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A comparative study on the heavy metal solidification/stabilization performance of four chemical solidifying agents in municipal solid waste incineration fly ash

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HIGHLIGHTS

- The solidification performance of four solidifying agents in fly ash were compared.
- Their leachability were analyzed in accordance with different extraction procedures.
- Solidifying agents with multiply hydrosulfide groups show excellent performance.
- The leaching content of Cd, Ni, Pb and Zn is higher than the thresholds in China.
- The excessive acetic acid makes its binding capacity stronger in HJ/T 300-2007.

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ABSTRACT

Investigated in this paper were the content, specification distribution, and risk assessment code (RAC) determination of six targeted heavy metals and potentially toxic metals in fly ashes from a municipal solid waste incinerator in China. Contained in it is a comparison of the solidification/stabilization performance of two novel solidifying agents of sixthio guanidine acid (SGA) and tetrathio bicarbamic acid (TBA) with sodium dimethyldithiocarbamate (SDD) and Na_2S, and analysis of their leachability in accordance with TCLP 1311 of the US EPA and the extraction procedures of China (HJ/T 299-2007 and HJ/T300-2007). The total concentration of Zn, Cu, Ni, Pb, Cr, Cd is 37383.47, 3080.77, 1583.92, 1356.43, 566.15, and 77.83 mg/kg, respectively. Cr (3.7%) and Pb (7.50%) pose low risk; and Ni (12.93%) and Zn (15.45%) have a medium risk; while Cu (69.84%) and Cd (82.5%) have a very high risk according to their RAC score. Compared with SDD and Na_2S, SGA and TBA show an excellent overall solidifying performance due to their multiply hydrosulfide groups that bind with heavy metals very efficiently. The obtained results indicate that the leaching content of Cd, Ni, Pb and Zn is higher than the thresholds prescribed in GB5085.3-2007, and the excessive acetic acid makes its binding capacity stronger in HJ/T 300-2007 than in TCLP 1311.

1. Introduction

With economic development and improvement in people's living standards in China, municipal solid wastes (MSWs) are produced in increasing quantity [1]. A total of 260 million tons of MSWs were generated in 2013 in China [2], and this amount increases at an annual rate of about 8% to 10%. How to dispose these MSWs has become one of major concerns to environmental managers [3]. At present the main method of MSW disposal is still landfill burying, even though it can cause groundwater pollution [4]. However, due to rapid urbanization in recent years, landfilling space has become ever scarce in China which, in turn has increased the cost of disposal [5]. Another method of disposal known as municipal solid waste incineration (MSWI) is gaining popularity due to its environment friendliness [6], advantages of hygienic control over solid wastes, and high capacity that can reduce waste material by about 90% in volume and 70% in weight. Besides, energy from incineration can be used to generate electricity [1,5,7–11]. Thus, it has become

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an attractive alternative for MSW disposal in China. For instance, MSWI has been increasingly adopted by a number of municipalities in recent years, with 18% of MSW disposed in this way [1,5,12–17].

However, the MSWI method of disposal faces the problem of how to deal with the substantial quantity of solid residues which fall into two groups of bottom ashes and fly ashes (FA) [8]. The former is not a hazardous waste that can be recycled as construction materials [18]. The latter also contains a high level of potentially toxic metals such as Pb, Cd, and Zn which can be easily precipitated into the surface, leached into the groundwater if not treated properly. This may cause significant harm to the environment and human health [11]. Consequently, MSWI fly ashes are considered as hazardous waste in many countries [11,18–21].

Generally, the various treatment methods for eliminating the harmful impact of these metals in MSWI FA can be grouped into three classes [8,21]: (i) metal isolation using water-extraction and electrodialytic [11,22–24]; (ii) heat treatment, such as sintering, melting, or vaporization [6,25–28], in which FA is melted at temperatures around 1300–1400 °C [27]; and (iii) solidification/stabilization (S/S) in which regulated potentially toxic metals are leached and their mobility reduced via physical encapsulation and chemical stabilization [31]. Although many toxic metals and problematic substances can be extracted for recovery and recycling using the isolation method [11], this process is too complex, and requires post-treatment of wastewater. In the second method, heavy metals are either incorporated in the vitrified residue or separated from the residue via evaporation [27], but some metals cannot be completely vaporized. The remnants of unevaporated metals could cause secondary pollution [27–30]. By comparison, the last method does not have such disadvantages as pollutant mobility is reduced via solidification with cement-based materials [32–35], which makes the final mass double in volume [8]. In order to solve this problem, both inorganic chemical solidifying agents, such as ferrous sulphate, iron oxides [36–39], sodium hydrosulphide hydrate [40], sodium sulfide or polysulfide [18,41]. hydroxide, carbonates [8], H_3PO_4 [42], phosphates [43], silicates [31,44], geopolymers [10,45]; and organic solidifying agents or chelators [46], such as ethylene diaminetetracetic acid (EDTA) and thiodiglycolic acid (TGA) [47], thiourea [11,15,41,48], sodium diethyldithiocarbamate trihydrate [8], pyrrolidines, imines, carbamates and thiols [49,50] have been used to stabilize such metals. Of the two chemical solidifying agents, organic solidifying agents have received more attention due to their low cost, room temperature hardening, flexibility and capability to immobilize and stabilize hazardous wastes without additional pre-treatment (such as pH control) required [10,51]. More importantly, they require much less area and dosage than inorganic agents. For instance, the dosages of organic solidifying agents required are generally around 2–5% of waste residues [49], while the dosages of inorganic solidifying agents may exceed 10% [42,49]. Therefore, organic solidifying agents have been explored extensively. So far carbamates have been the most common chelating agents owing to their complexion of heavy metals with the organic sulphide group [51–53]. However, it is not so stable as it contains only a single dithiocarboxy chelating group. Thus, there is a need to develop new heavy metal solidifying agents with more chelating groups which can potentially improve their stability [23].

In a previous work, the authors have managed to successfully synthesize two heavy metal chelating agents, tetrathio bicarbamic acid (TBA) with two organic sulphide chelating groups, and sixthio guanidine acid (SGA) with three organic sulphide chelating groups [54–56], and tested their performance in precipitating heavy metals in printed circuit board (PCB) wastewater treatment and in situ remediation of heavy metal-contaminated soils [54–56]. Experiment results showed that both TBA and SGA exhibit good stability, which suggests that such agents with multiple chelating groups may be effective at stabilizing or solidifying heavy metals in MSWI FA.

Furthermore, the hazard imposed by potentially toxic metals is related not only to their total metal concentration but also to their mobility and toxicity [15,57]. Therefore, leaching investigations are ordinarily required to predict both the potential mobility of heavy metals to groundwater and their bioavailability to plants under natural conditions [58]. Many countries released their own toxicity characteristic leaching procedure. Among them, TCLP 1311 [59] (EPA 1311 of US EPA) has been extensively used in previous studies. While in China, HJ/T 299-2007 [60] and HJ/T 300-2007 [61] have been applied to assess the leaching toxicity of MSWI FA in the literature. However, the nature controlling the leachability difference in the TCLP 1311, the HJ/T 299-2007 and HJ/T 300-2007 has not been studied in-depth yet.

This paper investigates the content, specification distribution, and risk assessment code of targeted heavy metals and potentially toxic metals in FA collected from a MSWI plant in China. This study aims to (1) evaluate the heavy metal S/S efficiency of two novel chemical solidifying agents (SGA and TBA) and compare their performance with that of two traditional ones (SDD and Na_2S) in stabilizing MSWI FA; and (2) assess heavy metals leachability before and after FA is solidified/stabilized according to the TCLP 1311, the HJ/T 299-2007 and HJ/T 300-2007, which will contribute to a better understanding of the nature of the leaching process.

2. Materials and methods

2.1. Materials and chemicals

Analytical-grade guanidine hydrochloride, hydrazine hydrate, carbon disulfide, acetone, ethanol, potassium hydroxide, potassium phosphate, sodium sulfide, chlorhydric acid, perchloric acid, nitric acid, acetic acid, hydroxylamine hydrochloride, hydrogen peroxide, and ammonium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and Nanjing Chemical Reagent Co., Ltd. (China). SDD were obtained from Aladdin-reagent Co., Ltd. (China). All the materials were utilized without any further purification. SGA and TBA was synthesized according to the prescribed procedures [55–57], respectively (see Supplementary information page for further details).

The FA used was collected from a MSWI plant in Shenzhen, China on a typical day of operation in May of 2013. The waste incinerator used is Keppel Seghers' robust multi-stage reciprocating grate flip, and flue gas cleaning is used by Keppel Seghers' semi-dry scrubbing- activated carbon-fabric filter system. Its waste incineration and fly ash stabilization process is summarized as a flowchart in Scheme 1 according to the industrial treatment process.

The FA sample was homogenized after collection, dried in an electrically heated drying cabinet (Shanghai Jing Hong Laboratory Instrument Co., Ltd., DHG-9240A), and then sieved to <2 mm for analysis in this work.

2.2. Analytical apparatus and methods

2.2.1. Speciation identification of heavy metals in FA

The total concentration of targeted heavy metals in the dried FA was determined with the assistance of the X-ray fluorescence (XRF) elemental analyzer (XL3t, Thermo Scientific Niton Co., US) [10,27,45]. The FA sample was analyzed in triplicate, and the results reported in this study were the average values with standard deviation.

A modified three-step sequential BCR extraction procedure (Table S1) was used to examine speciation of heavy metals in the FA sample before and after S/S [62,63]. The concentration of cer-