J Mater Cycles Waste Manag (2008) 10:14–18
DOI 10.1007/s10163-007-0192-y

SPECIAL FEATURE: ORIGINAL ARTICLE

The 4th International Conference on Combustion, Incineration/Pyrolysis and Emission Control (4th i-CIPEC)

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Lead immobilization in mechanochemical fly ash recycling

Received: March 15, 2007 / Accepted: August 31, 2007

Abstract In previous studies, we focused on a mechanochemical process for recycling fly ash for use in cement; this process was expected to immobilize heavy metals in the fly ash, a desirable outcome in light of the fact that recycled fly ash is commonly used in the synthesis of inorganic materials. Here, we investigated the leaching of lead (Pb) from fly ash treated by a mechanochemical process and from cement prepared from the treated fly ash. We used lead oxide (PbO), a typical Pb compound in fly ash, as a model substance. Mechanochemical treatment of the fly ash inhibited Pb leaching by 93%, and further inhibition (more than 99.9%) was observed in cement produced from the treated fly ash. During the mechanochemical treatment, PbO was reduced to Pb by iron from the stainless-steel mill used for processing, and the lower solubility of Pb in water resulted in immobilization of the Pb.

Key words Mechanochemical process · Fly ash · Leaching · Lead (Pb) · Immobilization mechanism

Introduction

Fly ash generated by municipal solid waste incinerators is a controlled waste in Japan. It is hazardous because it contains high concentrations of dioxins and heavy metals such as lead; Japanese law requires that fly ash be rendered harmless before its disposal in landfills. Many existing landfill sites in Japan will reach their capacity within a few years, but there is insufficient space for new sites, and the construction of such sites is often opposed by local residents.[1] Alternative methods for disposal of solid wastes have been developed. For example, melting technology is promoted as a means of reducing the volumes of solid wastes such as fly ash to conserve scarce landfill space. This technology separates heavy metals from fly ash, decomposes dioxins, and produces recyclable fused slag by-products. However, melting facilities are costly to build and maintain, the exhaust gases must be treated, and high-temperature treatment carries a risk of accidents.[2] An eco-cement plant that produces cement from incinerator residues such as bottom and fly ash has been operating in Chiba, but this process faces concerns similar to those faced by melting technologies.[3,4] Because of these problems with existing technologies for the detoxification and recycling of fly ash, the development of a novel method that is reliable and environmentally safe is urgently required.

In previous studies, we focused on mechanochemical (MC) treatment with a ball mill to recycle fly ash for use in cement. MC treatment, in which mechanical energy transmitted via balls to a target substance is used to drive certain chemical reactions, is beginning to be applied in other areas,[5–8] for example, as a novel approach to the degradation of hazardous substances such as organochlorine compounds in polluted soil.[9–12] The MC treatment of fly ash in the presence of calcium oxide (CaO) as an additive results in the degradation and dechlorination of dioxin in the fly ash.[13] To recycle fly ash for use in cement, dioxins must be degraded and the leaching of heavy metals must be prevented. MC treatment has been used as a method to improve the physical and chemical properties of various inorganic materials and to develop new inorganic materials[14–16]; especially, there are various reports on the MC reduction of metal oxides by grinding with metal or inorganic compounds such as Al, carbon, and SiO_2.[17–20] Therefore, we expected that this process might be useful for immobilizing heavy metals in fly ash.

MC treatment requires no heating and produces negligible gas emissions. Thus, a large plant with sophisticated facilities is not needed, and simple closed-system designs are more likely to be accepted by local residents. The immobilization of heavy metals and the degradation of the dioxins in fly ash by MC treatment may therefore be a practical

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pretreatment method for the safe recycling of the fly ash as a component in cement.

The immobilization effect of MC treatment on the leaching of heavy metals from fly ash and from the cement prepared from the fly ash must be investigated, along with the mechanism of immobilization. Lead (Pb) is one of the most abundant heavy metals in fly ash and is a risk to human health.[21] Therefore, we investigated the leaching of Pb from mechanochemically treated fly ash and from the cement prepared from the fly ash; we also investigated the mechanisms for the observed immobilization of Pb.

Materials and methods

Materials

Fly ash generated from the stoker firing process in a municipal solid waste incinerator was used. CaO (purity 99%; Kanto Chemicals, Tokyo, Japan) was used as an additive to promote the degradation of dioxins during MC treatment[13,22]; before use, the CaO was treated at 800°C for 2h to eliminate water. Aluminum sulfate [$Al_2(SO_4)_3$; purity 99%; Wako, Osaka, Japan] was used as a binder in the production of cement from the MC treatment residue. Lead oxide (PbO; purity 99%) was purchased from Wako.

MC treatment

For the MC treatment process, we used a planetary ball mill (Pulverizette-7; Fritsch, Idar-Oberstein, Germany) with a pair of stainless steel pots (45 cm^3), in each of which seven steel balls (15mm in diameter) were placed; the pots were placed on a rotating disk in such a way that the pots and the disk rotated in opposite directions.

Fly ash (1g) and CaO (4g) were charged into each pot under atmospheric conditions. The planetary ball mill was then operated for at least 2h at 700rpm to ensure dioxin degradation, with a 15-min cooling interval every 15min.[22] After MC treatment, the residue was removed from the pots for Pb leaching tests and for use as a component in cement. In the experiment to investigate the behavior of Pb during MC treatment, 1.8g of PbO was added to the fly ash and CaO mixture.

To confirm that the MC treatment residue could be used as a component in cement, the residue (5g) was cemented with 2g of $Al_2(SO_4)_3$ as a binder, and then water was added to obtain a 60% water content on a weight basis. The mixture was put into a Petri dish (9cm) and cured in water for 1 week and subsequently in air for 1 month to allow the water to evaporate. The resultant cement was subjected to leaching tests.

Analysis

The leaching of Pb from the MC treatment residue and from the cement prepared from the residue was investigated by a leaching test according to Notification No. 46 from the Ministry of the Environment of Japan. In the leaching test, the cement produced from the MC treatment residue was ground to a particle size of less than 2mm, whereas the MC treatment residue was tested without any pretreatment. Distilled water was added to the test samples at 10ml/g and then the mixtures were subjected to reciprocal shaking at 200rpm for 6h. After centrifugation at 1560g, the supernatants were filtered through a membrane filter (0.45µm) and the filtrates were analyzed for Pb by means of atomic absorption spectrometry. The Pb species in the MC treatment residue were also identified by X-ray diffraction (XRD) analysis.

Results and discussion

Pb leaching

The Pb concentration in the leachate from cement prepared with untreated fly ash was 60.8mg/l. From the fly ash content in the cement, the amount of Pb leached from the fly ash in the cement was calculated to be 540µg/g fly ash, which indicates that about 13% of the Pb in the fly ash (4.05mg/g fly ash) was leachable. However, Pb leaching was completely inhibited by the combination of MC treatment and subsequent production of cement with $Al_2(SO_4)_3$ (Table 1). Pb in the leachate from the cement prepared with treated fly ash was below the detection limit (<0.005mg/l), which is less than half the level of the environmental quality standard in Japan (0.01mg/l). Although these results confirmed the immobilization of Pb, we did not know whether the immobilization was the result of MC treatment or of the subsequent cement production. Therefore, we compared the leachability of Pb from the MC treatment residue and from its cement product.

Table 2 summarizes the results of leaching tests on treated and untreated fly ash and on cement prepared with the treated fly ash. After 2h of MC treatment, the amount of Pb leached was reduced by 92.8%, to 39µg/g fly ash. This result confirmed that the inhibition of Pb leaching from the

Table 1. Pb leaching from the cement product of fly ash treated mechanochemically for the indicated grinding times

Grinding time (h)	Not treated	2	4	8
Pb leaching (mg/l)	60.8	<0.005	<0.005	<0.005

Table 2. Comparison of the amount of Pb leaching from untreated fly ash, fly ash treated mechanochemically, and the cement product

Sample	Pb in leachate (µg)	Inhibition of leaching (%)
Untreated fly ash	540	–
Mechanochemical treatment	39	92.8
Cement product	<0.4	>99.9

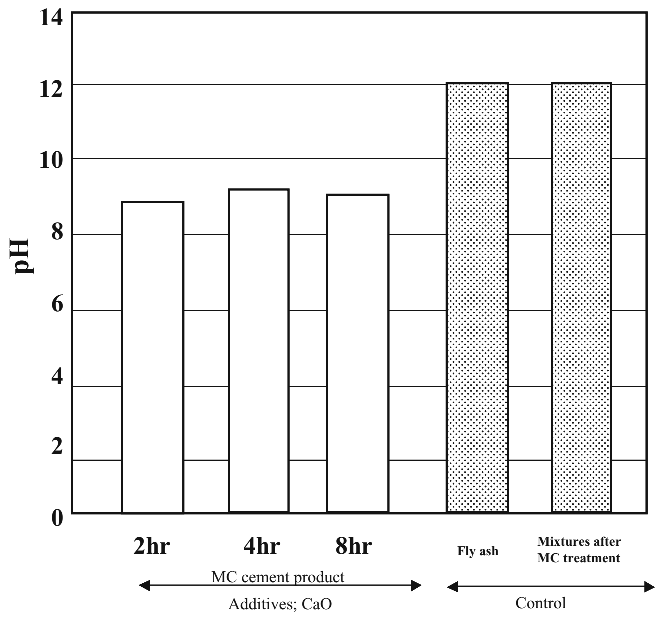

Fig. 1. Suppression of alkali elution from cement product made from fly ash after mechanochemical (*MC*) treatment with CaO

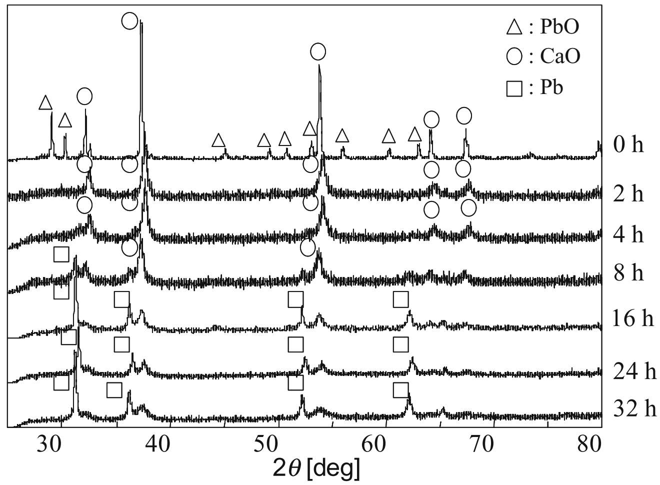

Fig. 2. X-ray diffraction analysis shows the changes in the crystal pattern of PbO-spiked fly ash during MC treatment for different processing times using CaO

cement product was mostly due to the MC treatment, although cement production was necessary for complete inhibition of Pb leaching.

Grinding not only pulverizes and homogenizes solid materials but also induces MC reactions that produce new substances.[14–16] The MC reaction induced during the grinding of fly ash and CaO may cause a chemical change in the Pb in the mixture that results in its immobilization.

Factors that are supposed to be involved in the solidification of cement are as follows: (a) microparticulation of the cement component by grinding increases the surface area of the component, producing a high-energy, unstable particulate, and the addition of water stabilizes it by means of hydrate formation; and (b) homogeneous dispersion of the particulates in water leaves few air spaces.[23] In fact, the eluates from the fly ash or the mixtures after MC treatment had a strong alkaline pH of 12, whereas the pH of eluates from the cement product made from mixtures treated mechanochemically was depressed to about 9, as shown in Fig. 1. This reduction in pH may result from CaO incorporation in hydrated form during the solidification of cement, decreasing the existence of free CaO soluble in water. Thus, there is a possibility that this pH depression contributes to the inhibition of Pb leaching. On the other hand, because the energy from the stress imposed on the solid substances during the grinding process is preserved in the resulting powder,[14] Pb species in the fly ash may remain activated after grinding. Further inhibition of Pb leaching by the production of cement from the MC treatment residue may be caused by the Pb species activated by the MC treatment becoming surrounded by hydration products and bound chemically or physically (or both) to those products during the hydration process.

Mechanism of Pb immobilization

For practical use of the MC treatment residue as a cement component, the mechanism of Pb immobilization needed to be determined. The results of the leaching tests indicated that the immobilization of Pb was due mostly to the MC treatment, which produced a change in the Pb species present. We therefore identified the Pb species in the fly ash by XRD analysis. To obtain fly ash typical of that derived from municipal waste,[24] we spiked the fly ash with 1.8 g of PbO before MC treatment, using CaO as an additive.

Figure 2 shows the changes in the crystal pattern of PbO-spiked fly ash mechanochemically treated with CaO. The PbO peaks rapidly disappeared, and a peak for Pb appeared after 8 h of MC treatment. These results clearly indicate that PbO was reduced to Pb during MC treatment, probably in a process similar to the MC reduction of metal oxides reported in previous research.[17–20] Because the solubility constant of PbO (0.107 g/l) in water is much higher than that of Pb (3.1×10^{-4} g/l), the immobilization of Pb by MC treatment may result from the reduction of the PbO.

Although XRD analysis confirmed that Pb was produced by MC treatment, the identity of the reductant remained unknown. We hypothesized that it was derived either from the stainless-steel pot and steel balls or from the fly ash itself, because SiO_2 and/or metals such as Al act as reductants during MC reduction of metal oxides.[17] To identify the reductant, we subjected PbO (4 g) alone to MC treatment for 48 h. The crystal pattern obtained by XRD analysis showed a weak Pb peak after 48 h of treatment (Fig. 3). This result indicates that the components of the stainless-steel ball mill may have been involved in the reduction of PbO compounds to Pb.[18] To verify this, we subjected the following sample mixtures to MC treatment with a zirconium ball mill: (a) PbO (4 g); (b) fly ash (1 g) and PbO (1.8 g); and (c) CaO (4 g), fly ash (1 g), and PbO (1.8 g). Pb was not produced with the zirconium ball mill under any conditions,

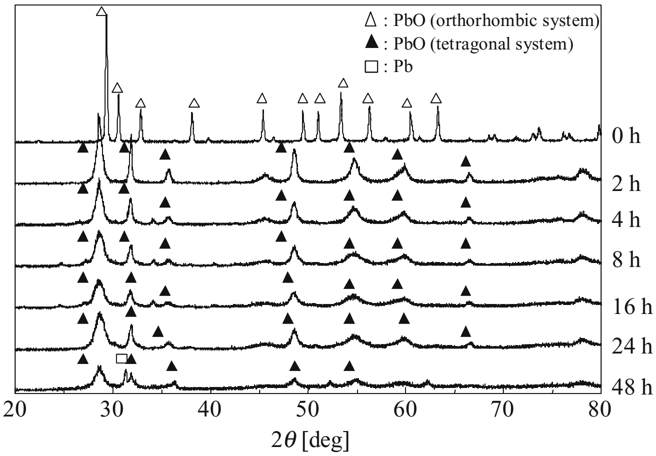

Fig. 3. Crystal patterns of PbO samples milled for the indicated times in a stainless steel mill

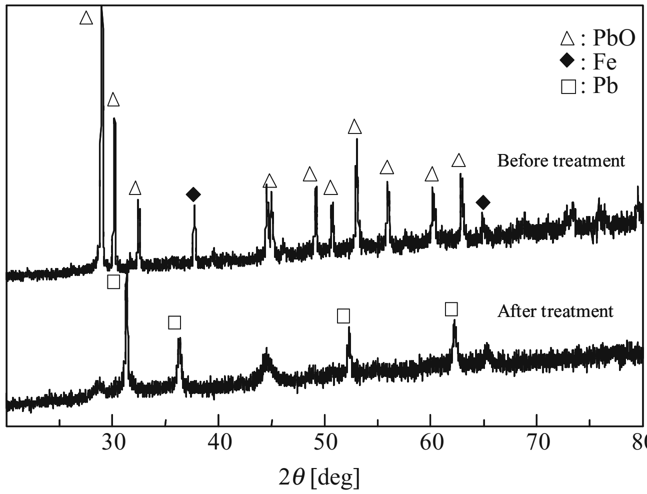

Fig. 5. Crystal patterns of a mixture of PbO and Fe before and after 24 h of MC treatment using a zirconium ball mill

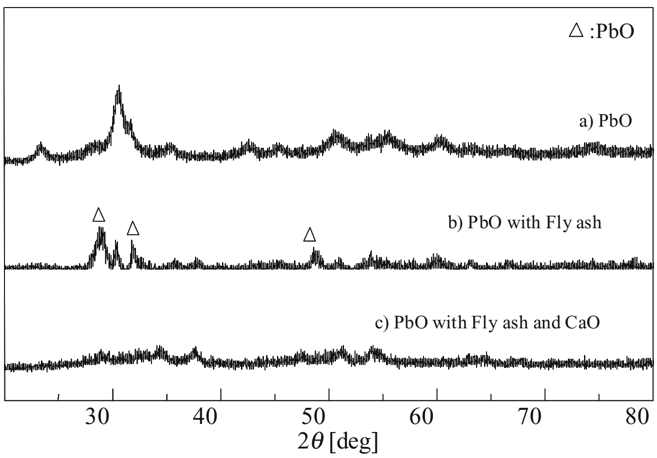

Fig. 4. Comparison of the crystal patterns of PbO samples milled alone (*a*), milled with fly ash (*b*), and milled with fly ash and CaO (*c*) using a zirconium ball mill for 72 h

even after 72 h (Fig. 4). This result indicates that the stainless steel in the ball mill was involved in the reduction to Pb during MC treatment.

Iron, which makes up 70% of stainless steel, may have acted as a reductant in the ball mill.[18] To investigate this possibility, we used a zirconium ball in the mill with PbO and Fe in a 1:4 molar ratio and then ran the mill for 24 h. (Note that a new ball mill was used to avoid any possible effects of reductants that might be present on the surface of a previously used mill.) Figure 5 shows the crystal patterns obtained by XRD analysis before and after the MC treatment. The formation of Pb and the disappearance of PbO were observed, confirming that Pb is produced in the presence of Fe; therefore, Fe was most likely generated from the stainless-steel pot and balls by means of abrasion during grinding, and the Fe reduced the Pb.

XRD analysis indicated that the MC treatment process produced a transition from orthorhombic PbO to tetragonal PbO and that the tetragonal form persisted (Fig. 3). Similar phenomena, such as phase transitions and changes in the configuration of atoms, molecules, and ions, have been reported as a result of grinding.[15] After 48 h of grinding, PbO remained in the tetragonal form, although Pb was also produced. This finding suggests that the crystal form of the PbO in the fly ash was changed before the production of Pb by MC treatment. The solubility of tetragonal PbO in water (0.0502 g/l) is about half that of orthorhombic PbO (0.107 g/l), and the solubility reduction due to this transition may be partly responsible for the inhibition of Pb leaching from fly ash subjected to MC treatment. A leaching test with PbO treated mechanochemically for 2 h confirmed that about 90% of Pb leaching was inhibited by the treatment process (data not shown). These findings could be useful in the treatment and recycling of fly ash by means of a grinding process. Other species may also play a role, and further studies are necessary for a full understanding of the mechanisms involved.

Here, we used PbO as a model for the Pb compounds contained in fly ash, and we investigated its behavior during MC treatment to elucidate the mechanism of immobilization. Demonstration of the immobilization of other Pb compounds, such as lead chloride, which is also abundant in fly ash,[24] would provide additional useful information. In addition, the mechanism of the immobilization of Pb observed in the production of cement from fly ash treated mechanochemically must be determined; before recycled fly ash can be used as a component of cement, we must demonstrate that the Pb immobilized in the cement product is stable and not subject to reoxidation on exposure to air. It is expected that MC processes will have the advantage of not only treatment safety but also simplification of cement production processing, such as the omission of cement pyroprocesses and a reduction of curing time for the solidification process. It is essential for the practical application of MC treatment as a novel cement production technology to demonstrate the advantages. We will investigate these issues in future studies.

Conclusions

Our results can be summarized as follows:

1. MC treatment of fly ash inhibited Pb leaching by 93%, and further inhibition (99.9%) was observed on the production of cement from the treated fly ash.
2. During MC treatment, PbO was reduced to Pb.
3. The pH depression observed by the production of cement is one of the reasons for the further inhibition of Pb leaching.
4. The immobilization of Pb during MC treatment can be explained by changes in the Pb species: the solubility constant of PbO (0.107 g/l) in water is much higher than that of Pb (3.1×10^{-4} g/l).
5. The transition of PbO crystals from orthorhombic to tetragonal, which resulted in a decrease in the solubility constant (to 0.0502 g/l), provides another possible explanation for the inhibition of Pb leaching from fly ash on MC treatment.
6. Fe abraded from the stainless steel of the ball mill was confirmed to act as a reductant during MC treatment.

Acknowledgments This work was supported financially by the Steel Industry Foundation for the Advancement of Environmental Protection Technology and was funded by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science. All support is greatly appreciated.

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