Synthesis and efficiency of a new chemical fixation agent for stabilizing MSWI fly ash

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Abstract

In this study, a novel chemical fixation agent, colloidal aluminate oxide (CAO), has been synthesized and characterized in detail. CAO does not require cementitious additives, and can be used as a stabilizer of lead in the fly ash from municipal solid waste incineration (MSWI) plants. CAO reveals a high reduction ratio for the leachability of Pb of 94.8% when compared with three commercial fixation agents, MF-103, BTS-03 and POCAT, and two fine chemicals, ethylene diaminetetracetic acid (EDTA) and thiodiglycolic acid (TGA). A possible mechanism for CAO stabilization of lead is formulated based on the results of Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) spectra.

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1. Introduction

About 19 large-scale municipal solid waste incineration (MSWI) plants have been in operation in Taiwan since 2001. The total amount of MSW combustion residues produced, including boiler ash, scrubber ash, precipitator ash, and bottom ash, is approximately 2000 t/day [1]. Currently, the flue gas from MSW incinerators in an MSWI plant is treated by a spray-drying scrubber combined with a bag-filter. A solution suspension of lime is usually used as the neutralizer of acid gas and is sprayed into the scrubber of flue gas. The ash collected at the bottom of the scrubber is called "*reaction product* (*RP*)" or "*reacted fly ash*", and contains the reacted lime, condensed heavy metals, and dust particles. The ash collected from the baghouse is called "*reactive fly ash* (*RFA*)", and contains the original lime and lighter dust particles [2]. The term "*fly ash*" generally pertains to a mixture of both RP and RFA. However, the ratio of RP to RFA from the same incinerator is not constant [2]. Taiwan's Agency of Environmental Protection (EPA) regulates that, before disposal, the MSWI fly ash must be stabilized physically,

chemically or thermally, using cement-based solidification, chemical stabilization or thermal treatment.

Huang and Chu [2] argued that both RP and RFA are cement-like materials with reference to the results of their chemical compositions. Huang and Chu [2] also reported that RFA consists of the original lime and reacted-lime of more than 45 wt.%. MSWI fly ash is one type of industrial hazardous waste, due to its high leaching toxicities of heavy metals (e.g. Pb(II) and Cd(II)). An increase in the alkalinity of MSW fly ash increases the difficulties of stabilization and disposal, i.e. the long-term leaching behaviors of heavy metals of solidified fly ash [3].

Cement-based solidification currently appears to be the best effective procedure for heavy metal-containing wastes [3,4]. Cement-based solidification treatment [1] has been widely used in Taiwan for stabilizing MSWI fly ash, and has been implemented by mechanically mixing the fly ash with 15–30 wt.% of cement and 1–3 wt.% of chemical fixation agent. The chemical fixation agent normally includes carboxylic, thiol, and carbamate functional groups [3–6].

Otherwise, several inorganic compounds have been used as chemical fixation agents, such as the phosphoric acid, the apatites [7–10], or some cementitious materials (i.e. CaO, $Ca(OH)_2$, and $CaCO_3$) [3,11,12]. Under a strongly acidic environment or a basic environment, the hydroxyapatite de-

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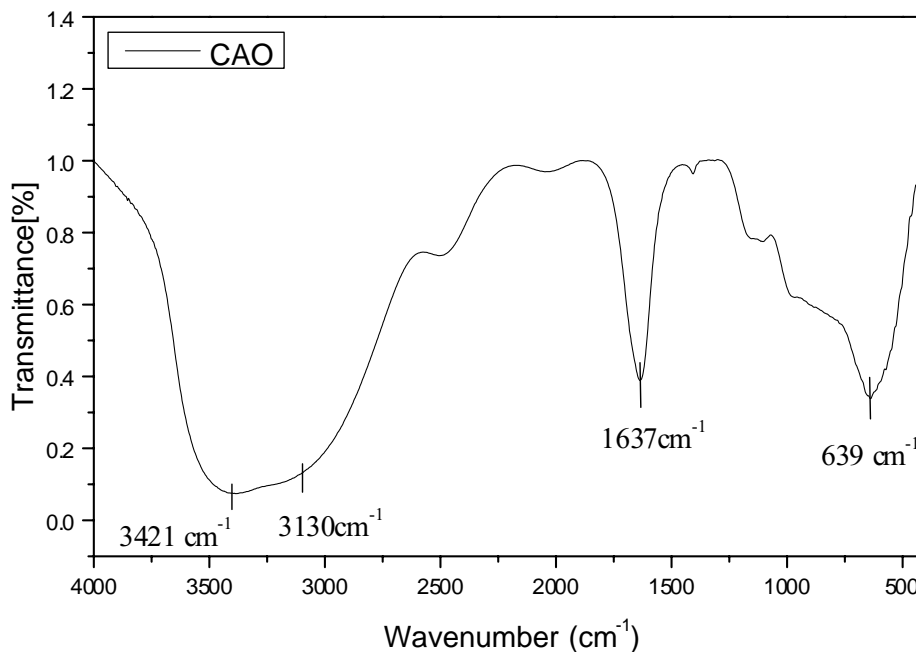*E-mail address:* wjhuang@mail.npust.edu.tw (W.-J. Huang).

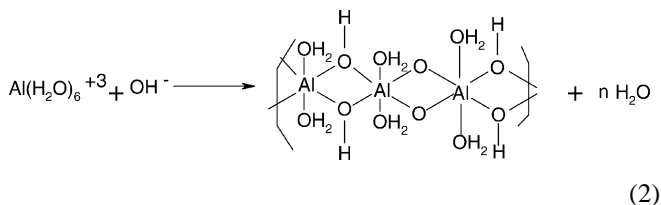Fig. 1. FT-IR spectrum of dried CAO powder.

polymerizes into low molecular weight and water-soluble phosphate. As a result, hydroxyapatites can penetrate deeper into pores and react with heavy metals more effectively. However, a higher dosage amount is required for hydroxyapatites relative to other agents [9].

The authors have synthesized a new chemical fixation agent, colloidal aluminate oxide (CAO), for the stabilization of heavy metals in the MSW fly ash. CAO is able to reduce the alkalinity of fly ash and the leachability of lead in fly ash. This study reports the details of the synthetic method and the proposed stabilization mechanism for CAO.

2. Experimental

2.1. Synthetic method of colloidal aluminate oxide

The synthetic procedures for CAO are as follows: 9 g of pre-dried $AlCl_3$ powder were dissolved by 270 mL of de-ionized water in a 500 mL beaker under a temperatures ranging from 0 to 5 °C, then 30 mL of 6 wt.% sodium hydroxide solution was slowly poured into the beaker. NaOH was used as the catalyst for the hydration reaction of $Al(H_2O)_6^{3+}$, as shown in Eqs. (1) and (2):

$$AlCl_3 \xrightarrow{H_2O} Al(H_2O)_6^{3+} \qquad (1)$$

$$Al(H_2O)_6^{+3} + OH^- \longrightarrow [\text{structure}] + n\,H_2O \qquad (2)$$

After 10–15 min of reaction time, a colorless and slightly viscous liquid was obtained.

The as-produced CAO solution has a pH of 5.0 and a solids content of 3 wt.%. The structural identifications of dried CAO powder were determined by Fourier-transform infrared spectroscopy (FT-IR) and with an X-ray diffraction (XRD) spectrometer. Fig. 1 shows the FT-IR spectrum, as well as the three main peaks of 639, 1637 and 3130–3420 cm^{-1} identified as the vibration motions of the bonds for –O–Al–O– and the bridged –OH, respectively. In addition, the broad peak of 3130–3420 cm^{-1} is identified as the vibration motions of the complexed water towards the Al atom. Fig. 2 shows the XRD pattern, in which a strong-diffraction peak of a 32° and a weak-diffraction peak of 45.5° were observed, and both of them correspond to the crystals of Al_2O_3.

2.2. Operation procedures of fly ash chemical stabilization

The MSW fly ash was sampled from the air-pollution-control devices at three large MSW plants located in southern Taiwan. All incinerators were of the mass-burn type and designed to control air pollution by a spray-drying scrubber combined with a fabric filter. The fly ash was collected from the manhole of the baghouse, and stored carefully under a condition of constant temperature and moisture. The fly ash was stabilized by adding the chemical fixation agent and a proper amount of water, and these solidified samples then were cured at room temperature for 7 days.
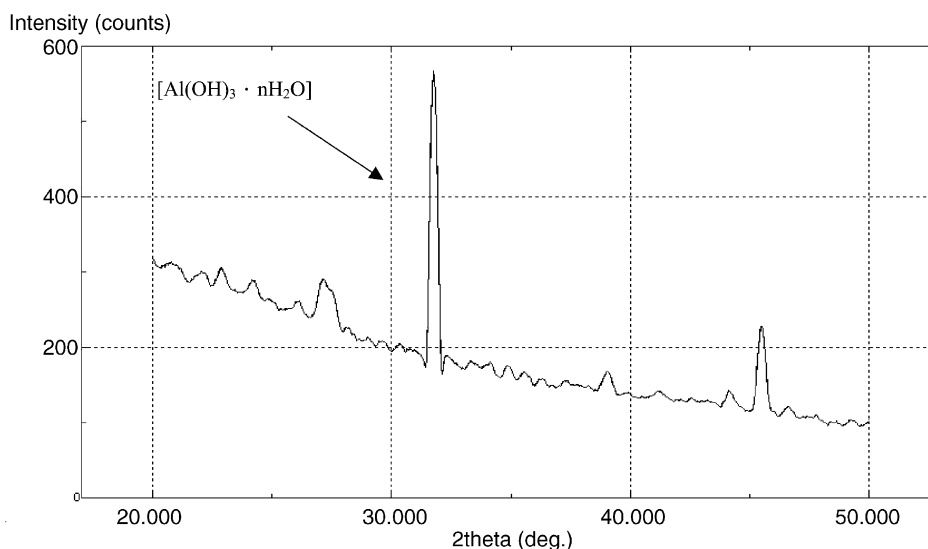
Intensity (counts)

Fig. 2. X-ray diffraction spectrum of dried CAO powder.

2.3. Toxicity characterization leaching procedure (TCLP) test

The TCLP test was performed in accordance with USA EPA method # 1311 and the metal species in the leachant were analyzed according to USA EPA method # 7420. The concentrations of heavy metals in the leachant were determined by a flame atomic absorption spectrometer (Unicam Instrum. Co., SOLAR-960).

Briefly, the TCLP procedures are as follows: the solidified fly ash was graded into the size of <10 mm and passed through the standard sieve with 10.0 mm openings. An acetic acid-based extractant (pH = 2.88) was mixed with the graded and solidified fly ash at a liquid-to-solid ratio of 1–20 (1:20) by weight. The mixture then was mechanically agitated at a speed of 300 rpm for 18 h.

2.4. Fourier-transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) measurements

The X-ray diffraction (XRD) measurement was performed with the Shimadzu diffraction meter (type XRD-6000) and a light source of Cu Kα line. The sweeping range was set to be from 5° to 75°, with a scanning rate of 2°/min at room temperature.

The Fourier-transform infrared spectroscopy (FT-IR) spectrum of the sample was determined using a Bruker Vector-22 FT-IR, with a scanning range of 4000–400 cm^{-1}, and the resolution was set to be 4 cm^{-1}. Before the FT-IR tests, the solidified fly ash was mixed with a proper amount of the pre-dried KBr powder, and the mixture was compressed into a thin disc film by a hand compressor.

The pH of the TCLP leachant was determined by Fisher Scientic Accument pH-meter 25. Three commercial chelating agents, MF-103, BTS-03 and POCAT supported by Transtar Co. (in Taipei) were used for testing. Thiodigly-

colic acid (TGA) and *N,N,N′,N′*-ethylene diamino tetra acid (EDTA), were also used as chemical fixation agents and were purchased from the Aldrich Chemical Co.

3. Results and discussion

3.1. Efficiency assessment of chelating reagents

The stabilization of Pb(II) in fly ash was emphasized in this study, because lead has a higher leachability than other heavy metals in fly ash [2]. Three commercial agents (MF-103, BTS-03 and POCAT) and two kinds of fine (pure) chemicals (EDTA salt and TGA) were utilized to stabilize the lead in fly ash. Table 1 summarizes the Pb(II) concentrations ([Pb]) of the TCLP leachants from the stabilized P3 fly ash, and the lowest concentration of 6.6 ppm is correlated with the mixture stabilized by TGA of 3% dosage amount. However, all concentrations of Pb(II) were higher than the regulatory level at 5.0 ppm set by Taiwan's EPA. In addition, all pH values of the leachant were greater than

Table 1
TCLP data of Pb(II) of P3 fly ash stabilized by commercial agents and fine chemicals

Agents	Chemical composition of chelators	Concentration of lead (ppm)				
		0%	1.5%	3%	9%	12%
TGA	Thiodiglycolic acid	25.8	22.7	6.6	12.5	11.7
MF-103	Phosphates	25.8	10.6	10.1	10.6	9.9
BTS-03	Water-soluble silicates	25.8	13.0	11.6	17.4	12.1
EDTA	EDTA disodium-dicalcium salt	25.8	33.2	13.5	33.5	37.4
POCAT	Polyethyleneimine with thiol side group	25.8	13.0	11.6	17.4	12.1

Dosage amount is based on the weight ratio of reactive fly ash to agent volume.

Table 2
TCLP data of Pb(II) of CAO stabilized fly ashes from various sources

Plants	Concentration of lead (ppm)				
	0%	1.5%	3%	9%	12%
P1	36.78	1.92	1.48	N.D.	N.D.
P2	12.69	4.28	3.76	3.67	3.52
P3	25.8	4.85	4.61	2.97	5.08

Table 3
TCLP data of five metals of CAO stabilized Plant 1 fly ash

Concentrations	Concentration of lead (ppm)				Regulatory level in Taiwan (ppm)
	1.5%	3%	9%	12%	
[Pb]	1.92	1.48	N.D.	N.D.	5
[Zn]	0.05	0.04	N.D.	0.04	25
[Cu]	0.01	N.D.	0.04	0.06	25
[Cd]	0.01	N.D.	N.D.	N.D.	1
[Hg]	N.D.	N.D.	N.D.	N.D.	0.2

12.0, indicating that the stabilized fly ash also has a high alkalinity.

Table 2 shows the concentration of lead ([Pb]) of the CAO stabilized fly ash from Plant 1, and the concentrations of cadmium, copper and zinc ([Cd], [Cu] and [Zn]) are shown in Table 3. In Table 2, the [Pb] of the leachant decreased significantly from 36.7 to 1.9 ppm by CAO addition. The concentrations for [Cd], [Cu] and [Zn] in Table 2 are all far below the regulatory levels of Taiwan's EPA. Fig. 3 shows the leaching curves for the MF-103, BTS-03 and CAO for stabilizing the fly ashes from P1 and P3. In Fig. 3, only the results of the more effective fixation agents among commer-

cial agents listed in Table 1 are presented. The other chemical fixation agents have randomized stabilization efficiency for the reduction of Pb. Common to all, CAO was the agent with the highest efficiency (94.8%) for immobilizing Pb(II), without simultaneously enhancing the leaching of the other heavy metals.

3.2. Basic stability for MF-103, BTS-03 and CAO

To test the stability of each chemical fixation agent in the basic environment of fly ash, several drops of 1.0 M $NaOH_{(aq)}$ solution were added into the solutions of MF-103, BTS-03, or CAO. Then, the attenuation curve of pH versus mixing time was recorded. Fig. 4 displays The pH attenuation curves for the CAO, MF-103, and BTS-03 solutions are displayed in Figs. 4–6, respectively. The CAO solution has a stepwise decrement with increasing mixing time, which is in contrast to the behaviors for the MF-103 and BTS-03 solutions that maintain the original pH value over the entire test. Thus, the CAO solution is capable of reducing the pH of the fly ash. This may be caused by the degradation reaction of CAO chains. Therefore, if the CAO dose is acceptable, the hydrolytic polymer might serve as an alternative chemical fixation agent for stabilizing heavy metals in fly ash, such as poly(DL-lactic acid) [13], poly(4,4-methylenedianiline) [14], Schiff base [15] deviators, or polycarpine [16].

3.3. Stabilizing mechanism of CAO

In an attempt to understand the stabilization mechanism of the CAO on the lead in the fly ash, 5 mL of the CAO solution was poured slowly into 50 mL of the 1000 ppm lead standard solution (with a pH = 12), and a gel-like white precipitate immediately formed at the bottom of beaker. After
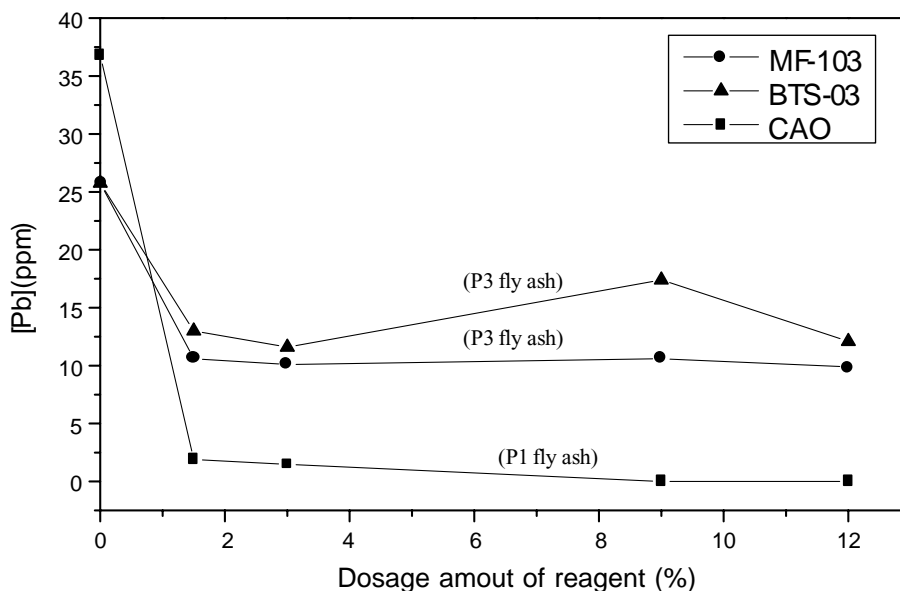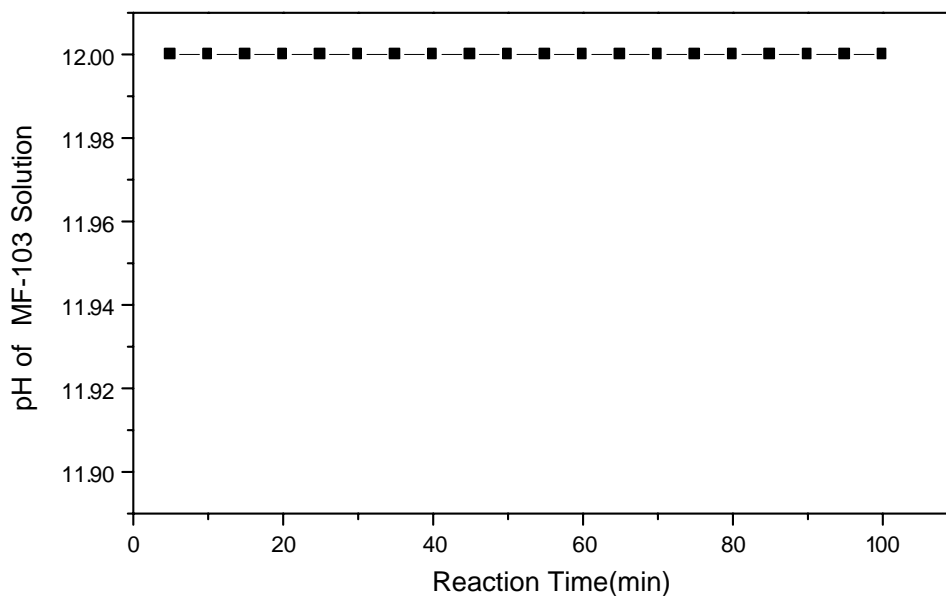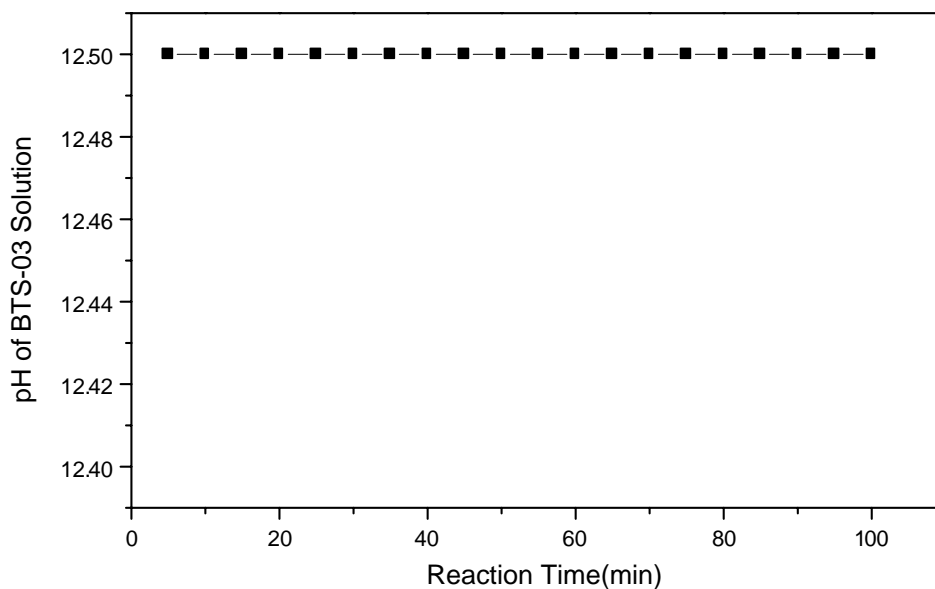

Fig. 3. The fixation curves of MF-103, BTS-03 and CAO of Plant 1 fly ash.

Fig. 4. The base stability of MF-103 reacting with $NaOH_{(aq)}$.

Fig. 5. The base stability of BTS-03 reacting with $NaOH_{(aq)}$.

steadying for 10 min, the precipitate was collected by vacuum filtration and dried at 105 °C. Figs. 7 and 8 show FT-IR spectra for the dried CAO, $Pb(OH)_2$ powder and the precipitate. Figs. 9 and 10 show the X-ray diffraction patterns for the dried CAO powder, $Pb(OH)_2$ and the precipitate. Based on the spectroscopic data, a "micro-crystal encapsulation mechanism" is formulated for the CAO stabilization of Pb(II), and the mechanism includes following steps, also illustrated by Eqs. (3) and (4): firstly, the CAO chain is a attacked by hydroxide ions and complexed water-ligends and bridged =OH groups are formed and secondly the Pb(II) binds on the active Al–OH site to form $Al(OH)_3/Pb(OH)_2$ crystals.
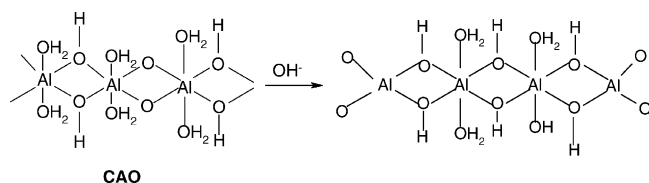
(3)
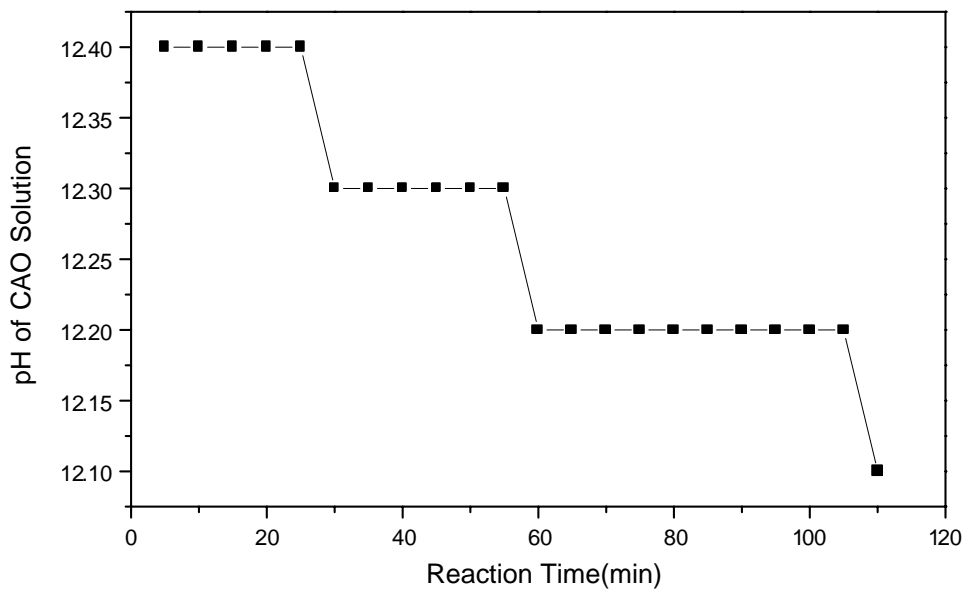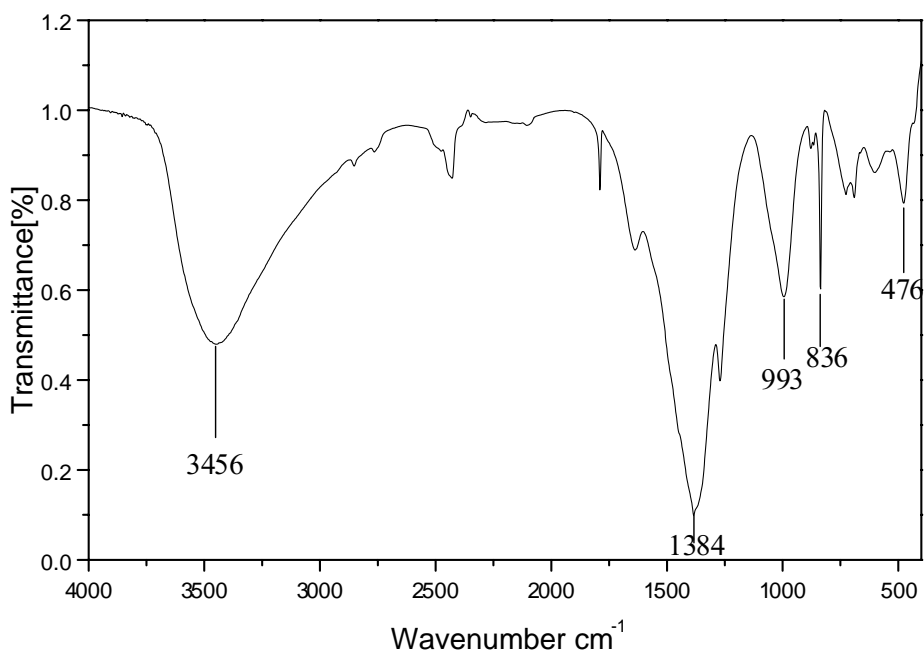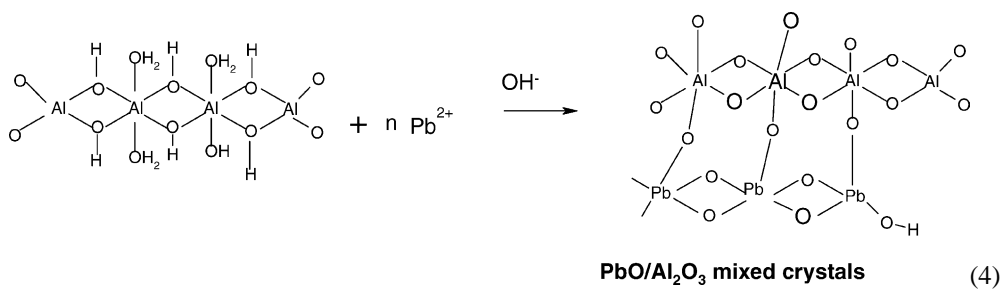
Fig. 6. The base stability of CAO reacting with $NaOH_{(aq)}$.

Fig. 7. FT-IR spectrum of CAO/Pb(II) precipitate.

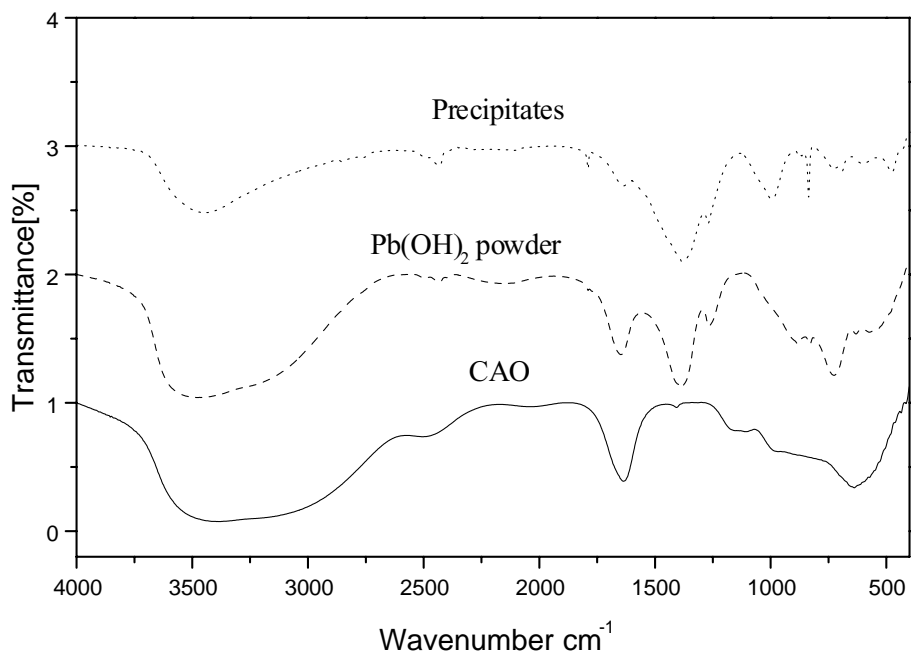**PbO/Al$_2$O$_3$ mixed crystals** (4)

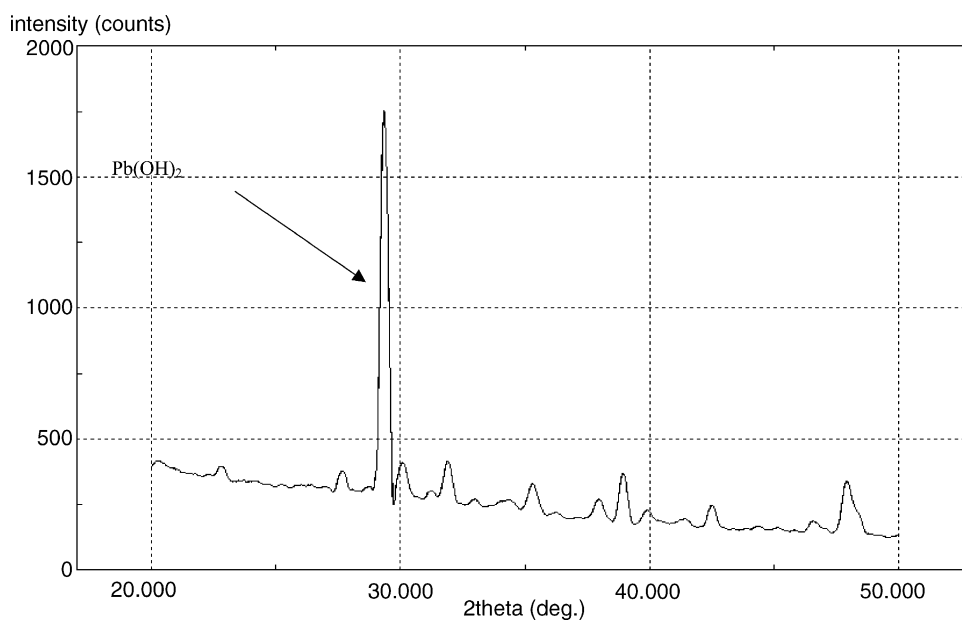Fig. 8. FT-IR spectra of dried CAO, Pb(OH)$_2$ powder and precipitate.

Fig. 9. X-ray diffraction spectrum of Pb(OH)$_2$ powder.

To the authors' knowledge regarding the fixation mechanisms of heavy metals, the "micro-crystal encapsulation mechanism" for the CAO is different from the complexation–precipitation mechanism for organic polymeric chelators [5–7], the absorption–crystallization mechanism for some cementitious materials [3,11,12,17], and the dissolution–precipitation mechanisms for apatites [9,10,18] and silicates [19].
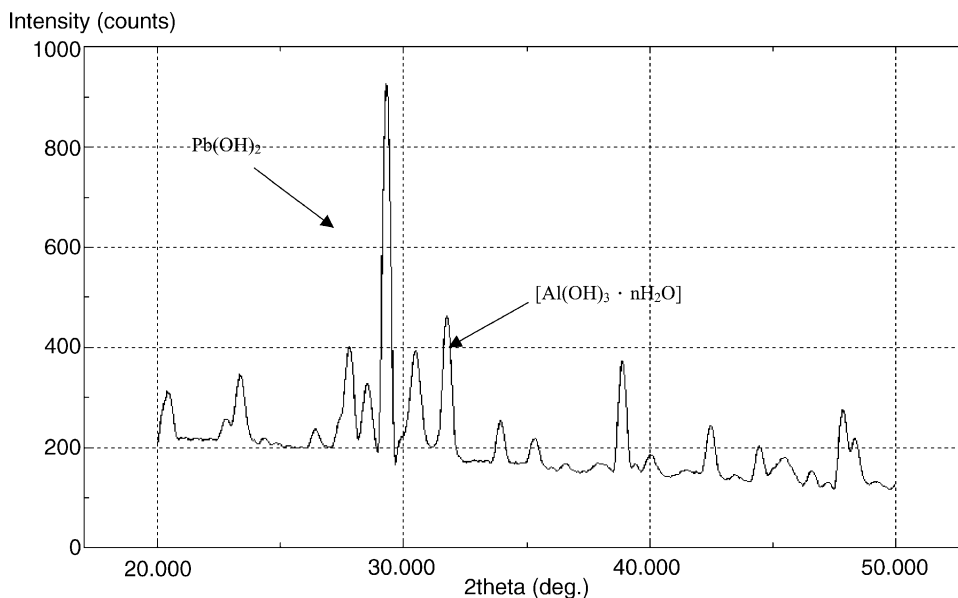
Fig. 10. X-ray diffraction spectrum of CAO/Pb(II) precipitate.

4. Conclusions

In this study, a colloidal aluminate oxide was synthesized, characterized, and tested as a chemical fixation agent for the lead in MSW fly ash. The CAO shows a good efficiency (94.8%) for reducing the leachability of the lead in the fly ash, without enhancing the leaching of other heavy metals. A fixation mechanism of the CAO stabilizing the lead in fly ash is proposed, with the critical process being the formation of the $Al(OH)_3/Pb(OH)_2$ crystals.

Acknowledgements

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