Meso-2, 3-dimercaptosuccinic acid as a novel chemical agent to stabilize heavy metals in MSWI fly ash

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Abstract: The fly ash from municipal solid waste incineration (MSWI) is generally classified as hazardous material. Fly ash often contains large amounts of potentially toxic metals (e.g. Pb, Cd), which can cause harm to the environmental and human health if released from the ash. The leaching concentration of heavy metals in fly ash usually beyond the standard limits and fly ash must be treated before disposal. Chemical stabilization for heavy metals in fly ash was explored. It was found that sodium sulfide (Na_2S) and sodium phosphate (Na_3PO_4) were effective for heavy metal stabilization since they can convert soluble and leachable heavy metals into insoluble and non-leachable forms. In addition, meso-2, 3-dimercaptosuccinic acid (DMSA) showed great superiority in heavy metal stabilization process compared to Na_2S and Na_3PO_4. In this work, the heavy metal stabilization efficiency of DMSA was experimentally studied, which was also compared with sodium sulfide and sodium phosphate, and typically Hg was stabilized more effectively by using DMSA.

Introduction

Since incineration can reduce waste volume efficiently and the heat generated from incinerator can be reused, incineration has become a popular method for municipal solid waste (MSW) treatment in many developed countries and would be more widely used in the coming future in China [1]. Typically, a large amount of incineration residues, bottom and fly ash, as well as waste gas are produced in the process of incineration [2]. Among them, the fly ash contains high level of chloride compounds of calcium, sodium and potassium, while it also contains considerably hazardous substances, e.g., toxic heavy metals such as Pb, Hg, Zn, Cu, As. Cd and toxic organic materials such as dioxin which are concentrated in the fly ash [3], therefore fly ash is generally classified as hazardous waste [4]. In practice, dioxins can be detoxified into carbon dioxide through vitrification process at high temperature, but heavy metals cannot be decomposed [5]. There is much concern over the emission of heavy metals to the environment due to their associated health hazard [6]. With regard to toxicity, fly ash is most harmful because of its high content of leachable heavy metals. Therefore, to avoid secondary pollution, the fly ash has to be well treated before disposal [7].

Usually, the fly ash is treated by one of the following methods, thermal treatment [8], cement solidification [9], chemical stabilization [1,2], and acid extraction [3]. Among these options, chemical stabilization of the residues may be an interesting alternative, using specific chemicals such as hydroxides, sulfides, silicates, carbonates, phosphates and chelating agents to achieve the goal of converting pollutants into less soluble or less toxic forms [10]. Over the last 20 years, sodium sulfide has been considered to be effective because of the stability of the products and the reductive character of the sulfide ion [11]. Soluble phosphates are the mostly tested additives [12,13,14]. The high efficiency of phosphates for stabilizing lead, zinc and copper is pointed out in various studies [12,13,15].

Meso-2, 3-dimercaptosuccinic acid (DMSA) is an effective oral or injected chelator in heavy metal detoxification which has also been widely used in medicine [16]. Through the complexation of metals with the sulfhydryl, DMSA can be also used for metal chelation. In this work, the effect of DMSA, Na_2S and Na_3PO_4 were studied in order to prevent the release of the heavy metals from fly ash into the environment. It is expected that DMSA would has better stabilization effect on Hg and enhance the long-term stabilization of the heavy metals.

Materials and methods

Fly ash sampling

The fly ash used in this work was collected from Shanghai Jiangqiao MSW Incineration Plant. Original fly ash samples used for the determination of total metal levels were digested by HNO_3/H_2O_2 mixture solution at 180˚C and then analyzed by inductively coupled plasma emission spectrometry (ICP-AES). The major heavy metal elements of the original fly ashes are summarized in table 1.

Table 1 Primary heavy metal composition of the fly ash [mg/kg]

Zn	Ba	Pb	Cu	Cr	Cd	As	Ni	Hg
9345	6327	4859	1300	627	450	389	335	321

Treatment process of fly ash

To assess the effects of DMSA on heavy metals in fly ash, a fly ash stabilization experiment was conducted. Analytical sodium sulfide and sodium phosphate were used as stabilization agents for comparing with DMSA stabilization effects. Agents applied to the treatment process were on a weight basis at 0.3%, 0.5%, 1%, 2%, 3%, 5%, 7.5% and 10%. Each agent was dissolved into the distilled water and then thoroughly mixed with 100g fly ash within 2L polyethylene bottles. Treated fly ash were adjusted to 40% of moisture content and then incubated for seven days at room temperature and then air-dried for further analysis.

Leaching toxicity analysis

The leaching toxicity of fly ash samples was determined using the Test method standard for leaching toxicity of solid waste-Horizontal vibration extraction procedure (GB 5086.2-1997). Adding 100 g of the fly ash whose diameter <5 mm into a polyethylene bottle (2L), then deionized water was added according to Liquid/Solid=10, then fixes the bottle on the machine of reciprocating horizontal oscillation with 110 ± 10 rpm and amplitude of 40 mm for a duration of 8 h followed by 16 h standing at 25 ˚C. The liquid phase is separated by the 0.45μm millipore filter in a mutche filter. The filtered solution is handled by microwave digestion and analyzed by ICP-AES.

Effect of pH on the leachability of the fly ash

The pH of the leachate is one of the major factors influencing the leaching concentrations of heavy metals of fly ash. Using extracting agents with different pH is also called pH-stat experiment. This pH range corresponds to values expected for open leaching systems. It is a prediction method to assess if or not the stabilized products can keep long-term stabilization when the environment situation changes [1]. The pH-stat experiment was conducted according to the experimental steps of HVEP. The extracting solutions were NaOH a.q. (0.25~1.0 mol/L), distilled water and HNO_3 a.q. (0.10~1.20 mol/L).

Results and discussion

Leaching characteristics of heavy metals of original fly ash

The method of HVEP was applied to test leaching toxicity of heavy metals of fly ash, the results of leaching toxicity of original fly ash are shown in Table 2.

Table 2 Leaching toxicity of original fly ash [mg/l]

Metals	As	Cd	Cr	Cu	Ni	Pb	Zn	Hg
Leaching toxicity	0.038	0.125	0.292	0.183	0	9.701	0.151	0.227
China toxicity standard [17]	1.5	0.3	10	50	10	3	50	0.05

It can be seen from Table 2 that the leaching concentrations of lead and mercury in fly ash are beyond the scope of toxicity standard. MSWI fly ash belongs to hazardous wastes and must be treated before discharge properly.

Stabilization of fly ash

Fly ash was stabilized with three agents DMSA, Na_2S and Na_3PO_4 according to the method mentioned in 2.2 and the adding dosages were 0.3%, 0.5%, 1%, 2%, 3%, 5%, 7.5%, 10%. Figure 1 shows the stabilizing effect of dosage on the leachability of Pb and Hg which were beyond the national standard limits.

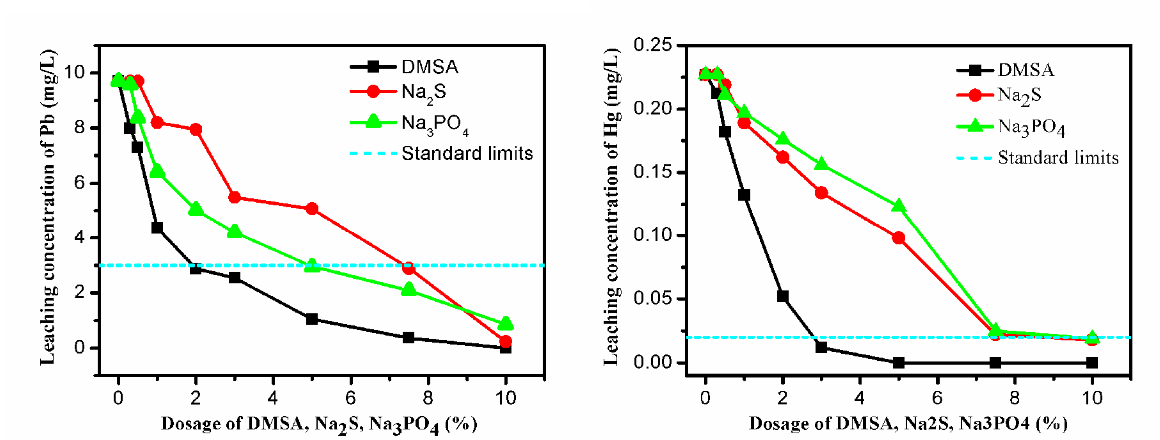

Fig. 1 Effect of dosage on leachability of Pb and Hg

It can be concluded from the results in Figure. 1 that to increase the dosage leads to a decrease of leaching concentration of Pb. For DMSA, when the dosage was 2%, the leaching concentration of Pb was lower than the standard limits. However, in order to satisfy the standard, the adding dosage of inorganic agents like Na_2S, Na_3PO_4 had to be increased to 8%. Similarly, the leaching concentration of Hg decreased with the increasing of the adding dosage. For three agents above, in order to realize the leaching concentration of Hg satisfy the standard limits, their dosages had to be more over than 3%, 10%, 10% respectively. Obviously, the stabilizing effect of DMSA on Hg is superior to inorganic agents like Na_2S and Na_3PO_4.

Effect of pH on the leachability of the fly ash

The leaching concentrations of heavy metals at different pH values of untreated and treated fly ash at chemical dosage of 3% are shown in Figs. 2.

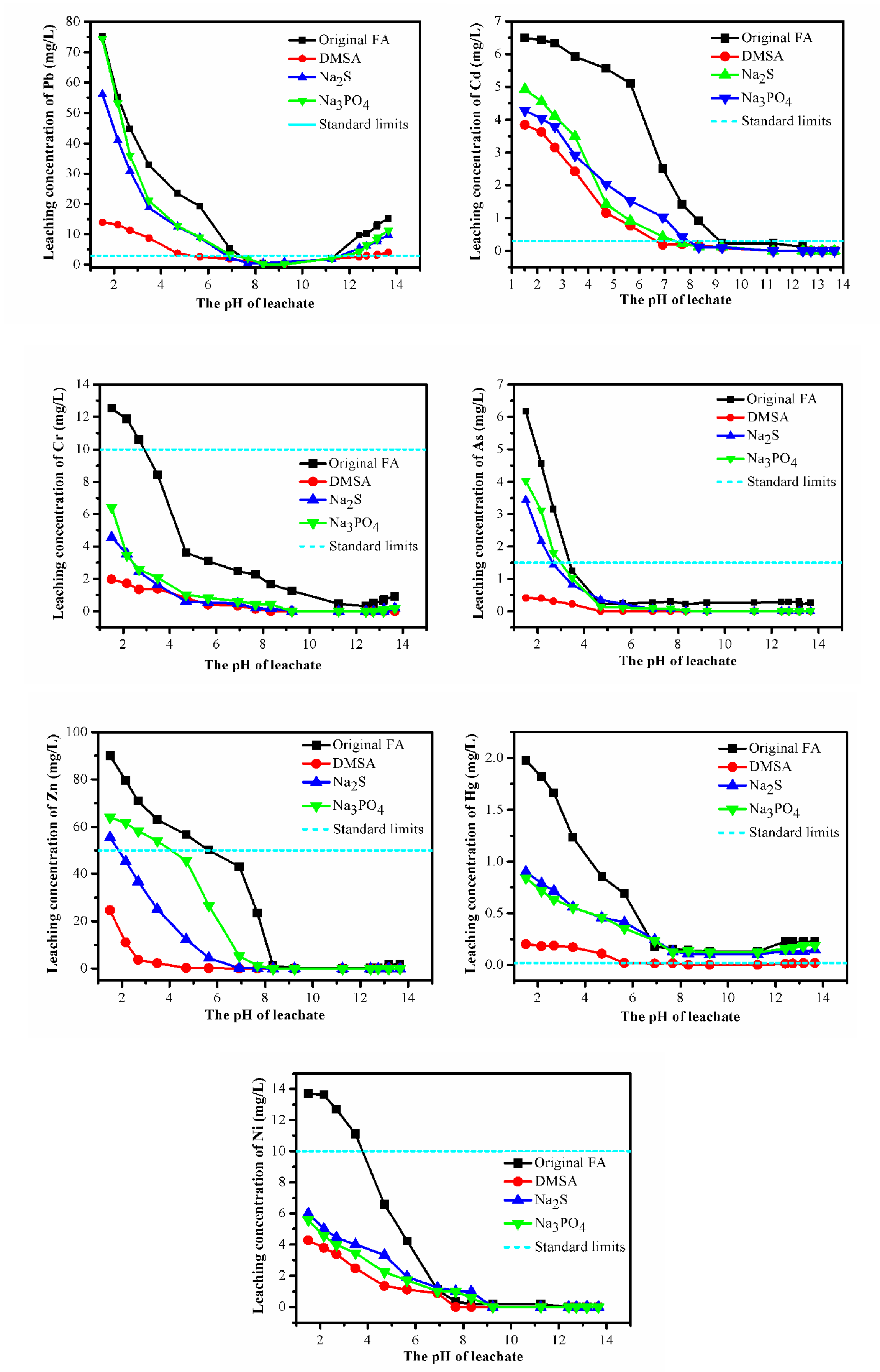

Fig. 2 Leaching concentration of heavy metals at different pH value under 3% chemical dosage

The figures above showed that the leaching amount of heavy metals in fly ash changed dramatically with the pH value shifting. And DMSA is superior to inorganic agents Na_2S, Na_3PO_4. In terms of Pb, after stabilization with the chemical dosage of 3%, the leaching concentration of heavy metals in the fly ash stabilized by DMSA was below standard limits within the pH range of 5.65~12.73, while for Na_2S and Na_3PO_4, the leaching concentration could satisfy the standard limits only within the pH range of 7.68~11.25. DMSA has broader adoptive range of pH value. For some other heavy metals, the adoptive pH ranges of these agents are shown in Table 3. Typically, Hg can be stabilized more effectively by DMSA, while Na_2S and Na_3PO_4 seem to be useless in the stabilization of Hg within the whole pH range.

Table 3 Adaptive range of pH of different stabilized fly ash

Heavy metals	DMSA	Na_2S	Na_3PO_4
Pb	pH 5.65~12.73	pH 7.68~12.73	pH 7.68~12.73
Cd	pH 6.92~13.65	pH 7.68~13.65	pH 8.33 ~13.65
Cr	pH 1.51~13.65	pH 1.51~13.65	pH 1.51~13.65
As	pH 1.51~13.65	pH 2.68~13.65	pH 2.68~13.65
Zn	pH 1.51~13.65	pH 2.16~13.65	pH 4.70~13.65
Hg	pH 5.65~13.65	~	~
Ni	pH 1.51~13.6	pH 1.51~13.65	pH 1.51~13.65

Conclusions

The heavy metals in fly ash can be stabilized more effectively by adding DMSA than inorganic stabilization chemicals such as Na_2S and Na_3PO_4. And the results also indicate that DMSA is more superior on Hg stabilization. The leaching toxicity of heavy metals in fly ash stabilized by DMSA can be least affected by pH, thus the treated products can enhance long-term stabilization and what's more, the risk of secondary pollution of treated fly ash can also be decreased.

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