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Heavy metal stabilization in municipal solid waste incineration flyash using heavy metal chelating agents

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Abstract

Heavy metal chemical stabilization with synthesized heavy metal chelating agent was assessed for flyash from municipal solid waste incinerator. Flyash can contain heavy metals (e.g. Pb, Cd) which can leach. A new kind of heavy metal chelating agent showed more attractive competition than inorganic chemicals in stabilizing flyash. The synthesizing method of this kind of heavy metal chelating agent was explained in this paper, and the technology process and treatment efficiency of the chelating agent in treating flyash were experimentally studied, which was compared with the results of inorganic chemical agents such as sodium sulfide and lime. The heavy metals in flyash were stabilized more effectively by using heavy metal chelating agents than by using sodium sulfide and lime, furthermore, the stabilized products using the chelating agents can meet the landfill disposal controlling standards for heavy metal waste. pH-dependent leaching experiment showed the stabilized flyash by treatment with heavy metal chelating agent could keep long-term stabilization within a broad range of pH value. Thus, the risk of secondary pollution for the stabilized products was reduced dramatically when the environment condition changes during its disposal period.

Keywords: Heavy metal chelating agents; Flyash; Chemical stabilization; Heavy metals; Sodium sulfide; Lime; Stabilization/solidification

1. Introduction

Statistically, the total municipal solid waste (MSW) generation was 0.118 billion tonnes in China in 2000 (China Statistic Almanac 2001), and the figure increased to 0.135 billion tonnes in the next year in China (China Statistic Almanac 2002). And it was estimated that the annual MSW growth rate would be 8–10% in China, to be compared with an annual growth rate of 3.2–4.5% in the developed countries and an increasing rate of 2–3% in other developing countries, respectively [1]. Therefore, to dispose of all the generated municipal solid waste without environment pollution needs a huge amount of high-standard sanitary facilities (e.g. landfills) to be constructed in China. But the fact of huge population with a relatively shortage of arable land required more efficient technologies to minimize and recycle municipal solid waste in China. Since incineration can reduce waste volume efficiently and the heat generated from incinerator can be reused in many sources, incineration would be more widely used in MSW treatment in the coming future in China. Typically, 2–5% flyash collected by the filters will be generated from MSW incineration, and different kind of heavy metals, such as zinc, copper, lead, chromium and cadmium may contain in flyash. There is much concern over the emission of heavy metals to the environment due to their associated health hazard, especially, heavy metals can exert a range of toxic health effects including carcinogenic, neurological, hepatic, renal and haematological [2,3,8]. With regard to toxicity, flyash is most harmful because of its high content of leachable heavy metals. Therefore, a good way must be found to treat flyash from incineration before its disposal to avoid secondary pollution [9].

Flyash can by treated in several different ways. The traditional method, such as direct disposal, has been prohibited. The most frequent means of flyash disposal used include: (1) placement in a well-designed landfill; (2) immobilization through solidification/stabilization and then landfill or reuse; (3) separation of heavy metals by volatilization at high temperature or hydrometallurgical extraction by

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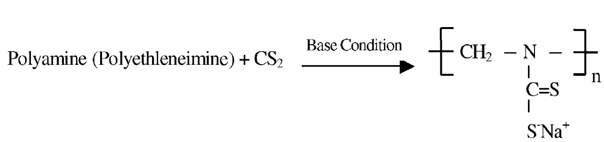
dissolution in acidic or alkaline medium [5,6]. Where chemical stabilization technology is strongly recommended and used to treat flyash because of its environmental safety and cost effective [4].

The traditional stabilization technology in treating with heavy metal wastes includes cement stabilization/solidification, lime stabilization and coal ash stabilization [7]. But for these main stabilization technology, several problems must be paid attention to: one is that the volume of the treated waste will be increase using cement or lime as the stabilization/solidification agents and this cannot meet the objective of waste volume reduction; another is long-term stabilization of the stabilized waste in landfills, especially the heavy metal ions would be leached again while the pH value changes [8,10]. Chemical stabilization is one method of reducing the leachability of heavy metals in waste materials and will not increase the volume of the stabilized products. The principal aim of chemical stabilization is to form new, less soluble mineral phases that are more geochemically stable in leaching environments, and one stabilization agent of recent is chemical agents [12]. Chemical stabilization processes are strongly recommended for the practical uses, in terms of the volume reduction and environmental safety of the stabilized products and cost balances, in comparison with the traditional cement or lime solidification methods [6].

In this paper, the objectives were to develop a cost effective and environmental safety stabilization process for flyash by chemical stabilization. A new kind of heavy metal chelating agent was synthesized. The heavy metal stabilization effects for flyash using the chelating agent was also compared with inorganic chemicals of lime and sodium sulfide. It is expected that the heavy metal chelating agent would enhance the long-term stabilization of the heavy metals in treated flyash so that the risk for environmental pollution may be reduced.

2. Synthesizing of heavy metal chelating agents

The heavy metal chelating agents can be synthesized experimentally through the reaction by different types of polyamine or polyethleneimine and carbon disulfide in alkaline conditions [1]. There is an active hydrogen atom over the nitrogen atom within the molecule of polyamine or polyethleneimine, so the active hydrogen atom can be replaced by carbon disulfide and thus the function bond group of disulfide carbamate can be formed theoretically. Since this agent can capture and encapsulate heavy metal ions tightly, we call it heavy metal chelating agents. The reaction can be expressed as following:



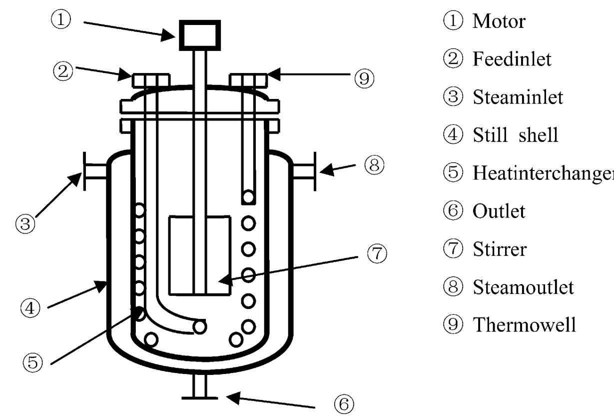


Fig. 1. Sketch view of the autoclave.

Heavy metal chelating agents was synthesized in an autoclave reactor (see Fig. 1). First, add polyamine or polyethleneimine solution to the autoclave via feed inlet, then, add a certain ratio of 5 M NaOH solution according to the reaction to the autoclave. Keep the temperature in the reactor between 25 and 35 °C, and add CS_2 very slowly at violent stirring. After all the CS_2 added to the reactor, heating-up the reactor to 60–70 °C, and keep stirring for 5–8 h at this condition.

3. Materials and methods

3.1. Flyash samples

The flyash samples were taken from Shenzhen Municipal Solid Waste Incineration Plant built in 1985, which was the earliest incineration plant in China. The plant used stoker incinerators and semi-dry adsorption gas cleaning process. The particle size of the flyash is between 1 and 1000 μm, and 50% of the flyash particle size is less than 100 μm.

3.2. Flyash composition analysis

The samples (approximately 0.5 g accurately weighed) of flyash were digested in a 5:1 ratio of hydrofluoric acid (HF) and nitric acid (HNO_3) and evaporated to near dryness. Further nitric acid was added and digested for 8 h. The solution was then filtered and quantitatively diluted to 50 ml prior to introduction to iductively coupled plasma coupled with atomic emission spectrophotometer (ICP–AES) system [3]. The main species of the heavy metals are element heavy metal, metal oxide and metal chloride.

3.3. Flyash treatment process

In this study, an experiment lab-scale treatment formulation was selected to ensure that stabilization and reaction products could be detected. The flyash material used in the experiment was further processed to provide a size fraction less than 1 mm. Fig. 2 shows a schematic diagram of the

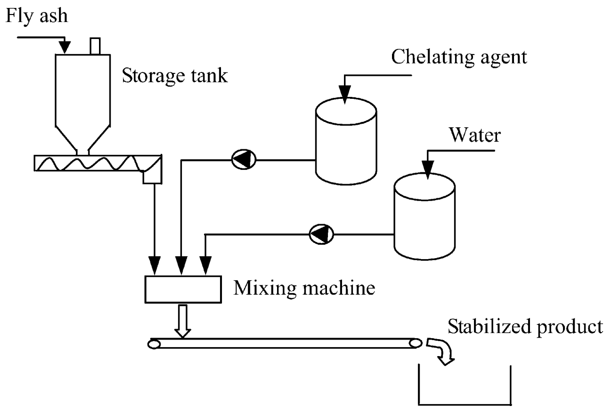


Fig. 2. Schematic diagram of the flyash treatment process.

flyash treatment process by adding heavy metal chelating agents and equipments used in the experiment.

3.4. Total availability leaching procedure

The toxicity of the flyash samples was determined using toxicity characteristic leaching procedure (TCLP). TCLP method is a standard method to determine the waste leaching toxicity, and it was improved on the basis of hazardous waste extraction procedure (EP) by USEPA. Its objective is to explore the leaching property of hazardous components from the treated waste under landfill conditions and to determine its pollution on the groundwater or not.

The experimental schematic diagram for TCLP test refers to Fig. 3.

3.5. pH-dependent leaching

pH-dependent leaching procedure is a means of determining the equilibrium behavior over a range of pH values. This pH range corresponds to values expected for both regulatory leaching tests and open leaching systems (e.g. landfills). It is a prediction method to assess if or not the stabilized products can keep long-term stabilization when the environment situation changes [4,11], for example, how about the availability leaching when the stabilized products exposed to extremely low or high pH value environment.

Table 1
Primary heavy metal composition of flyash (mg/kg)

	Pb	Cd	Zn	Cr	Hg	Cu	Ni
Sample 1	1870	45.2	6100	36.0	11.3	240	–
Sample 2	1170	86.2	8900	20.4	31.3	340	–
Average	1520	65.7	7500	28.2	21.3	290	–

Table 2
Leachability toxicity of the flyash (mg/l)

	Metals						
	Pb	Cd	Zn	Cr	Hg	Cu	Ni
Leaching concentration of flyash	38.5	1.87	7.2	0.18	0.006	0.11	–
Hazardous waste toxicity standard	3.0	0.3	50	1.5	0.05	50	10
Hazardous waste landfilling control standard	3.0	0.3	–	1.5	0.05	–	15

4. Results and discussion

4.1. Heavy metal composition

Heavy metals of the samples were determined by ICP–AES using flyash composition analysis method. Table 1 shows the primary heavy metal composition of the flyash samples (elemental composition of the flyash was not shown).

4.2. Leachability of the flyash

Heavy metals of the filtrate using TCLP method were determined by ICP–AES. Table 2 shows the leachability toxicity of the flyash samples. Comparatively, the Chinese Standards for Hazardous Waste Distinguish—Toxicity Leaching Distinguish [13] and Chinese Standards for Hazardous Waste Landfill Control [14] were also listed in Table 2.

4.3. Stabilization of flyash using chelating agent and inorganic agents

This experiment included three different groups, heavy metal chelating agents group, sodium sulfide (Na_2S) group

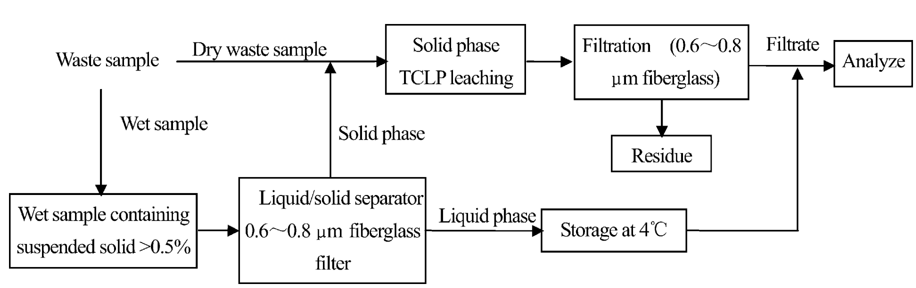


Fig. 3. Schematic diagram of toxicity characteristic leaching procedure (TCLP).

Table 3
Leachability of the stabilized products using chelating agent to be compared with Na_2S and lime (mg/l in the leaching solution)

	Run no.									
	0	1	2	3	4	5	6	7	8	9
Dosage (%)	–	0.2	0.4	0.6	0.2	0.4	0.6	0.2	0.4	0.6
pH of leachate	–	5.5	5.5	6.0	8.0	9.5	12.0	9.0	10.5	11.5
Pb	38.5	3.12	0.68	0.26	10.3	2.50	1.85	12.4	4.5	2.7
Cd	1.87	0.32	0.21	0.16	1.23	0.78	0.50	1.30	0.97	0.61
Zn	7.2	1.8	0.72	0.37	2.6	1.63	0.58	3.42	2.91	1.27
Cr	0.18	ND	ND	ND	0.04	0.02	0.02	0.05	0.04	0.03
Hg	ND	–	–	–	–	–	–	–	–	–
Cu	0.11	–	–	–	–	–	–	–	–	–

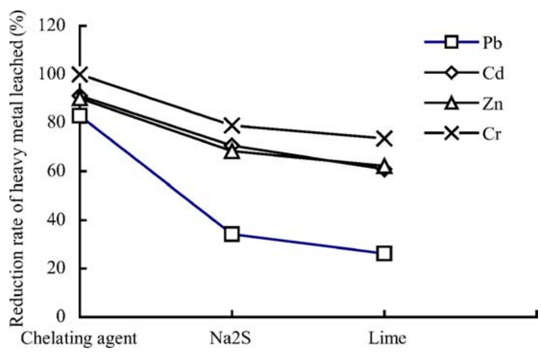


Fig. 4. Comparison of reduction rate of heavy metal leached at 0.2% chemical dosage.

and lime group. The experiment dosage of different chemicals in each group was 0.2, 0.4 and 0.6% by weight, respectively. The heavy metal leaching from treated flyash were listed in Table 3, where, experiment run 0 was the leaching data for untreated flyash, runs 1–3 were treated flyash groups using heavy metal chelating agent, comparatively, runs 4–6 and runs 7–9 were treated flyash groups using sodium sulfide and lime, respectively. Figs. 4–6 focus on the comparison of reduction rate of heavy metal leached from treated flyash using different chemical agents at different experimental dosage.

It can be concluded from the results shown in Figs. 4–6 that the leached heavy metals of stabilized flyash (such as Pb, Cd, Zn and Cr) can be reduced by over 85% using heavy metal chelating agent at a chemical dosage of 0.2% by weight, and the reduction rate of the leached heavy metals can be higher than 90% at a chemical dosage of 0.4 and 0.6% using the chelating agents. For a comparison, the leached heavy metals of stabilized flyash using inorganic agents for sodium sulfide and lime were much higher (see Table 3), and the reduction rate of the leached heavy metals was much lower than 80% even if the chemical dosage was reached 0.6% by weight.

As shown in Table 3, the leached heavy metals of the treated flyash in heavy metal chelating agent group were much lower than that of the untreated flyash, and the treated flyash can meet China Hazardous Waste Landfilling Control Standard when the heavy metal chelating agent used amount was 0.6%. In contrast, the treated flyash using Na_2S and lime cannot meet the Standard.

4.4. pH-dependent leaching

Fig. 7 shows the schematic process of pH-value dependent leaching procedure. Flyash was treated with different chemical agents including synthesized heavy metal chelating agents, sodium sulfide and lime, then stabilized products was desiccated for leaching. Each extraction was performed at a L/S ratio of 10, ensuring solid phase control. Ten grams of sample was placed into a Teflon vessel to which 1000 ml

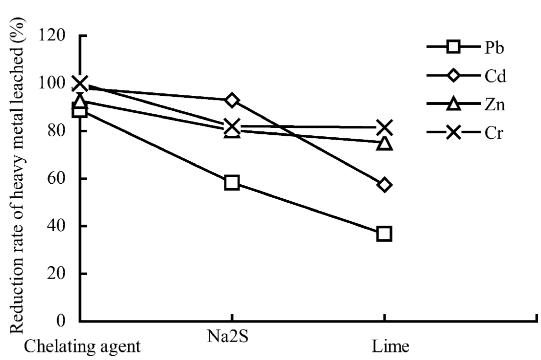


Fig. 5. Comparison of reduction rate of heavy metal leached at 0.4% chemical dosage.

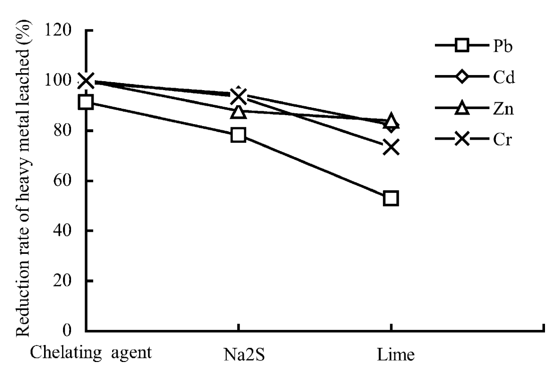


Fig. 6. Comparison of reduction rate of heavy metal leached at 0.6% chemical dosage.

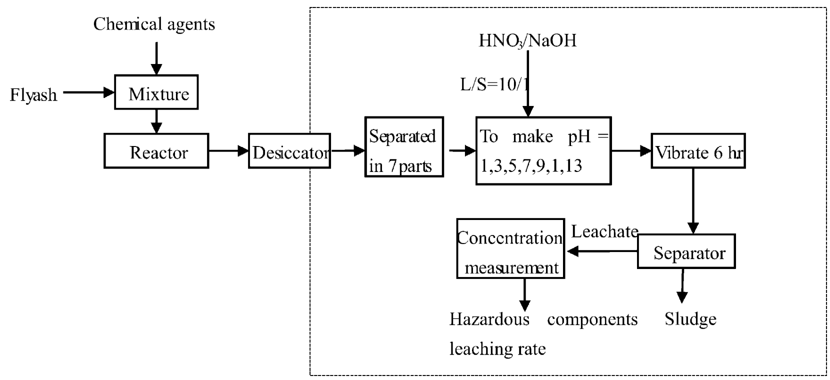


Fig. 7. Schematic process of pH-dependent leaching procedure.

of distilled, deionized water was added. High purity 3N HNO_3 was used to control the pH at various set points (1, 3, 5, 7, 9, 11, 13) for 8 h. Then the leachates were filtered and analyzed by ICP–AES.

During the pH-dependent leaching the initial pH of the untreated and treated flyash at chemical dosage of 0.2% was measured in distilled water at an L/S ratio of 10. The untreated flyash pH ranged from 10.2 to 10.6. The treated flyash pH ranged from 6.0 to 6.5 for heavy metal chelating agents, 8.0 to 8.4 for sodium sulfide and 10.2 to 11.1 for lime, respectively.

The experiments of chemical used dosage for heavy metal agents, sodium sulfide and lime were done at 0.4 and 0.6% by weight, and the pH ranged from 1 to 13. Leaching concentrations for Cd and Pb were determined by ICP–AES. The TCLP leaching concentrations of Cd and Pb at different pH values of untreated and treated flyash were showed in Figs. 8–11.

The maximum allowable TCLP leaching amount of waste was referred to the Japanese standards in Environment Notice No. 13 which was stricter than Chinese standards, and the leaching amounts for Cd and Pb are both 3 mg heavy metal per kilo gram waste.

Treatment resulted in a considerable reduction of Pb and Cd in leachate as shown by the pH-dependent leaching.

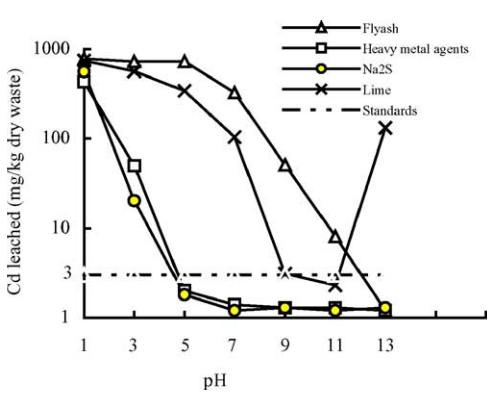


Fig. 8. Leached concentration of Cd at different pH value under 0.4% chemical dosage.

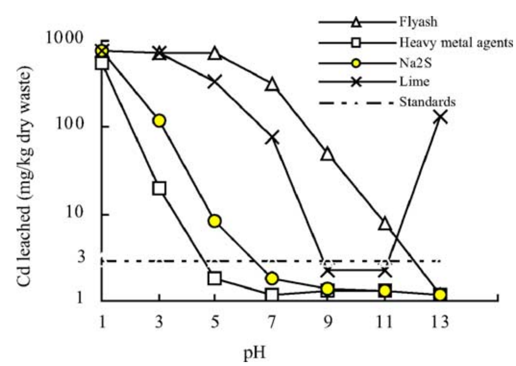


Fig. 9. Leached concentration of Cd at different pH value under 0.6% chemical dosage.

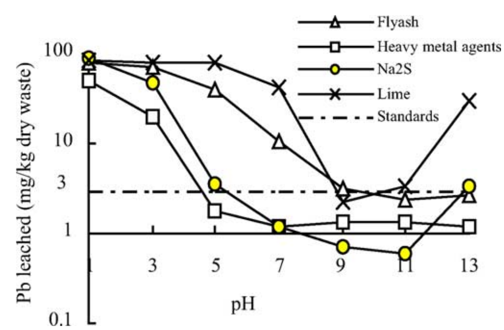


Fig. 10. Leached concentration of Pb at different pH value under 0.4% chemical dosage.

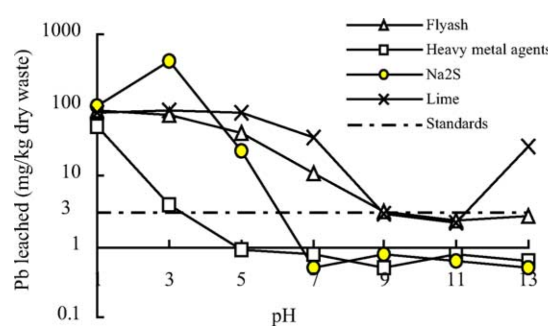


Fig. 11. Leached concentration of Pb at different pH value under 0.6% chemical dosage.

Figs. 8–11 shows that the leaching amount of heavy metals in flyash changed dramatically with the pH value shifting, and the leaching concentration of Cd and Pb can be both less than 3 mg/kg which meets the landfill control standard when the pH value was higher than 12 and 9, respectively. When the heavy metal chelating agent was used, the leaching concentration of Cd can meet the standard when the pH value was higher than 3.8 and 3.6 (chemical dosage was 0.4 and 0.6% by weight, respectively), similarly, the leaching concentration of Pb can meet the standards when the pH value was higher than 4.2 and 3.2, respectively. In contrast, when sodium sulfide was used, the leaching concentration of Cd can meet the landfill control standard only when the pH value was higher than 10 and 6.5 (the chemical dosage was 0.4 and 0.6% by weight, respectively), and the leaching concentration of Pb can meet the standard only when the pH value was higher than 7.4 and 5. At the same time, the leaching concentration of the main heavy metals in the treated flyash can meet the landfill control standard only when the pH value was between 9 and 11 when lime was used.

According to the leached heavy metal from treated flyash to meet the landfill control standard, for the heavy metal chelating agent, the range of pH value was expanded for 8.2 and 4.8 unit for Cd and Pb, respectively, at a dosage of 0.4% by weight, and at a dosage of 0.6%, the range of pH was expanded for 8.4 and 5.8 unit for Cd and Pb, respectively. For compare, the range expansion of pH value for the Na_2S treated flyash to reach the landfill control standards was clearly lower than that for heavy metal agents treated flyash, and it was the same for the lime treated flyash.

5. Conclusions

The heavy metals in the flyash generated in MSW incinerators can be stabilized more effectively by adding heavy metal chelating agents than by adding inorganic stabilization chemicals such as sodium sulfide and lime. The experiment results also demonstrated that the treated flyash using heavy metal chelating agents can keep stabilization at a relatively wider range of pH value, thus it enhanced long-term stabilization of the heavy metals in the treated flyash when the environment pH value and other conditions change, so that the risk of secondary pollution of treated flyash can by reduced.

Acknowledgements

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