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Utilization of washed MSWI fly ash as partial cement substitute with the addition of dithiocarbamic chelate

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Abstract

The management of the big amount of fly ash as hazardous waste from the municipal solid waste incinerator (MSWI) has encountered many problems in China. In this study, a feasibility research on MSWI fly ash utilization as partial cement substitute in cement mortars was therefore carried out. MSWI fly ash was subjected to washing process to reduce its chlorine content (from 10.16% to 1.28%). Consequently, it was used in cement mortars. Ten percent and 20% replacement of cement by washed ash showed acceptable strength properties. In TCLP and 180-day monolithic tests, the mortars with washed ash presented a little stronger heavy metal leachability, but this fell to the blank level (mortar without washed ash) with the addition of 0.25% chelate. Therefore, this method is proposed as an environment-friendly technology to achieve a satisfactory solution for MSWI fly ash management.

Keywords: MSWI fly ash; Heavy metals; Leaching; Compressive strength; Dithiocarbamic chelate

1. Introduction

Incineration has become a preferred option to dispose municipal solid waste (MSW) in big cities (e.g. Shenzhen, Shanghai, Beijing, Tianjin, Guangzhou, Hangzhou) in China. Nowadays, there are about 70 MSW incinerators (MSWI) and the total capacity has reached 33010 t/d (China Statistical Yearbook, 2006). The pollutants generated in the incineration process are trapped in the air pollution control system with production of a big amount of fly ash. MSWI fly ash with concentrated heavy metals (e.g. Cd, Cr, Cu, Ni, Pb) and organochlorine compounds is considered as hazardous waste and requested to be disposed of in hazardous waste landfills after the immobilization of heavy metals. However, most cities have no hazardous waste landfill and although a few cities (e.g. Shenzhen, Shanghai, Tianjin) have such, their limited landfill capacity is not enough to contain the MSWI fly ash. In addition, MSWI fly ash is almost out of control. Hence, finding an alternative way for the disposal of MSWI fly ash has been an essential issue in these cities.

The reuse of industrial waste in basic municipal constructions has been a common practice for a very long time now. For instance, coal fly ash is reused successfully in cement, concrete, and roadbed. It has been shown that without pollutants and chlorine, MSWI fly ash is mineralogically similar to coal fly ash, and hence has pozzolanic properties (Huang and Chu, 2003). MSWI fly ash can also be added into cement mortars or concrete as substitute or inert aggregate (Collivignarelli and Sorlini, 2002). Rémond et al. (2002) had incorporated fly ash into the hydration model. The results showed that the MSWI fly ash essentially affects the hydration of the aluminate phases of the cement by particularly forming Friedel's salt. The reactions between chlorides and aluminates lead in particular to a high sulfate concentration in the interstitial solution of cement pastes, which slows down the transformation of ettringite into monosulfoaluminate. Chlorine concentrations from 5% to 20% in MSWI fly ash exceed

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the maximum allowable concentration in most cement mixtures. In the meantime, Mangialardi (2004) found a four-stage washing process to be able to convert the raw MSWI fly ash into a material with improved chemical characteristics for its incorporation into cementitious matrices. As a result, the cementitious mixtures incorporating washed fly ash in place of raw fly ash were found to exhibit better performance characteristics in terms of setting, dimensional stability, compressive strength, and environmental quality. Specifically, it has been demonstrated MSWI fly ash that was subjected to a washing process to reduce its chloride content has about the same property on the concrete 28-day compressive strength as common coal fly ash when the 30% of the cement was replaced by ashes (Bertolini et al., 2004). Moreover, the physical properties of fresh and hardened concrete are not deteriorated (Aubert et al., 2004). Aubert et al. (2006) developed a conventional process based on the washing, phosphation and calcinations of MSWI fly ash to make the utilization of MSWI fly ash in blended cement safe and feasible, and furthermore, a modified process intended to eliminate metallic aluminum and sulfate to improve the quality of the ash.

Another essential issue regarding the reuse of MSWI fly ash is the environmental impact of the pollutants. The removal of organochlorine compounds is generally done by the melting process (Abe et al., 1996) or a low-temperature dechlorination process (Ishida et al., 1998; Wang et al., 2006). The leaching behavior of heavy metals from fly ash is mainly pH dependent due to the solubility product of hydroxide, so the heavy metal leachability would increase in the long-term as pH decreases in the condition of acid rain or organic acid solution. The most common stabilization/solidification (S/S) processes are based on the use of hydraulic binders or chemical agents. The use of cement for hazardous waste S/S disposal has an extensive documented history and well-established technology (Glasser, 1997), but the increase volume of products leads to a high landfill cost. Cement S/S has encountered some difficulties in MSWI fly ash, like the enhancement of leachability of amphoteric heavy metals (Pb and Zn), for instance. Mizutani et al. (2000) compared different chemical agents (a chelating agent, phosphate and ferrite) used for the treatment of MSWI fly ash. The authors concluded that the chelating-treated material showed a high reducing capacity and strong retention for metals over a wide pH range, while the phosphate-treated material showed a significant decrease in availability (especially for Pb), and the ferrite treated material showed an increased physical retention. Moreover, Jiang et al. (2004) investigated heavy metal stabilization in MSWI fly ash by heavy metal chelating agents. The results indicated that the heavy metals in fly ash can be stabilized more effectively by using a kind of dithiocarbamic chelate than by using chemical agents such as sodium sulfide and lime by the formation of coordinated complex. Also, the coordinated complex is stable and then the heavy metal leachability is not pH dependent.

Therefore, the aim of this study is to achieve a safe utilization of MSWI fly ash. Fly ash was subjected to a washing process to reduce its chlorine content before use, while chelate was added to reduce heavy metal leachability. We focused on compressive strength property and heavy metal leachability from mortars to evaluate the physical properties and environmental impacts of this utilization.

2. Materials

MSWI fly ash used in this study was from the Hangzhou MSW Incineration Plant. The plant uses reciprocating stoker incinerators and semi-dry lime adsorption and bag filters as air pollution control system. The ash samples were stored in dry and sealed containers (avoiding hydration and carbonation). Table 1 shows the heavy metal content of MSWI fly ash. Notably, Pb and Zn were the most abundant species. The total amount of heavy metals was about 2.65% of the dry weight of MSWI fly ash. Meanwhile, Table 2 shows the results of the toxicity characteristic leaching procedure (TCLP, a standard method to determine waste leaching toxicity by US EPA) of MSWI fly ash. The concentration of Cd and Zn inflected the potential toxicity and inapplicability of considering MSWI fly ash as normal waste.

The cement used as received was ordinary Portland cement 32.5R, and the sand was the China standard sand produced by Xiamen ISO Standard Sand Co., Ltd. The water used for making and curing cement mortars was tap water, and for the leaching test was de-ionized water (pH = 7.67). The chemical agent used to stabilize heavy metals was a kind of dithiocarbamic chelate. The chelate was synthesized experimentally through the reaction by different types of polyamine or polyethyleneimine and carbon disulfide in alkaline conditions (Jiang et al., 2004). The schematic structure of the chelate and the heavy

Table 1
The heavy metal content in MSWI fly ash (g/kg)

Sampling date	Cd	Cr	Cu	Ni	Pb	Zn	Total
4/16/2005	0.29	0.24	0.74	0.08	5.33	17.61	24.29
4/27/2005	0.35	0.28	0.39	0.09	5.67	19.30	26.07
5/10/2005	0.41	0.24	0.37	0.10	5.44	22.72	29.27
Average values	0.35	0.25	0.50	0.09	5.48	19.88	26.54

Table 2
TCLP test results of MSWI fly ash (mg/L)

Sampling date	Cd	Cr	Cu	Ni	Pb	Zn
4/16/2005	1.12	0.05	0.88	0.36	0.42	42.34
4/27/2005	3.05	0.27	0.92	0.23	0.56	43.84
5/10/2005	2.35	0.42	0.21	0.14	0.43	36.99