



# Chemical stabilization of MSW incinerator fly ashes

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## Abstract

In this work, the relationship between heavy metal content of fly ash and that of the solid wastes incinerated was correlated and compared. It is found that the former is a function of the latter. Hence, it is important to prevent heavy metal-rich wastes from being incinerated in order to reduce the content of toxic metals in the fly ash. The leachability of fly ash from incineration was usually beyond the scope of toxicity standard and must be properly treated before discharge. Secondly, chemical stabilization for the heavy metals in fly ash was explored. Among the chemicals used, it was found that sodium hydroxide was not suitable for the adequate extraction of the heavy metals from the fly ash. Ethylenediaminetetraacetic acid disodium salt (EDTA) was also tested and seems to be effective for the leaching of toxic metals from the fly ash. On the other hand, sodium sulfide and thiourea are one of excellent chemicals for the effective treatment of fly ashes, since they convert soluble and leachable toxic metals into non-leachable and insoluble forms such as lead and zinc sulfide or their similar forms of thiourea. These chemical species are supposed to be stable in nature. A comparison between chemical stabilization noted above and cement or asphalt solidification methods is made. Chemical stabilization processes, especially using sodium sulfide as the chemical agent, are strongly recommended for the practical uses, in terms of the volume expansion and environmental safety of the stabilized products and cost balances, in comparison with the traditional cement or asphalt solidification methods.

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## 1. Introduction

Municipal solid wastes (MSW) incineration is one of means of disposing of incineration waste generated by municipalities. It was adopted in Europe fairly early (first attempts were

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made over 100 years ago) in order to recover energy and to reduce the volume of the waste [1,2]. Compared with landfills, MSW incineration is certainly more expensive, however, its future cost will be lower, since landfills will pose environmental threats for decades. The main concerns for MSW incineration are the emission of toxic flue gas to the atmosphere and the release of harmful substances of the incineration residues, especially fly ash and bottom ash (slag).

The flue gas impurities can be grouped into four categories: (1) acidic gases such as HCl, HF, SO<sub>2</sub>, HBr, NO<sub>x</sub>; (2) products of incomplete combustion (hydrocarbon, CO, dioxins and furans); (3) dust with heavy metals; (4) volatile heavy metals. These impurities are mainly a result of the composition of the wastes being incinerated. Only few impurities are created by the incineration process itself or by the interaction between different impurities. These impurities may be from multiple sources. For example, Hg may come from thermometers, electronic components, batteries, and Cd from paints, batteries, stabilizers and softeners. Generally, the presence of used batteries, paints, electronic products, diapers, and plastics, in the wastes greatly contributes to the toxicity of flue gas and ashes. Preliminary sorting and separation of these specific wastes containing high contents of heavy metals will reduce the contents of heavy metals in the ashes [3–6].

Emission control legislation has been posed in nearly every country. However, the emission limits vary from country to country, depending on economic development level. According to the legislation in the most countries, 99% of HCl and HF, 90% of SO<sub>2</sub> and Hg, 95% Cd and dioxins, 85% NO<sub>x</sub>, and 99.8% particulate should be removed from the flue gas from MSW incinerators. The dust (particulate) removal can be realized by dry or wet dust removal technologies. The dry removal technologies include the electrostatic precipitator and the fabric filter (bag house). Both technologies are very efficient. The fabric filter, however, is limited by a relatively low operating temperature, the electrostatic precipitator has relatively high investment costs. The wet dust removal includes Venturi scrubbers and wet electrostatic precipitators. Venturi scrubbers are quite efficient for particle removal and have low investment costs but they have a high pressure drop. The wet electrostatic precipitators, on the other hand, are very efficient especially for the fine particulates but they are quite expensive. Most of the heavy metals can be captured as solids by dust removal technologies. Volatile heavy metals (Hg, As, Ti) are trapped in wet scrubbers or in reactors with active carbon [1].

Typically, 20–50 kg filter (fly) ash collected by the filters and 100–250 kg slag, will be generated from the incineration of 1000 kg of MSW, after the bulk metals are removed manually or magnetically. In the fly ash, 3.3–5.9 Zn, 1.2–2.4 Cu, 1.8–2.4 Pb, 0.6–1.1 Cr, 0.1–3 Ni, 0.022–0.06 Cd and 0.00003 Hg (all in g/kg) may contain in the slag, and much higher contents in the fly ash. From the point of view of toxicity, the fly ash is the most harmful component because of its high content of leachable heavy metals. According to the existing legislation of most countries, the slag may be directly disposed of in landfills without solidification or other treatment.

Fly ash can be treated in several different ways. The traditional method, such as direct disposal, has been prohibited. The most frequent means of fly ash disposal used include: (1) placement in a well-designed landfill, (2) immobilization through solidification (cement) and then landfill or reuse or vitrification, (3) separation of heavy metals by volatilization at high temperature or hydrometallurgical extraction by dissolution in acidic or alkaline medium [7–12].

The placement of fly ash in a landfill developed for this material will result an irreversible effect on the environment, as the heavy metals in the ash will never disappear [13]. Moreover, the cost for such a disposal method is unacceptably high in many cases. Immobilization using cement and other solidification agents often yields relatively low stabilization efficiency according to its long-term leachability tests [8,14–16]. The capability of cement matrix to capture and stabilize the heavy metals is limited and the resultant compound may deteriorate after long-term storage in the landfill or recycled use such as road pavement materials upon stabilization [17,18]. Moreover, the volume of the solidified products usually increases considerably, leading to an increase in the cost of disposal.

Modifications have been used to increase the long-term stabilization of the cement method. Three principally different cement solidification technologies exist: (1) solidification of unwashed (original) fly ash, (2) solidification after neutral/basic washing, and (3) solidification after acid washing. The first method result in a residue with high chlorine and high heavy metals contents. Consequently, a large amount of expensive high quality cement with good hydraulic properties is used. In the second technology, the soluble heavy metals chlorides are transformed to heavy metals hydroxides, which precipitate. After filtration and solidification with a low amount of cement, this process yields a residue with low chlorine content but having high heavy metals [1]. However, the heavy metals will continuously be released, though slowly, in a wet environment, as shown in this work. Most heavy metals may be removed if the fly ash is washed in an acidic medium. This process is actually a hydrometallurgical process as most of the metals may dissolve in the acidic solution. The post-solidification treatment for the resultant residue seems unnecessary.

Evaporation or vitrification of heavy metals in the fly ash at a high temperature has obvious shortcomings due to an extremely high-energy consumption and high investment in equipment. This process is not cost-effective for a small and medium scale incinerators [19–23].

The objectives of this work were to develop a cost-effective stabilization process for fly ash by chemical immobilization. Sodium sulfide, thiourea, sodium hydroxide, and ethylenediaminetetraacetic acid, were used. The solidification effects of these chemical agents were also compared with those of cement and asphalt. A combination of chemical stabilization and cement or asphalt solidification for fly ash is proposed. It is expected that such a combination would enhance the encapsulation of the heavy metal in the stabilized products so that the risk for environmental pollution may be reduced.

## 2. Experimental

### 2.1. Fly ash sampling

There are several MSW incineration plants in China, of various sizes ranging from 50 to 1000 t per day [24]. The fly and bottom ashes used in this work were taken from Changzhou MSW Incineration Plant, which is 150 km from Shanghai. The fly ash is collected by a bag house at the plant. Table 1 shows the elemental composition of the fly ashes. The solid samples were firstly dissolved in concentrated nitric acid solution while heating and then analyzed with ionization coupled plasma (ICP) or atomic emission spectrophotometer (AES). Over 99.5% of samples can dissolve in the acid solution.

Table 1  
Composition of the fly ashes used in this research as obtained from Changzhou incinerator bag house (mg/kg)

	Hg	Zn	Cu	Pb	Cd	Ni	Cr	Fe
Sample I	49	4382	296	1480	24.6	60.1	115	25742
Sample II	55	4389	330	1512	26.4	61.5	121	25812
Average	52	4386	313	1496	25.5	60.8	118	25777

## 2.2. Toxicity test

The toxicity of the fly ash samples was determined using the China leachability toxicity standard method as described below. To 100 g of the samples, adds 900 ml of water, adjusts the pH using NaOH or sulfuric acid to a range of 5.8–6.3, and then dilutes to 1000 ml. The pH value in the leaching solution must be kept in this range. If the pH deviates outside this range NaOH or sulfuric acid solutions should be added during the leaching operation. The sample is leached by rotating in a mechanical shaker with an oscillating frequency of  $110 \pm 10 \text{ min}^{-1}$  for 8 h at 25 °C. The sample is allowed to settle for 16 h and filtered. The supernatant is analyzed using by ICP or AES.

## 2.3. Chemical treatment of fly ash by NaOH and EDTA solutions

To 10 containers containing 10 g of the fly ash sample, add 100 ml of 0.1, 0.5, 1, 2 and 5 mol/l of NaOH solution, or 100 ml of EDTA solutions with 0.01, 0.02, 0.05, 0.1 and 0.2 mol/l, to each container, respectively, stirred on an oscillator with a frequency of  $110 \pm 10 \text{ min}^{-1}$  for 8 h at 25 °C, and then allowed to settle for 16 h. The supernatant was filtered, and analyzed. The resultant leaching residue was dissolved in nitric acid solution, and then the heavy metal contents of Zn, Pb and Cd were determined with ICP.

## 2.4. Chemical stabilization of fly ash by sodium sulfide and thiourea

To 12 containers containing 10 g of the fly ash, add 0.1795, 0.5, 1, 2, 4 and 6 g  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , and 100 ml water, or add 0.1795, 0.5, 1, 2, 4 and 6 g thiourea and 100 ml water, to each container, respectively. Leached for 8 h at 25 °C on an oscillator with a frequency of  $110 \pm 10 \text{ min}^{-1}$ , allowed to settle for 16 h and then filtered. Pb and Cd in the supernatant are determined by ICP.

The solidification and stabilization methods for the fly ash by the binders used as well as preliminary treatment and leaching procedures for the solidified/stabilized products obtained are described in the following sections. The experiments were carried out in duplicate for the solidification and stabilization procedures, and in triplicate for pH tests on the leachability of fly ash and solidified and stabilized products. In general, the agreement of results for the repeated experiments was found to be excellent, with <1–2% difference in two parallel tests.

### 3. Results

#### 3.1. Comparison of the elemental composition in the fly ash and the MSW incinerated

Table 2 provides a statistical comparison of the concentration of elements from MSW in Switzerland [19] and China [24]. From Tables 1 and 2, it can be seen that the concentration of elements in the fly ash and MSW from China and Switzerland roughly decreased in the following sequence: Hg < Cd < Ni < Cr < Cu < Pb < Zn < Fe. Therefore, one can conclude that the contents of toxic heavy metals in the fly ash are directly related to those found in the MSW incinerated.

Moreover, the elemental contents of the fly ashes are also closely related to the melting and boiling points of the elements (metals or compounds) concerned (Table 3). In general, the lower the melting and boiling points for either elements or compounds (oxides, sulfates, and chlorides), the higher contents for the corresponding elements in the fly ash.

Fig. 1 shows the boiling and melting points of metals of interest and their compounds. The temperature ranges of incineration in Changzhou MSW Incinerator are also shown as being between the two dotted lines on the figure. Metals of Ni, Cr and Fe, oxides of Zn, Ni, Cr, and Fe, would be relatively less volatilized, as the melting points of oxide and the metals are above the incineration temperature range. However, the melting points of all the chlorides and most sulfates, and metallic Hg, Zn, Cu, Pb and Cd, fall in or below this range, which implies that these substances would be more volatile under the incineration conditions.

Table 2  
Typical elemental contents in the MSW generated in China and Switzerland

Element	Concentration (g/kg)	
	China	Switzerland
C	29 ± 5	37 ± 4
S	–	1.3 ± 0.2
P	0.65 ± 0.10	0.73 ± 0.16
Cl	–	6.9 ± 1.0
K	2.1 ± 0.21	2.5 ± 0.4
Na	–	5.7 ± 1.4
Ca	–	27 ± 5
Si	–	39 ± 8
Mn	–	–
Fe	25 ± 3	29 ± 5
Co	–	–
Ni	–	–
Cu	–	0.7 ± 0.2
Zn	1.3 ± 0.2	1.4 ± 0.2
Al	–	11 ± 2
Be	–	–
Pb	–	0.7 ± 0.1
Hg	0.005 ± 0.001	0.003 ± 0.001
Cr	0.18 ± 0.02	–
Cd	0.3 ± 0.1	0.011 ± 0.002
As	0.03 ± 0.01	–

Table 3  
Physical properties of metals and their compounds

Metals	Melting point (°C)	Boiling point (°C)	Oxides (°C)	Chlorides (°C)	Sulfates (°C)
Hg	-39	357	Decomposable above 400	m.p. 275, b.p. 301	Decomposable at the m.p.
Zn	419	907	Volatilization at 1800	m.p. 283, sublimation under calcination	Decomposable under calcination
Cu	1083	2595	m.p. 1026	m.p. 620, decomposable at 993	Decomposable at 560
Pb	327	1744	m.p. 886, b.p. 1516	m.p. 501, b.p. 950	m.p. 1170
Cd	321	767	Sublimation at 900	m.p. 570, b.p. 960	m.p. 1000
Ni	1555	2837	m.p. 1980	m.p. 1001	m.p. 99
Cr	1900	2480	m.p. 2435, b.p. 3000	m.p. 83	Decomposable at high temperature
Fe	1535	3000	m.p. 1377, Decomposable at 3410	m.p. 282, b.p. 316	Decomposable at high temperature

Hence, it may be hypothesized that the heavy metals in the fly ash may originate from the volatilization of chlorides and sulfates of Zn, Ni, Cr and Fe, and chlorides, sulfate and oxides for the other metals, and metallic elements of Hg, Zn, Cu, Pb and Cd. Moreover, the metallic forms may be oxidized into oxides in the incineration process and then volatilized in the flue gas, as confirmed in the following leachability tests.

### 3.2. Leachability of the fly ash

Table 4 shows the leachability toxicity of the fly ash determined using the China TCLP standard, as described previously. It can be seen from Table 4 that 49% Cd, 16% Pb, 13%

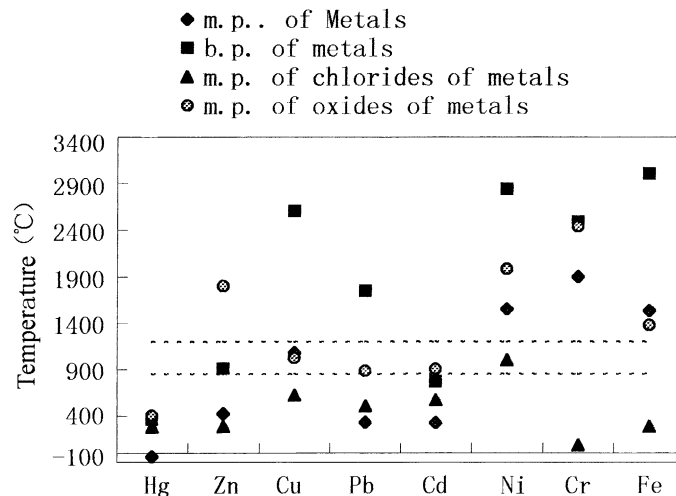


Fig. 1. Melting and boiling points of the metals of interest and their compounds.

Table 4  
Leachability toxicity of the fly ash (mg/l)

Metals	Concentrations in the leach solution			Leachability (%)	China toxicity standards
	First analysis	Second analysis	Average		
Hg	0.0346	0.0309	0.03275	0.6	0.05
Zn	56.66	57.80	57.23	13.05	50
Cu	0.71771	0.70567	0.71169	2.27	50
Pb	23.96	25.15	24.56	16.42	3.0
Ni	0.30101	0.38794	0.34448	5.67	25
Cd	1.2057	1.3145	1.2601	49.42	0.3
Cr	0.13881	0.13575	0.13683	1.16	1.5

Zn, 6% Ni, and few other metals can be leached from the ash. Because of the high solubility of chlorides and sulfates of Zn, Cu and Ni, these elements should be present predominantly as insoluble oxides in the fly ash. Nevertheless, as described above, the volatilization of oxides of these metals is poor. This finally implies that the oxides in the fly ash should originate from the chemical reactions taking place during the incineration process, including decomposition of sulfates and chlorides. However, it is somewhat difficult to reach such a conclusion for Hg, Pb, and Cr, as the solubility of their salts is markedly lower and as a result the leachability would also be lower. Hence, the leachability toxicity of the fly ash may be reduced if the heavy metals could be transformed into oxides.

### 3.3. Effect of pH on the leachability of the fly ash

The results are presented in Table 5. Increases in pH in the leaching solution will lead to a decrease of leachability of the heavy metals in the fly ash because insoluble hydroxides will form at higher pH.

### 3.4. Solidification of fly ash using cement and asphalt

For a comparison, both traditional solidification methods using cement and asphalt, as well as the latest methods using chemicals were studied. For cement and asphalt solidification methods, two types of ordinary portland cements, denoted as nos. 425 and 325 according

Table 5  
Effect of pH values on the leachability of heavy metals from the fly ash (mg/l in the leaching solutions)

Metals	pH = 1.5	pH = 3.0	pH = 4.5	pH = 6.0	pH = 7.5	pH = 9.0
Zn	94.45	88.56	75.43	57.23	28.64	18.65
Cu	2.2416	1.9567	1.3954	0.71171	0.50362	0.17363
Pb	45.37	42.36	38.75	24.56	8.3217	2.3451
Ni	0.95461	0.81150	0.60310	0.34448	0.23151	0.10321
Cd	2.3459	2.0147	1.7956	1.2601	0.84530	0.54281
Cr	0.22431	0.21242	0.15463	0.13683	0.062354	0.024235

Table 6  
Leachability of the solidified products using different quality of cement and asphalt (mg/l in the leaching solution)

	Sample no.				
	1	2	3	4	5
	3:1 (1200:400) <sup>a</sup>	2:1 (1000:500) <sup>a</sup>	1:1 (800:800) <sup>a</sup>	1:2 (500:1000) <sup>a</sup>	1:3 (400:1200) <sup>a</sup>
No. 325 cement					
Zn	12.937	3.3359	2.4326	2.4780	1.5321
Cu	0.67589	0.38451	0.22357	0.24510	0.17645
Pb	4.8976	1.8462	1.0024	1.0243	0.86542
Cd	0.10234	0.031274	0.020135	0.021347	0.021084
Ni	0.28025	0.31279	0.62590	0.72395	0.69637
Cr	0.28579	0.20965	0.19435	0.17463	0.17652
No. 425 cement					
Zn	15.024	4.2924	2.8618	2.5493	1.7405
Cu	0.70040	0.43212	0.25989	0.21370	0.18839
Pb	5.5777	1.9180	1.0596	1.0286	0.81516
Cd	0.10560	0.032977	0.019462	0.022526	0.021084
Ni	0.26025	0.14633	0.18070	0.38694	0.42217
Cr	0.37570	0.20271	0.18290	0.21820	0.23739
Asphalt					
Pb	4.2377	1.2180	0.87822	0.45861	0.31516
Cd	0.014867	0.012342	0.0086957	0.0078541	0.0061711

<sup>a</sup> Ratios of fly ash to the cement or asphalt (g:g).

to China National Standard in which the content of CaO in the former is higher than that in the latter, were used. A given weight of cement or asphalt was mixed with a known weight of fly ash, water was added, the mixture stirred and then injected into a mould 70.7 mm × 70.7 mm × 70.7 mm. The sample was naturally dried at room temperature. After 4 weeks of drying, the solidified products were broken into fine particles and screened (5 mm pore). The screened powder was used for toxicity analysis. The results are presented in Table 6. Higher concentration of cement or asphalt in the solidified products will result to lower leachability. The selection of the mix ratios depends on the toxicity leach limit. According to the China TCLP standard, the ratios of fly ash to cement should be lower than 2:1 for both types of cements and the asphalt so that the leachability of all heavy metals can meet the standard.

However, the solidification seems unable to strongly immobilize the heavy metals in the matrix of the solidified products when they are exposed to an aqueous solution for a long time (Figs. 2 and 3). Here, only Zn and Pb were tested, as the other metals have a lower leachability.

Obviously, the leachability of Zn and Pb increases as the leaching time increase. It is easy to get an equation for no. 2 sample as shown in Figs. 2 and 3:

$$y = 3.491 \ln(x) - 2.876, \quad \text{for zinc} \quad (1)$$

and

$$y = 0.6805 \ln(x) + 0.5917, \quad \text{for lead} \quad (2)$$



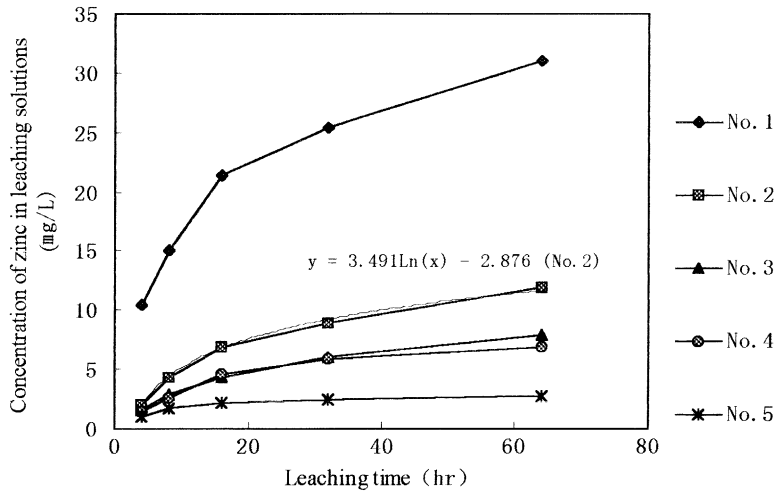


Fig. 2. Effect of leaching time on the leachability of Zn from the cement-solidified products.

where  $y$  is the concentrations of zinc or lead in the leaching solutions (mg/l) and  $x$  the leaching time (h). It can be calculated that it would take 438 years for Zn concentration and 34 h for Pb to reach the toxicity standard set by China, under the leaching conditions used (pH 5.8–6.8, while stirring). Hence, Pb would be more easily leached and should be especially controlled. Certainly, the solidified products would not expose to such an

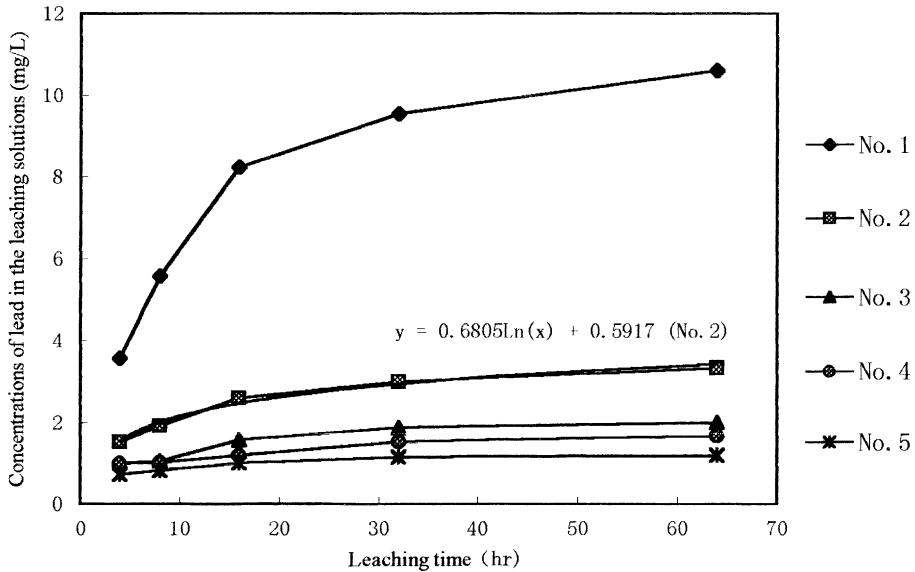


Fig. 3. Effect of leaching time on the leachability of Pb from the cement-solidified products.

environmental medium, and the leaching rate would be much lower in practice. However, it can be concluded that the cement-solidified product is not a long-term solution as required by the increasingly stringent environmental constraints, because the encapsulated heavy metals in the solidified products will release gradually in the ultimate disposal sites.

### 3.5. Chemical solidification

There are many naturally stabilized chemical forms of heavy metals in nature. Hence, it is possible to convert the heavy metals in fly ash to naturally stabilized chemical forms, such as sulfides. An alternative is to extract the heavy metals from the fly ash by acidic or alkaline treatment so that their contents can be reduced to the environmentally acceptable level. In this work, four types of chemicals were used, (NaOH, ethylenediaminetetraacetic acid disodium (EDTA), sodium sulfide, and thiourea), to explore the possibility of chemical stabilization for fly ash treatment.

#### 3.5.1. Treatment using NaOH solution

Table 7 shows Pb and Cd contents in both leaching solutions and residues after the fly ash is treated by NaOH solutions. The extraction of lead increases with an increase of the initial NaOH concentration. This result is the same as with alkaline treatment of Electric Arc Furnace dusts and oxidized zinc ores [10–12]. Inorganic compounds of lead, especially oxides, carbonates, phosphates, arsenates, etc. can dissolve in both strong acidic and alkaline solutions. However, as predicted, the extraction of Cd is unchanged as the initial NaOH concentration increases. Comparison with the data in Table 5 shows the leaching of Cd in pH 9 is consistent with leaching in 5 M NaOH solution.

If the data in Tables 5 and 7 are combined and Fig. 4 is obtained, the dependence of lead and cadmium leaching on pH and NaOH concentrations clearly shows that extraction of lead increases significantly while that of cadmium decreases as the pH value or NaOH concentration increases. The chemical reactions are shown below.

Table 7  
Leaching of the fly ash using NaOH<sup>a,b</sup>

	NaOH concentration (mol/l)				
	0.1	0.5	1	2	5
<b>Pb</b>					
Concentration in the leaching solutions (mg/l)	29.83	36.21	60.98	72.18	85.02
Pb leached (%)	19.94	24.20	40.76	48.25	56.83
Content in the leaching residues (mg/kg)	1196	1122	868	763	628
<b>Cd</b>					
Concentration in the leaching solutions (mg/l)	0.53290	0.53316	0.52143	0.50499	0.52917
Cd leached (%)	20.90	20.91	20.45	19.80	20.75
Contents in the leaching residues (mg/kg)	20.40	20.15	20.27	20.45	20.19

<sup>a</sup> Weight of the fly ash = 10 g.

<sup>b</sup> Volume of NaOH solution = 100 ml.

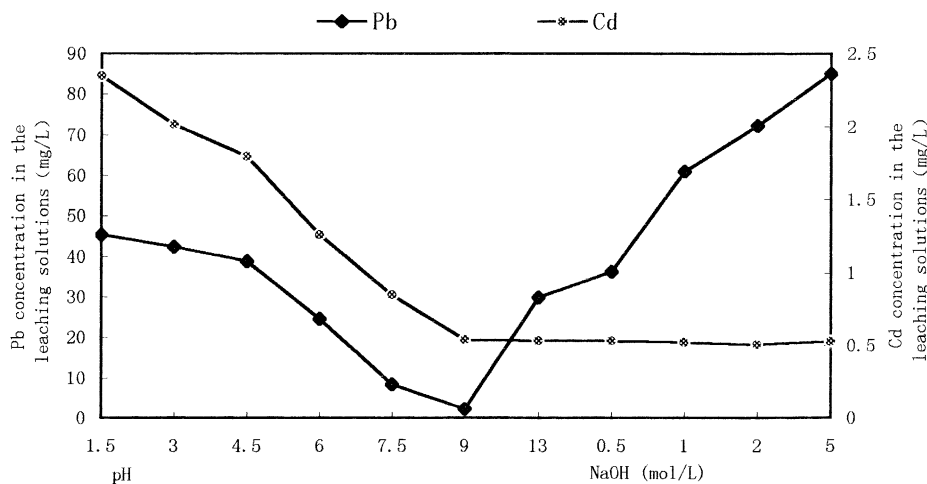


Fig. 4. Dependence of the leaching of lead and cadmium from the fly ash on the pH and NaOH concentrations.

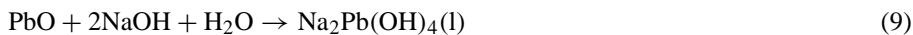
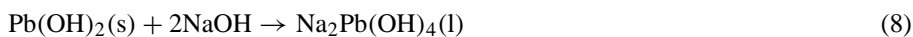
At lower pH values, the oxides of lead and cadmium dissolved in the acidic leaching solutions:



As pH values increases, insoluble lead and cadmium hydroxides forms so that the leaching rate decrease until pH 9:



Lead hydroxides dissolve when the pH (NaOH concentrations) increases so does the leaching of lead increases, while the leaching of cadmium is less:



In the strong NaOH solutions,  $\text{PbSO}_4$  can also dissolve to form soluble  $\text{Na}_2\text{Pb}(\text{OH})_2\text{SO}_4$ :



The Pb and Cd in the leaching residues were 628 and 20.19 mg/kg, respectively, even if the fly ash is treated with 5 M NaOH solutions. According to Table 4, approximately 16.42 and 49.42% of Pb and Cd can be leached. Then the concentrations in the leaching solutions of the residues would be 10.3 mg/l for Pb and 0.998 mg/l for Cd, which are beyond the limit

of the leachability toxicity standard. Therefore, NaOH solutions can be used for the part extraction and recovery of lead and zinc from but not for ultimate detoxification of the fly ash.

### 3.5.2. Treatment using EDTA solution

Ethylenediaminetetraacetic acid disodium salt (EDTA) is an excellent complex agent and can be used for the removal of heavy metals in the fly ash by dissolving the soluble salts so that the leachability toxicity can be reduced, as shown below:

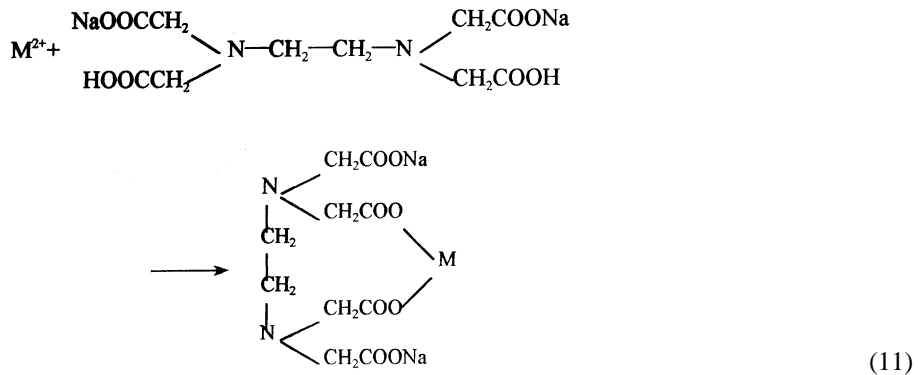


Table 8 shows the effect of initial EDTA concentrations on leaching efficiencies of heavy metals from the fly ash. It is clear that extraction of both lead and cadmium from the fly ash increases with increasing of EDTA concentrations. More than 70% of both Pb and Cd can be leached at EDTA concentration of 0.1 M. Hence, the leachability toxicity would be reduced after the fly ash is treated by EDTA solutions.

Table 8  
Extraction and stabilization of the fly ash by treatment with EDTA solutions

	Sample no.				
	1	2	3	4	5
	0.01 <sup>a</sup>	0.02 <sup>a</sup>	0.05 <sup>a</sup>	0.1 <sup>a</sup>	0.2 <sup>a</sup>
<b>Pb</b>					
Concentration in the leaching solutions (mg/l)	27.91	35.74	90.63	108.6	118.2
Pb leached (%)	18.66	23.89	60.58	72.59	79.01
Concentration in the leaching residues (mg/kg)	1226	1137	568	434	314
<b>Cd</b>					
Concentration in the leaching solutions (mg/l)	1.2875	1.3950	1.8020	1.8673	1.9128
Cd leached (%)	50.49	54.70	70.67	73.23	75.01
Concentration in the leaching residues (mg/kg)	12.75	11.47	7.651	6.630	6.375

<sup>a</sup> EDTA (mol/l).

When the EDTA concentrations is increased from 0.05 to 0.1 mol/l, the leaching of Pb and Cd increase from 60.58 and 70.67% to 72.59 and 73.23%, respectively. Hence, EDTA solutions with a concentration of 0.05 mol/l may be used as the leaching agent. In this case, the contents of Pb and Cd in the leaching residues are 568 and 7.6 mg/kg, which may meet the current leachability toxicity standard of China.

### 3.5.3. Stabilization with sodium sulfide

The sulfides of lead, zinc, cadmium, and other methods, have been present in the nature for a long time. Hence, it is an effective approach to stabilize the heavy metals by transferring the soluble forms to insoluble sulfides. The solubility products of the heavy metals decreases in the following sequence:  $\text{Hg}^{2+} \rightarrow \text{Ag}^+ \rightarrow \text{As}^{3+} \rightarrow \text{Bi}^{3+} \rightarrow \text{Cu}^{2+} \rightarrow \text{Pb}^{2+} \rightarrow \text{Sn}^{2+} \rightarrow \text{Zn}^{2+} \rightarrow \text{Co}^{2+} \rightarrow \text{Ni}^{2+} \rightarrow \text{Fe}^{2+} \rightarrow \text{Mn}^{2+}$ . The first metal will be preferably precipitated over the last one.

Table 9 shows the leachability of  $\text{Na}_2\text{S}$ -stabilized products of fly ash. As ( $\text{Zn}^{2+} + \text{Pb}^{2+} + \dots$ ) in the table means the sum of the heavy metals in the leaching solutions, calculated from Table 4. It can be seen in Table 9 that leaching decreases with an increase in the amount of sodium sulfide added. When the sodium sulfide concentration ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) reaches 0.5 g (5% of the fly ash weight) and 0.18 g (1.8% of the fly ash weight), Pb and Cd can be stabilized to a level satisfying leachability toxicity standard. The volumetric increase in the sulfide-stabilized ash is negligible. Hence, sodium sulfide should be an excellent stabilizer for the fly ash.

### 3.5.4. Stabilization by thiourea

Heavy metals can form insoluble forms with thiourea, an organic precipitant. For comparison, in this work, thiourea was also used as one of the stabilizers. The results are shown in Table 10. When the amount of thiourea added reaches 0.076 g (0.76% of the fly ash) and 0.046 g (0.46% of the fly ash), the leachability of the stabilized products will be below the standard limits. The quantity of thiourea needed is much lower than that of sodium sulfide.

Table 9  
Stabilization of the fly ash by  $\text{Na}_2\text{S}$

	Sample no.					
	1	2	3	4	5	6
$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ added (g)	0.1795	0.5	1	2	4	6
$\text{S}^{2-}$ (mol)	0.00075	0.00208	0.00416	0.00833	0.01665	0.02498
Sodium sulfide/fly ash (wt.%)	1.8	5	10	20	40	60
$C = (\text{Zn}^{2+} + \text{Pb}^{2+} + \dots)$ (mol)	$1.0301 \times 10^{-4}$					
$\text{S}^{2-}/C$ (molar ratios)	7.3	20	40	81	161	243
Contents in the leaching solutions (mg/l)						
Pb	7.265	2.737	1.265	0.73712	0.12579	0.10112
Cd	0.12342	0.10659	0.095372	0.089752	0.053296	0.044881

Table 10  
Stabilization of the fly ash by thiourea

	Sample no.					
	1	2	3	4	5	6
Thiourea added (g)	0.0460	0.0760	0.1649	0.3928	0.7950	1.5345
Thiourea (mol)	0.00060	0.00100	0.00217	0.00516	0.01044	0.02016
Thiourea/fly ash (wt.%)	0.46	0.76	1.65	3.93	7.95	15.34
C = [Zn <sup>2+</sup> + Pb <sup>2+</sup> + ...] (mol)	1.0301 × 10 <sup>-4</sup>					
Thiourea/C (molar ratios)	5.8	9.7	21	50	101	196
Contents in the leaching solutions (mg/l)						
Pb	3.572	1.256	0.9798	0.5589	0.09182	0.08782
Cd	0.11220	0.10220	0.084152	0.067321	0.039271	0.025245

In Tables 9 and 10, it can be seen that the sodium sulfide and thiourea added is much more greater than the stoichiometric prediction, implying that part of the stabilizers are consumed for the formation of other soluble metals such as Fe, Ca, Mg, etc.

For comparison, one can calculate that 5% of Na<sub>2</sub>S·9H<sub>2</sub>O (0.00208 mol for 10 g of the fly ash) is equivalent to 0.76% of thiourea (0.001 mol H<sub>2</sub>NCSNH<sub>2</sub> for 10 g of the fly ash), in terms of the leachability level of Cd and Pb from the fly ash. Hence, the stabilization capability of thiourea is stronger than that of sodium sulfide. The chemical reactions between thiourea and heavy metals are unavailable in the literature, and it is proposed in this paper as shown below (for Pb):



Table 11  
Comparison for fly ash stabilization by the chemicals used

	NaOH	EDTA	Sodium sulfide and thiourea
Mechanism	Dissolution of zinc, lead from the ash to reduce the leachability toxicity of these two metals	Dissolution of most heavy metals to reduce the leachability toxicity	Transferring the soluble forms of heavy metals into the insoluble forms
Advantages	Possible recovery of the dissolved metals	Possible to reach the leachability toxicity standard without volume expansion	Excellent stabilization for the heavy metals with no or little volume expansion. Few amount of agent needed
Disadvantages	Impossible to make the leaching residues to reach the leachability toxicity	Difficult to regenerate the complex agent due to the stability of the complexes formed	Possible dissolution of the sulfides when exposing to the acidic rain or environment such as in a MSW landfill

### 3.5.5. Comparison of the four stabilizers

The results are shown in Table 11. Obviously, thiourea is preferable for sodium sulfide, and sulfide over EDTA. NaOH alone can not be used for the stabilization of the fly ash.

## 4. Discussions

The main purpose of stabilization or solidification of fly ash is to reduce the long-term dissolution rate of the heavy metals in a landfill or other disposal site, using the current leachability toxicity standards as the assessment tool [5,6,22,23]. The immobilization of heavy metals depends on the stabilization and solidification methods used. Traditional methods include cement and asphalt solidification. However, the life of cement and asphalt products is limited, depending on the quality of the cement or asphalt used. These solidified products can be used as materials for road pavement, substitution for bricks for construction sites, or just placed in a landfill. However, as these products age, the encapsulated heavy metals will be gradually released.

One of main purposes for MSW incineration is to reduce the volume of the wastes. However, such a volume reduction will be reversed when the fly and bottom ashes are solidified with cement or asphalt. Hence, such a solidification method is not the preferred solution to the disposal problem as shown in Eq. (8).

The most obvious advantage for chemical stabilization is the negligible volume expansion. Addition of sulfides to the fly ash changes the soluble forms of heavy metals into the insoluble forms, which have existed in the nature as mineral ores for a long time [11]. That process should become the preferred method for fly ash treatment. However, the chemically stabilized products should not be exposed to an acidic environment to prevent the heavy metals from dissolution, as the case of cement and asphalt solidified products.

The long-term effects of the environment on chemically stabilized products should be explored to justify the effectiveness of the proposed stabilization of process for these products. Nevertheless, from the viewpoint of economy, the cost for chemical stabilization should be relatively less than that for high temperature volatilization and evaporation of heavy metals or vitrification.

From the viewpoint of long-term stabilization of the stabilized or solidified ash, combinations of cement and asphalt solidification and chemical stabilization may be more effective. Before cement or asphalt solidification, the heavy metals in the fly ash are first chemically stabilized using chemical agents such as sodium sulfide. As a result of this treatment, the leachability toxicity may be much lower in comparison than with a single means of solidification. On the other hand, if the heavy metals in the fly ash can be extracted to some extent by chemical agents such as sodium hydroxide and EDTA and then solidified using cement, the leachability toxicity would also be reduced. It is expected that such a combination of treatment process would be much safer for the fly ash discharged to the environment.

The quantity of the cement or asphalt or chemical agent needed for safe disposal of the fly ash depends on the content and chemical forms of heavy metals, as well as the leachability toxicity standards that must be met. Stricter standards may be promulgated in the future due to the environmental constraints. In this case, the disposal methods should be selected so that the resultant stabilized products can meet the legal requirements.

## 5. Conclusions

The heavy metals in the fly ash generated in MSW incinerators can be stabilized effectively by adding sodium sulfide and thiourea. The volume expansion due to the addition of the foregoing chemicals is negligible. Another effective treatment method for the fly ash is to leach the heavy metals from the ash by using complex agents such as EDTA. NaOH can be used for the leaching of zinc, but the resultant leaching residues should be treated further and, therefore, NaOH is not a suitable chemical agent. Comparing cement and asphalt solidification to chemical stabilization is made, it is noted that the former may be suitable for recycling of fly ash as construction materials, although the volume expansion is significant and the encapsulated heavy metals may be released gradually. The latter process results in little volume expansion. The advantage of a combination of chemical treatment or stabilization with traditional cement or asphalt solidification is discussed.

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## References

- [1] A. Jakob, Municipal solid waste incineration—flue gas and ash treatment, in: Z. Youcai (Ed.), *Proceedings of Sino-Swiss Workshop on Solid Wastes Management and Technology*, Tongji University Press, Shanghai, China, 1998, pp. 93–102.
- [2] H. Belevi, Sustainable management of municipal solid waste, in: Z. Youcai (Ed.), *Proceedings of Sino-Swiss Workshop on Solid Wastes Management and Technology*, Tongji University Press, Shanghai, China, 1998, pp. 59–69.
- [3] A. Bagchi, D. Sopcich, Characterization of MSW incinerator ash, *Env. Eng.* 115 (2) (1989) 447–452.
- [4] E.F. Barth, An overview of the history, present status and future direction of solidification/stabilization technologies for hazardous waste treatment, *J. Haz. Mater.* 24 (2/3) (1990) 103–109.
- [5] J.H. Tay, A.T.C. Goh, Engineering properties of incinerator residue, *J. Env. Eng.* 117 (3) (1991) 224–235.
- [6] J.H. Tay, Sludge ash as filler for portland cement concrete, *J. Env. Eng.* 113 (2) (1987) 345–351.
- [7] S.C. Poon, Z.Q. Chen, Comparison of the characteristics of flow-through and flow-around leaching tests of solidified heavy metal wastes, *Chemosphere* 38 (3) (1999) 663–680.
- [8] L. Song, Chemical stabilization of fly ash from MSW incinerators, Master thesis, Tongji University, Shanghai, 2000.
- [9] J.H. Tay, W.K. Yap, Sludge ash as lightweight concrete material, *J. Env. Eng.* 115 (1) (1989) 56–64.
- [10] Y.C. Zhao, R. Stanforth, Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium, *J. Haz. Mater.* 80 (2000) 223–240.
- [11] Y.C. Zhao, R. Stanforth, Production of Zn powder by alkaline treatment of smithsonite Zn–Pb ores, *Hydrometallurgy* 56 (2000) 237–249.
- [12] Y.C. Zhao, R. Stanforth, Extraction of zinc from zinc ferrites by fusion with caustic soda, *Min. Eng.* 13 (13) (2000) 1417–1421.
- [13] Y.C. Zhao, J.Y. Liu, R.H. Huang, G.W. Gu, Long-term monitoring and prediction for leachate concentrations in Shanghai refuse landfill, *Water Air Soil Pollut.* 122 (3/4) (2000) 281–297.
- [14] K.Y. Chen, P. Bishop, J. Isenburg, Leaching boundary in cement-based waste forms, *J. Haz. Mater.* 30 (3) (1990) 298–306.



- [15] C.F. Lin, T.H. Huang, Leaching characteristics of a model stabilization/solidification system: tricalcium silicate and copper oxide, *J. Haz. Mater.* 36 (2) (1990) 114–119.
- [16] C. Vipulanandan, S. Krishnan, Stabilization/solidification of phenolic waste with cementitious and polymeric materials, *J. Haz. Mater.* 24 (2/3) (1990) 123–136.
- [17] S. Shukla, Solidification/stabilization for disposal of pentachlorophenol, *J. Haz. Mater.* 30 (3) (1992) 288–294.
- [18] A. Roy, The effect of sodium sulfate on stabilization/solidification of a synthetic electroplating sludge in cementitious binders, *J. Haz. Mater.* 30 (3) (1992) 297–316.
- [19] H. Belevi, *Environmental Engineering of Municipal Solid Wastes Incineration*, ETH, Switzerland, 1994.
- [20] J. Wochele, S. Stucki, Similarity laws for the tubular furnace as a model of a fixed-bed waste incinerator, *Chem. Eng. Technol.* 22 (3) (1999) 209–222.
- [21] J. Wochele, S. Stucki, C. Ludwig, Factors influencing the volatility of heavy metals in MSW incinerators, *Wastecon /ISWA World Congress*, Charlotte, NC, 1998.
- [22] S. Biollaz, R. Bunge, M. Schaub, H. Kunstler, Better quality of MSW incinerator residues for lower cost, in: *Proceedings of the Third International Symposium on Incineration and Flue Gas Treatment Technology*, Brussels, 2001.
- [23] S. Stucki, A. Jakob, Thermal treatment of incinerator fly ash: factors influencing the evaporation of  $ZnCl_2$ , *Waste Manage.* 17 (1997) 231–236.
- [24] Y.C. Zhao, *Incineration Technology of MSW*, Chemical Industry Press, Beijing, 2000.