Cement solidification of the tailings after flotation of medical waste incinerator fly ash

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A B S T R A C T

Medical waste incinerator (MWI) fly ash contains a large amount of carbon constituents and dioxins, which could be removed by flotation. Simultaneously, chlorides could be washed out. In this paper, the cement solidification of the flotation products (tailings) was executed and compared with that of MWI fly ash. Results revealed that the water demand of cementitious mixtures with MWI fly ash was higher than that with the tailings, and the setting time of test block with MWI fly ash was longer than that with the tailings. The compressive strength and heavy metal stabilization effect of test block of the tailings was better than those of MWI fly ash. After 7d curing, the compressive strength of test block of the fly ash met the threshold of 0.35MPa for the landfill’s requirement only when above 70% cement ratio is mixed, and those of all test block of the tailings meets the requirement. In order to make the leaching concentration of heavy metals in test block meet landfill standard, the ratio of fly ash and the tailings in test block should be controlled below 30% and above 60%, respectively.

Keywords: Fly ash; Heavy metals; Cement solidification; Flotation; Chlorides

1. Introduction

Incineration is an effective approach to realize the harmlessness and reduction of medical wastes and has become popular in China [1]. Because of the presence of a large number of chlorine-containing plastics and disposable disinfectants (such as NaCl and KCl), the chlorine level in the typical medical wastes is 1.1–2.1%, which is approximately twice as high as that in domestic wastes [2]. After incineration, most of chlorine in medical wastes can migrate to medical waste incinerator (MWI) fly ash [3]. In addition, incinerator flue gas contained with a considerable amount of dioxins and heavy metals will be produced after incineration of medical wastes. These pollutants emitted from incinerators usually can be captured by the injected powder active carbon (PAC) and then removed by the bag filter in flue gas. The air purification system of the medical waste incinerator needs to inject more PAC than that of domestic waste incinerator (DWI) due to more amount of dioxin emission and the strict dioxin emission standard [4]. The injection amount of PAC can be up to 800 mg/Nm\(^3\) so as to purify the flue gas from MWI [5]. These PAC are accumulated in the bag filter originally and finally become a part of MWI fly ash. In addition, there are 3 wt.% to 10 wt.% of unburned carbon in MWI fly ash, and these two kinds of carbon constituents can lead to 11.4–91.0% of carbon content in MWI fly ash [6]. Besides, MWI fly ash was listed as hazardous waste because of its high levels of heavy metals (such as Pb, Cr, Cd, Cu, and Zn) and dioxins, which may pose environmental threat.

Flotation is a physicochemical separation technique, in which gas bubbles are brought in suspension liquid, according to the difference of hydrophobicity and hydro-
philicity of different materials. After adding flotation agent in the flotation device, the hydrophobicity material was separated from the suspension by buoyancy of bubbles [7]. In our previous studies, a novel flotation technology was proposed to treat MWI fly ash based on the absorptive characteristics of dioxins on carbon constituents and the hydrophobic and lipophilic properties of both dioxins and carbons. It was found that most chlorides in MWI fly ash were washed out, and dioxins in it were concentrated and transferred into the froth product by flotation [8], which finally could be decomposed by reburning as a fuel or microwave heating [4,9]. For tailings, the toxic equivalent (TEQ) of dioxins was significantly reduced and met the landfill standard value of 3 ng TEQ g⁻¹ for allowable thresholds for landfills, but heavy metal leaching concentrations exceeded the thresholds. Thus, a further treatment of the tailings is required to prevent the environmental pollution from heavy metals.

Cement solidification is recognized as one of the most effective approaches to reduce the mobility of toxic heavy metal pollutants, which is widely used to treat industrial residues, sewage sludge, heavy metal contaminated soil, and incinerator fly ash [10]. This technology involves the formation of hardened and durable cement solidification body (monolithic material) and the reduction of the leaching concentrations of heavy metals [11]. During cement solidification of incinerator fly ash, cement hydration might be delayed because of the existence of the mixed fly ash, which depended on mixed ratios, curing ages, and ash composition [12,13]. The characteristics of high chlorides and carbon content make it difficult for the cement solidification to be applied directly to the treatment of MWI fly ash. High-level of soluble chlorides in incinerator fly ash might hinder hydration in cementation and have a negative effect on the stabilization of the solidified matrix. Then, water washing pretreatment is proposed to remove chlorides and minimize its influence [9,14]. It was found that PAC existed in fly ash was beneficial to the adsorption of phenol in cement solidified bodies, but cement test block contained with PAC was found to have a lower compressive strength than that without PAC [15,16].

High chlorides and carbon contents are important characteristics for MWI fly ash, however, the effect of which on cement solidification is rarely reported. In this paper, the cement solidification of MWI fly ash and the tailings was executed and compared, and the water demand for normal consistency, setting time, compressive strength and leaching toxicity of both kinds of cement solidified bodies were tested. And the objective of this research is to investigate the effect of chlorides and carbon constituents on cement solidification and verify the feasibility of integrating the flotation and solidification techniques for the detoxification of MWI fly ash.

2. Materials and methods

2.1. Materials

The raw fly ash (ash sample) was collected from a MWI in South China. The flue gas purification method of the incinerator is PAC injection followed by bag filter. Ash sample was dried for 24 h under the atmosphere of 383 K before the subsequent operation. Part of fly ash was treated with flotation column with 30 mm in diameter and 950 mm in height [17]. Compressed air (0.06 m³/h) was introduced into the column through a rotameter. In every run, 3 g fly ash and 600 ml of deionized water was stirred in a hybrid mixer for 5 min. After that, 12 g/kg of collector (kerosene) and 2 g/kg frother (methyl isobutyl carbinol) were added subsequently and conditioned for 5 min. The slurry was then transferred into the column. Two types of product froths and the tailings were obtained, respectively. After flotation, the tailings products were carefully vacuum-filtered by the membrane filter (0.45 µm), dried for 24 h under the atmosphere of 383 K. Loss on ignition (LOI) was defined according to the standard of GB18485-2001 and determined as the weight loss of the subsample in the condition of 3 h and 873 ± 25 K [18].

2.2. Methods

Fly ash and 325 Ordinary Portland Cement (OPC) were mixed in a certain proportion, the mass ratios of fly ash in the mixture were 15%, 30%, 45%, 60% and 75%, respectively (referred to as F15, F30, F45, F60, F75). Deionized water was added to the mixture according to the measured standard consistency and stirred for 3 min. After mechanically stirring the mixture of fly ash, cement, and water to yield homogenous slurry, the sample was poured into 40 mm × 40 mm × 40 mm steel cube molds and compacted by means of a vibrating table to yield good packing of the mixture. Similarly, cement solidification of the tailings were executed and the mass ratios of tailings in the mixtures were 15%, 30%, 45%, 60% and 75%, respectively (referred to as T15, T30, T45, T60, T75). Besides, the water demand for normal consistency and setting time were tested according to Chinese National Standard GB/T 1346-2011. And the setting time of a cementitious mixture was referred to as the period when water was introduced into the mixture system to the onset of hardening.

After 24 h, these test blocks were demoulded and stored at 90%± 5% relative humidity, 20 ± 2°C for 3 d, 7 d, 14 d and 28 d, respectively. At different curing ages, the specimens were removed, and the unconfined compressive strength (UCS) was measured by YE-300. The crushed sample was washed in a mixture of anhydrous ethanol and acetone, and the hydration reaction was ended. Then the crushed sample was dried and stored for the subsequent leaching tests.

The sample were further crushed manually until the particle size was less than 9.5 mm and subjected to a leaching test specified in the Chinese solid waste extraction procedure for leaching toxicity-acetic acid buffer solution method (HJ/T300-2007). 17.25 mL reagent of glacial acetic acid was diluted using deionized water, the pH value of the solvent was adjusted to 2.64 ± 0.05. Subsequently, the extraction was performed for 18 ± 2 h at a liquid/solid ratio of 20:1 and the rotational speed was fixed at 30 ± 2 r/min. After the extraction, the leachate samples were filtered through a 0.45 µm and analyzed using AA800 to determine the concentrations of heavy metals of Cu, Zn, Cd, and Pb. To ensure validity and reliability of data, all the tests were carried out as a minimum in duplicate and the results were determined as the average of the measurements.
3. Results and discussion

3.1. Effect of flotation on ash characteristics

The chemical compositions and LOI of the MWI fly ash and the tailings were presented in Table 1. The major components of fly ash were CaO, SiO₂, Na₂O, and Cl. A considerable amount of Cl (31.4%) was observed in MWI fly ash, which may be related to the high chloride contents in raw medical wastes [9]. CaO, SiO₂, and Al₂O₃ emerged as major components in the tailings because of large amounts of chloride dissolution, which was mineralogically similar to coal fly ash and might have pozzolanic properties [18]. At the same time, chloride content in the tailings decreased to 4.8% after flotation. The LOI of fly ash reached up to 31.2%, which was approximately three times higher than that of the DWI fly ash [6]. Similarly, the flotation process removed large amounts of carbon from fly ash and resulted in 4.8% of LOI in the tailings. After flotation, the dioxin concentration in the tailings was only about 1.7 ng I-TEQ/g lower than the standard value for landfills in China (3 ng I-TEQ/g). On heavy metals, the large amount of Zn in medical waste may come from syringes, waste plastics, rubber, and medical adhesive plastic. The usage of PVC plastics in MW usually contributes to Pb- and Cd-loads in medical waste [19]. The plasticizers and adhesives included in the packaging of MW always contain Cu, Zn, and other heavy metals because of the frequent usage of aluminum foil, PET, PVC, and PP [20]. Most of Zn, Pb, Cu and Cd would migrate or concentrate in the fly ash during incineration of medical waste. Therefore, this paper mainly studies the leaching concentrations of Zn, Pb, Cu and Cd (Table 1). Heavy metals in the fly ash will be allocated between three products of the froths, waste water and the tailings after flotation. The content of Pb in the tailings was higher than that of fly ash, and the content of other heavy metals is relatively low. On the one hand, flotation was similar to the water-washing process and increases the content of heavy metals in the tailings because of the removal of soluble chloride [16]. On the other hand, the soluble state of some heavy metals will enter the wastewater, which would decrease the content of heavy metals in the tailings.

3.2 Effect of flotation on water demand for normal consistency

Water demand for normal consistency of cementitious mixtures with different ratio of fly ash and the tailings is shown in Fig. 1. With the increase of fly ash and the tailings were added, the water demand for normal consistency increased, which was similar to those reported by Shi [10]. The water demand of OPC was 29%. The water demand of fly ash increased from 35% to 53% when the fly ash ratio increased from 15% to 75%, correspondingly, that of the tailings increased from 34% to 46%. The water demand of cementitious mixtures with fly ash is obviously higher than that of the tailings, which may be related to the fact that fly ash contains more porous PAC. Besides, high water demand might reduce the compressive strength of solidified products and enhance the risk of heavy metal leaching [11].

3.3. Effect of flotation on setting time

It is reported that the initial and final setting time for OPC in China should not be less than 45 min and more than 10 h, respectively. The setting time which is the difference between final setting time and initial setting time of ash-cement mixture should generally be less than 48 h in Italy [21], but there are no relevant standards in China.

The setting time of cementitious mixtures with different ratios of fly ash is shown in Table 2. Both initial setting time and final setting time of test block with fly ash-cement mixture should generally be less than 48 h in Italy [21], but there are no relevant standards in China.

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3.4. Effect of flotation on compressive strength

UCS is an important factor to decide whether ash-cement test block can be put into a landfill. There is no definite standard for UCS of fly ash cement solidified body in China. According to the American strength standard, UCS of the test block must be greater than 0.35 MPa [22].

UCS of test block of fly ash at different curing time is shown in Fig. 2. The compressive strength decreased obviously with the increase of fly ash ratio. This phenomenon has also been confirmed by some researches [12,13], which can be analyzed from three aspects. Firstly, the cementitious activity of incineration fly ash was lower, and it would delay the hydration of cement as the addition of fly ash [10]. Secondly, the high ratio of fly ash resulted in the relative increase of water demand of test block and the increase of capillary pore, which decreased the strength of cement solidification in later period. Thirdly, carbon constituents in MWI fly ash not only might reduce the cement hydration products, but also destroy the connection structure of hydration products. At fly ash ratio of 15%, 30%, 45%, 60% and 75%, these test block limited 7-d compressive strength to 39.7%, 3.6%, 0.9%, 0.7% and 0.4% of that of OPC, respectively. Especially, the 7-d strength of ash-cement test block with above 30% fly ash ratio was lower than 0.35 MPa, which means that 70% cement should be added considering the compressive strength of ash-cement test block.

Comparing with MWI fly ash, the compressive strength of test block with the tailings was high at the same curing time and ratio (Fig. 3). Moreover, it was observed that 7-d compressive strength values of all the solidified samples exceeded the minimum guideline of 0.35 MPa [22]. The compressive strength of OPC at 7 d and 28 d were 16 MPa and 32.8 MPa, respectively. The early strength of specimen with above 30% ratio of the tailings was relatively less, but the differences between test block of OPC and those of the tailings were reduced in the later ages. This also proved that the cementitious activity of test block with the tailings was weak at early ages, but partial of the tailings still participated in hydration reactivity [10].

For MWI fly ash, only the samples with the ratio of 30% fly ash met the UCS regulation, but all the tailing samples were in compliance with the regulatory limits of landfill. The results might be related to the removal of chlorides and carbon constituents after flotation. Firstly, ettringite is one of the main products of cement hydration, which provides primarily the early strength of test block by the self-cementing ability [11]. High content of chlorides in the MWI fly ash essentially affect the hydration of the aluminate phases of the cement by particularly forming Friedel’s salt, which might reduce of formation of ettringite and slow down the development of the early strength [6,23]. Secondly, comparing with the tailings, high levels of carbon constituents in MWI fly ash might lower the strength by causing structural discontinuity within the test block. Especially, PAC distributed in the test block could impede hydration and pozzolanic reactions [14]. Thirdly, the compressive strength correlated nicely with the water demand and hydration degree [24]. For test block from MWI fly ash, water demand was higher than that from the tailings, which could produce bubbles and chinks in the solidified samples, and then reduce the compressive strength [14].

3.5. Effect of flotation on leaching concentration of heavy metals

The leaching concentration threshold of heavy metals such as Pb, Zn, Cd, Cu, Cr, Hg, As, Ni, Ba, Be and Se in...
waste is stipulated in the standard for pollution control on the landfill site of domestic solid waste (GB16889-2008). Heavy metals such as Ba, Be and Se are very few in the incinerator fly ash, and there is hardly any research on them. The volatile metal As and Hg mainly exist in gaseous form during waste incineration, a few remain in incinerator fly ash. Some lithophile heavy metals Ni and Cr with low volatility mainly exist in bottom ash, only a small amount of them is possibly carried into fly ash by solid particles in flue gases, and their leaching concentration in fly ash were relatively low, and no further research in this paper. Their leaching values in MWI fly ash and the tailings is presented in Table 3. The leaching concentrations of Zn, Pb and Cd in MWI fly ash and the tailing were much higher compared with the limit values, which mean that they cannot be filled in the landfill site of municipal solid waste.

Immobilization mechanisms of heavy metal during cement hydration process are very complex, which change with matrix materials structure [25]. The migration of heavy metal ions is hindered or absorbed by the products of the cement hydration reactions. Two important hydration products, C-S-H and AFt, are considered to play an important role in the solidification/stabilization of heavy metals. C-S-H with high-density hydrogen bonding and high specific surface area acts as a barrier onto the surface of the solid wastes, which can tightly bind heavy metals such as Pb$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$with strong chemical adsorption. C-S-H has significant cation exchange capacities, Ca$^{2+}$, Al$^{3+}$, and Si$^{4+}$ in the test block are easily replaced by heavy metal cation [26]. Heavy metal anions Zn$^{2+}$ can replace the Ca$^{2+}$ in C-S-H or react with Ca to produce less reactive (CaZn$_n$(OH)$_2$H$_2$O) [27]. Pb$^{2+}$ in C-S-H cannot replace Ca$^{2+}$, but it can be fixed in C-S-H in the form of (Pb(OH)Cl) and carbonate precipitation [11]. AFt can absorb and immobilize the heavy metals through the chemical adsorption and isomorphic replacement, and it have a very strong lattice binding effect on heavy metal ions. At same time, Cd$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, and other metal ions could replace Ca$^{2+}$ [26].

Leaching concentrations of heavy metals in test block of fly ash for 7 and 28 d are shown in Figs. 4 and 5, respectively. The stabilization effect on heavy metal ions is hindered or absorbed by the products of the cement hydration reactions. Two important hydration products, C-S-H and AFt, are considered to play an important role in the solidification/stabilization of heavy metals. The hydration product C-S-H increased and the porosity of the test block decreased.

The dashed line represents the limit of standard of Pb and Cd for landfill standard of domestic waste landfill. There is no dashed line of Zn and Cu on the graph, because their leaching concentration of all samples was below the regulatory limitation. Among the four heavy metals, the highest leaching concentration of Zn is related to its high content in fly ash. The leaching concentrations of Pb in F15 and Cd in F15 and F30 met the landfill standards after 7 d curing period, and that of Pb in F30 also satisfied the standards after 28 d. Leaching concentrations of heavy metals in test block of the tailings for 7 and 28 d are shown in Figs. 6 and 7, respectively. It can also be observed that the lower ratio of tailings is, the lower leaching concentrations of heavy metals are. At 7 d, the leaching concentrations of Pb and Cd met the landfill standards when the mass ratios of fly ash in the mixture are below 45%, and the leaching concentrations in T60 at 28 d can also keep in the range of landfill standard of domestic waste landfill (dashed line). Therefore, considering the stabilization effect of heavy metals, the ratio of fly ash in cement test block should be 30% or less, in contrast, the value of the tailings can reach 60%.

Compared with fly ash test block at the same time and the same proportion, the leaching toxicity of solidified
heavy metals from the tailings was obviously lower, though the content of all heavy metals in fly ash was higher. This is related to heavy metals such as Pb and Cd existing soluble form mainly include chloride and carbonate in fly ash. After flotation, part of the chloride of heavy metals might be dissolved in solution, the mobility of heavy metals in the tailings would be decreased. On the other hand, the hydration reaction of test block from the tailings was better than that of fly ash, incorporation of hydration product would decrease the mobility of heavy metals in the tailings [10]. During the process of hydration reaction of test block, the soluble chloride might migrate from inside to the outside of structure and re-precipitate on the surface. Thus, the high content of chloride in fly ash could degrade the performance of cement hydration and induce the structural discontinuity of the C-S-H gel, which would decrease the immobilization effect on heavy metals [28]. Therefore, the decrease in chloride content in the tailings might explain the decrease in the amount of leaching heavy metals. Furthermore, the large amount of chloride in fly ash would react with aluminate in cement and generate Friedel’s salt [24]. There was competition between the formation of Friedel’s salts and AFt, which would reduce the formation of AFt in solidified solids of fly ash. There are more AFt and C-S-H in test block of the tailings than those of the fly ash, which was beneficial to the stability of heavy metals [10].

In addition, high content of PAC in fly ash brought a lot of pore; acid buffer solution easily penetrated the pore of the test block during the extraction process, resulting in the leaching of heavy metals [29].

### 3.6. Proposed procedure combined with the flotation and cement solidification of MWI fly ash

As can be seen from the above results of both the compressive strength and heavy metal leaching, the maximum ratio of MWI fly ash in the cement test block before landfill disposal should be controlled below 30%, that is, the cement ratio should reach above 70%. Therefore, the disadvantages of direct cement solidification treatment of MWI fly ash were as follows. Firstly, high cement usage would cause environmental burden and economic impacts. At same time, it would increase waste volume, which would occupy a large amount of landfill space and significantly increase the capital investment of landfill construction. Secondly, cement solidification of MWI fly ash requires a long setting time because of the presence of high content of chloride salts and carbon constituents, resulting in low solidification efficiency. Thirdly, this process is inappropriate for long-term containment of toxic organics such as dioxins. Most organics do not react with the cement due to their large differences between hydrophobicity and polarity, which make hazardous organic contaminants being inefficiently immobilized within the test block [30]. Fourth, carbon constituents in MWI fly ash after solidification become useless and non-renewable resources, which cannot realize the utilization of MWI fly ash. From the point of view of environmental protection and sustainable development, direct cement solidification method is not suitable for treating MWI fly ash.

By employing flotation pretreatment, carbon constituents and dioxins will be separated from MWI fly ash (Fig. 8), and almost quantitative soluble chloride will be simultaneously washed out. After separation, the froth product enriched with carbon constituents and dioxins can be dried and delivered to the combustion chamber of incinerator for reburning, which can destruct of dioxins and recycle carbon constituents as energy. The toxicity of the tailing product will be decreased greatly, and their quality was reduced to less than 20% of fly ash. These tailings after simple dehydration can directly mix with cement to complete the solidification, and the process is relatively simple. Moreover, only 40% cement ratio is needed for solidification of the tailings, which greatly reduces the consumption of cement. After cement solidification, the stabilization efficiency of the heavy metals increases very much and their leaching toxicity concentrations are in the safety range due to no interference of chloride and carbon constituents on cement solidification.

Because the composition of fly ash is very complex, it is difficult to get a detailed effect mechanism of carbon constituents or chlorine salt on cement solidification/stabilization. To elucidate the effect mechanism, it is necessary to add different dosage of pure PAC and chloride such as NaCl in the tailings in our later research, respectively. In
additions, the effect of other interferences such as heavy metals and organic compounds on compressive strength of solidified sample should be further studied.

4. Conclusion

Cement solidification of MWI fly ash poses some problems such as high water demand, long setting time, low compressive strength, high volume of test block and high leaching concentration of heavy metals, because of the presence of high content of chloride and carbon constituents. Considering the compressive strength, it is necessary that a percentage of MWI fly ash in the test block is below 30%. Consideration of heavy metal leaching toxicity, the ratio of fly ash in cement test block must be 30% or less, and the value of the tailings can reach 60%. Direct cement solidification method is not suitable for treating MWI fly ash, and the techniques integrating the flotation and cement solidification for the detoxification of MWI fly ash is suggested.

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References


