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Extraction of metals from municipal solid waste incinerator fly ash by hydrothermal process

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Abstract

This work examined the extraction properties of metallic elements from municipal incinerator fly ash under hydrothermal conditions. The ash was firstly pre-washed by distilled water, then subjected to hydrothermal treatments. The pre-washing process was effective for Na, K, Ca extraction with extraction percentages of 67%, 76% and 48%, respectively. The optimum contact time was 30 min for the pre-washing process. Five types of acids were tested for the extraction experiments and hydrochloric acid was found to be most effective for metal extraction from the ash. Compared to room condition, hydrothermal treatment accelerated the dissolution of the ash, thus promoted the reaction of acid with hazardous metals such as Cr, Cd, Pb, and furthermore, the consumption speed of acid was slowed down under hydrothermal condition. The acid simultaneously reacted with all the metal in the ash under hydrothermal condition but preferentially reacted with Ca at room condition. The optimum hydrothermal treatment temperature, time and liquid/solid ratio were 150 °C, 5 h and 10:1 (ml:g), respectively.

Keywords: Hydrothermal extraction; MSW fly ash; Heavy metal; Crystallization

1. Introduction

Fly ash discharged from municipal solid waste (MSW) incineration plant has been classified as "hazardous waste requiring special control" in many developed countries for several years. In Japan, regulated by 1992 legislation [1], the fly ash is generally subject to treatment by any of the four ways, i.e. melting treatment, chemical stabilization, cement solidification, or extraction. Converting the ash into slag by melting process has been improved in recent years since the melted slag has the potential to be used as construction materials such as aggregates and ceramic linings [2,3]. The only shortcoming of this process is that it is much more costly compared with other methods, which makes it difficult for exact application. In-situ stabilization/solidification of heavy metals inside the fly ash using chelate agents or mixing the ash with Portland cement, on the other hand, is also practicing alternative nowadays for the relatively low treatment cost and ease of application. However, these processes present some drawbacks, namely slow releasing of heavy metals from the treated ash in a wet environment, which makes it still be hazardous for the environment [4,5]. Moreover, solidification with Portland cement could considerably increase the volume and weight of the residue, since the solidification operation usually adds 15–30 wt.% of cement and 1–3 wt.% of chemical reagent such as carboxylic, thiol or carbamate functional groups with the fly ash [4]. Comparably, extraction of heavy metals from the fly ash is an environmentally preferable method for the ash treatment. This process is actually a hydrometallurgical process as most of the metals may dissolve in the acidic solution.

The recovery of base metals such as Cu, Ni, Co, Zn and Pb from waste ashes provides an opportunity to convert the hazardous waste to innocuous material while at the same time extracting valuable pay-metals. To date, various hydrometallurgical methods using lixiviation reagents for metal extraction from waste ashes have been examined [6–8]. Among the reagents, mineral acids such as HCl, HNO_3, H_2SO_4, and alkaline solutions such as NaOH and aqueous NH_3, are frequently employed. Hydrochloric acid and nitric acid have the advantages of extracting almost all metallic elements, and sulfuric acid could dissolve many of the metals but leave Ca and Pb

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in the residue, while alkaline solutions have the advantages of selective extraction of amphoteric metals such as Zn and Pb and leave other metals in the solid residue. Nevertheless, a large amount of acids or alkaline solutions are generally needed for these processes, and furthermore, the resulting solutions are usually extremely acidic or alkaline with only low concentration of metals in the resulting leachate, which are difficult for recovery. Hence, these processes require high-level wastewater control, and are not suitable for ash disposal plants without wastewater treatment equipments.

Hydrothermal process is a functional way to active reactions whose major mechanism is via dissolution. In recent years, this technique has been applied to waste ash treatment so as to recycle the waste material. Many researchers have employed coal fly ash as a precursor material trying to convert the ash to zeolite-like materials in an alkaline condition. Thus far, many types of zeolite such as phillipsite, analcime, zeolite P, gismondine, and gmelinite have been successfully synthesized using fly ashes [9–11]. Recent reports also indicated that hydrothermal process could significantly increase fly ash pozzolanic reaction [12,13]. The resulting compounds can be used for immobilizing toxic wastes, and also have the potential to be used as the precursors of new kind of low-energy cements called fly ash belite cements. Furthermore, it has reported that hydrothermal treatment of MSW incinerator fly ash with water or alkaline solution could decompose dioxins such as PCDDs and PCDFs through dechlorination, especially at high temperature [14–16].

Many outstanding advantages have been demonstrated in waste ash recycle by hydrothermal treatment. To the knowledge of the authors, however, the leaching properties of heavy metals from fly ash under hydrothermal condition are less reported in the literature. In the present study, hydrothermal treatments on MSW incinerator fly ash were conducted so as to understand the extraction behaviors of metallic elements from the ash during hydrothermal process. The aim was to extract more metals using less acid. The optimum leaching conditions were established, and the crystalline and morphological properties of the residue were clarified.

2. Experimental

Fly ash was obtained from a MSW incineration plant in Nagoya, Japan. The plant has two 24 h running large-scale PLC based incinerators, and the furnace of each incinerator is design to dispose more than 5-tonne refuse per hour. The furnace room temperature is sustained within 850–1000 °C. The fly ash was captured by a bag-filter and was removed twice every day. The fly ash typically contains metallic elements such as Na 2.91%, Mg 1.08%, Al 2.83%, K 4.11%, Ca 22.5%, Cr 0.18 g kg^{-1}, Mn 0.97 g kg^{-1}, Fe 7.63 g kg^{-1}, Cu 0.90 g kg^{-1}, Zn 17.3 g kg^{-1}, Cd 0.14 g kg^{-1}, Pb 1.00 g kg^{-1} with variation limits around 0.03–1.23%, and non-metallic elements such as C 7.0%, Si 4.0%, P 0.28%, S 0.84%, Cl 28.3% with variation limits around 0.08–8.17%. Carbon content in the ash was determined using a CHN corder (Yanako, MT-6), and the other non-metallic elements were exmined using a scanning electron microscope (SEM, JSM-6330F) coupled with an energy-dispersive X-ray spectrometer (EDS, JED-2140). The details of the fly ash were presented in a previous report [17].

The fly ash was firstly vacuum dried at 105 °C for 24 h. Then a portion of the ash was pre-washed by distilled water. In the pre-washing process, a liquid/solid ratio of 20:1 (ml:g) was performed. The vibration time varied from 5 min to 20 h, and the temperature was approximately 20 °C. After vacuum filtration, metallic elements in the leachate were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer).

After separation, the pre-washed residue was vacuum dried at 105 °C for 24 h and subjected to hydrothermal treatments. A series of autoclaves were employed for the hydrothermal experiments. Each autoclave consists of a 50 ml Teflon interior and a stainless exterior. The pressures inside changes along with the temperature change, which were around 1.2–2.0 MPa. Hydrochloric acid, nitric acid, sulfuric acid, oxalic acid and citric acid were examined to compare their leaching effects. The treatment time varied from 1 to 70 h, and the temperatures varied from 100 to 200 °C. Liquid/ solid ratios of 3:1, 5:1, 10:1 and 20:1 (ml:g) were performed. After hydrothermal treatment, the autoclaves were immediately cooled using an electronic fan. Upon cooling, the supernatant solution was filtrated using a vacuum filter. Metallic elements in the leachate were determined by ICP-AES, and the pH of the solution was measured using a HORIBA D-21 pH meter. For comparison, parallel experiments were also conducted at room conditions.

The crystalline properties of the residue and the original ash were examined by a RIGAKU X-ray diffractometer (XRD, Rint 2000) at 50 kV and 100 mA using Cu Kα radiation (λ = 1.5418Å), and the surface morphology was examined by SEM. A high performance liquid chromatograph (HPLC, SHIMAZU) was employed for Cl^-, SO_4^{2-} and NO_3^- determination. Oxalic anion in the filtrate was precipitated with calcium chloride and determined by $KMnO_4$ titration, while citric anion was titrated with sodium methanolate in a 3:1 methanol/dimethylformamide mixture.

The quality and precision of metallic element analysis for the fly ash and other samples were controlled using four reference materials, i.e. coal ash (ZUK-1) from Institute of Geochemistry, Irkutsk (Russia), bone ash (NIST 1400) from National Institute of Standards and Technology (USA), and two sewage sludge (nos. 101 and 102) from National Institute of Agro-Environmental Science, Ministry of Agriculture, Forestry and Fisheries (Japan). The recoveries for the elements were: Na (94–97%), Mg (93–96%), Al (95–103%), K (101–106%), Ca (95–99%), Ti (102–110%), V (97–101%), Cr (106–115%), Mn (91–98%), Fe (102–108%), Co (95–99%), Ni (93–100%), Cu (98–106%), Zn (103–110%), As (99–100%), Sr (100–102%), Cd (101–103%), Ba (96–99%), Pb (99–101%), respectively.

3. Results and discussion

3.1. Pre-washing effects

In the metal extraction processes, the most economic approach is simply washing the fly ash with water to separate