatorname{Na_2Pb}(OH)_m \operatorname{S}_{(4-m)/2} (s) + k \operatorname{Pb}(OH)_2 (s) + p \operatorname{NaOH} (aq.)$$

5. Conclusions

Various methods for extraction of zinc from an EAF dust were tested. Zinc (95%) can be leached when dust was hydrolysed in water and then fused with caustic soda at 350° C, compared with 65% of zinc leached when dust was fused directly without previous hydrolysis. Only 38% of zinc can be leached by direct contact the dust with caustic soda solution. In saturation leach solutions, zinc, lead, and Al concentrations can reach 50, 3, and 1.2 g/l, respectively. The concentrations of other elements such as Fe, Cu, and Cd in the solutions were lower than 0.5, 0.4, and 0.1 g/l, respectively. Zinc can be electrowon directly from lead depleted alkaline solution by stainless steel electrodes after lead was removed by precipitation using sodium sulphide as precipitant. The resultant leaching residue contains lower than 1% of zinc, 0.5% of lead, 0.3% of copper, and 0.1% of cadmium, and over 35% of Fe.

References

- S.W.K. Morgan, Zinc and its Alloys, Industrial Metal Series, Macdonald & Evans, Estover, Plymounth, PL 12 7PZ, UK, 1977, pp. 88–112.
- [2] C.B. Gill, Nonferrous Extractive Metallurgy, Wiley, New York, 1981, pp. 18–279.
- [3] C.S. Brooks, Metals Recovery from Industrial Waste, Lewis Publishers, Michigan, USA, 1991, pp. 33-141.
- [4] M.J. Collie (Ed.), Extractive Metallurgy, Development Since 1980, Noyes Deta Cooperation, Park Ridge, New Jersey, USA, 1984, pp. 118–153.
- [5] S.R. Swarnkar, B.L. Gupta, R.D. Sekharan, Iron control in zinc plant residue leach solution, Hydrometallurgy 42 (1996) 21–26.
- [6] R. Stanforth, Method for reduction of heavy metal leaching from hazardous waste under acidic and nonacidic conditions, US Patent No. 5,037,479, August 1991.
- [7] E.C. Barrett, E.H. Nenniger, J. Dziewinski, A hydrometallurgical process to treat carbon steel electric arc furnace dust, Hydrometallurgy 30 (1992) 59–68.
- [8] F. Elgersma, G.F. Kamst, G.J. Witkamp, G.M. Van Rosmalen, Acidic dissolution of zinc ferrite, Hydrometallurgy 29 (1992) 173–189.
- [9] R.B. Tippin, R.L. Tate, Metal reclamation and detoxification of brass foundry waste sand, in: Proceedings of the 93rd Annual Meeting on American Foundrymen's Society Transactions, USA, Vol. 97, 7–11 May, 1989, pp. 513–520.
- [10] P. Edger, V.W. Grus, Removal of zinc and lead from iron and steel wastes via chlorine pyrohydrolysis, in: A. Takeshi (Ed.), Zinc Lead 95, Proceedings of the International Symposium on Extraction and Application, Zinc Lead, Tokyo, 1995, pp. 457–471.

- [11] J.R. Donald, C.A. Pickles, Kinetics of the reduction of the zinc oxide in zinc ferrite with iron, in: P.B. Queuneau, R.D. Peterson (Eds.), Proceedings of the 3rd International Symposium on Recycle Materials and Engineering Materials, Minerals, Metals & Materials Society, Warrendale, PA, USA, 1995, pp. 603–621.
- [12] J. Frenay, S. Ferlay, J. Hissel, Zinc and lead recovery from EAF dusts by caustic soda process, in: Electric Furnace Proceedings, Treatment Options for Carbon Steel Electric Arc Furnace Dust, Vol. 43, Iron Steel Society, 1986, pp. 171–175.
- [13] J. St. Pierre, M. Sider, D.L. Piron, Zinc electrowinning from alkaline and acidic chloride solutions, Zinc'85: in: Proceedings of International Symposium on Extractive Metallurgy of Zinc, Tokyo, Japan, 1985, pp. 297–311.
- [14] J. St. Pierre, D.L. Piron, Electrowinning of zinc from alkaline solutions at high current densities, J. Appl. Electrochem. 20 (1) (1990) 163–165.
- [15] J. St. Pierre, D.L. Piron, Electrownning of zinc from alkaline solution, J. Appl. Electrochem. 16 (1986) 447–456.