Using fume silica as heavy metals' stabilizer for high alkali and porous MSWI baghouse ash

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Abstract

In this study, we have proved that heavy metals in high porous and alkali baghouse ash could be fixed effectively by fume silica powder alone, or with the incorporation of colloidal aluminum oxide (CAO). The optimum amount is about 100 g of fume silica per kilogram of baghouse ash. Results have indicated that fume silica has a better fixation efficiency of lead in high porous baghouse ash. In addition, the reaction mechanism of fume silica is also discussed.
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Keywords: Lead; Baghouse ash; Chemical fixation agent; Fume silica; Municipal solid wastes incinerator (MSWI)

1. Introduction

At present, there are 19 large-scale municipal solid waste incineration (MSWI) plants in service in western Taiwan. The total amount of MSWI combustion residue produced, including boiler ash, fly ash, and bottom ash, is approximately 2000 t day^{-1} [1]. Currently, a spray-drying scrubber combined with a bag-filter (baghouse) treats the flue gas from incinerators in many MSWI plants. The chemical composition analysis of Taiwan's fly ashes (including baghouse ash and scrubber residue) has been reported [2]. The MSWI fly ash must be stabilized by physical, chemical or thermal methods such as cement-based solidification [3,4] and chemical fixation [5–17].

The organic chemical fixation agent normally includes carboxylic, thiol, and carbamate functional groups [5,6]; while the inorganic chemical fixation agent is mainly composed of colloidal aluminate oxide (CAO) [7], soluble phosphate [8], apatites [9–11], or some cementious matter (i.e. CaO, Ca(OH)$_2$, and CaCO$_3$) [3,12–13]. Among them, CAO and hydroxyapatite can be used in the waste with strong acid or basic environment. In addition to this, hydrolytic polymers also could be chemical fixation agents for MSWI fly ash, such as poly(DL-Iactic acid)[14],

poly(4,4-methylene dianiline) [15], Schiff base [16] deviators, or polycarpine [17]. Since the stabilization of heavy metals in fly ash is big business in hazardous materials control of MSWI air pollution residues, it is necessary to develop new chemical fixation agents for MSWI fly ash.

In our previous study [7], the authors stabilized baghouse ash by a synthesized aluminum-containing fixation agent, colloidal aluminate oxide (CAO). CAO was shown to have the ability to reduce the leachability of lead, the alkalinity, and the heat of solidification of baghouse ash [7]. Although CAO reveals a high reduction ratio of the leachability for Pb in most baghouse ash of up to 94% [7], but CAO is not being applicable for all baghouse ashes generated by different MSWI plants, especially for that with high porosity. In this paper, we would like to reduce the leachability of heavy metals from high porous baghouse ash through filling micro- or submicro-sized fine particles into the pores of the ash. In addition, the solid-state chemical fixation agent should possess the potential of forming insoluble salts with heavy metals.

2. Experimental

2.1. Ash sampling and characterization

Seven MSWI baghouse ash samples (named P1, P2, P3, P4, P5, P6, and P7) were collected from the manhole of the baghouse

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Table 1
The porosity and fractions of each size distribution of tested baghouse ashes

Items	P1	P2	P3	P4	P5	P6	P7
Size grades							
>2380 μm	0%	0%	1%	2.0%	0%	0%	0%
1190 μm	0%	0%	0%	2.0%	1%	0%	0%
590 μm	0%	0%	1%	21%	17%	0%	0%
297 μm	23%	4%	6%	36%	44%	0%	5.0%
149 μm	17%	20%	9%	23%	34%	2%	30%
74 μm	15%	48%	62%	13%	2%	17%	51%
<74 μm	45%	28%	21%	3%	1%	81%	14%
Chemical compositions (wt%)							
CaO	55.21	50.75	42.36	41.39	45.65	55.20	42.60
Al_2O_3	26.33	16.15	32.3	42.82	37.48	16.4	37.93
SiO_2	9.26	9.12	17.57	3.12	3.76	6.80	3.91
Fe_2O_3 and others	0.7	0.78	6.82	0.6	1.06	0.84	1.11
Porosity (%)	11.21	9.84	5.16	12.4	5.04	14.79	15.0
Total available amount of lead ions in the fresh ash (ppm)	115	84	127	264	147	80	173
[Pb] of TCLP of fresh ash (ppm)	12.4	4.80	0.15	51.78	37.85	4.37	42.6
[Pb] of TCLP of CAO stabilized Ash (ppm)	5.42	2.11	0.10	48.66	4.52	5.08	16.86
Is the ash being stabilized by pure CAO?	No	Yes	Yes	No	Yes	No	No

at large MSWI 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. After sampling, baghouse ashes were stored carefully controlling for constant temperature and moisture. Table 1 lists the weight percentages of sieved fractions in the size of 2380–74 μm and porosity.

2.2. Selection of primary and second chemical fixation agents

The synthesis method for colloidal aluminate oxide (CAO) has been reported [7] and was used as a primary fixation agent here. Five solid fixation agents were used as secondary fixation agents in this study: fume silica (SiO_2) powder, aluminum chloride ($AlCl_3$) powder, sodium silicate ($Na_2Si_2O_3$) powder, sodium carbonate (Na_2CO_3) powder, and ammonia hydrogen phosphate (($NH_4)_2HPO_4$). All these fine particles have a potential of forming insoluble salts with lead ($PbCl_2$, $PbCO_3$, $PbSiO_3$ and $PbHPO_4$) or are able to adsorb lead (Pb-fume silica).

Aluminum chloride, sodium silicate, sodium carbonate and ammonia hydrogen phosphate were purchased from SHOWA Chemical Co. Fume silica (Aerosil A-2000) made by Degussa Co. (Germany) was purchased from a local chemical company. The single particle size of the fume silica was near 0.012 μm, and the size of the aggregated clusters was 43.6 μm.

2.3. Chemical stabilization operation of ashes

Details of mixing receipts and TCLP data of stabilized concrete for P1, P4, P6 and P7 ashes are listed in Tables 2–5, respectively. In brief, ash was mixed with one or two kinds of chemical fixation agents and a proper amount of water, and then the solidified block followed a curing period for 7 days at room temperature. The secondary fixation agent was mixed with ash

powder first before the liquid mixture of primary fixation agent (CAO solution) and deionized water was added. In the cases of the addition of a CAO solution, the requirement of deionic water was reduced. Therefore, the (CAO + water)-to-ash ratio was kept at 70:100 by weight. The cured concrete was then crushed by hammer to pass through a sieve with a size of 10 mm.

2.4. Toxicity characterization leaching procedure (TCLP) test

The TCLP test was performed in accordance with the USA EPA Method # 1311 and then the metal species in the leachant was analyzed according to the USA EPA method # 7420. The concentrations of heavy metals in the leachant were determined by a flame atomic absorption (AA) 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 in and the solidified fly ash at a liquid-to-solid ratio that resulted was 1:20 by weight. The mixture was then sealed in a HDPE bottle equipped on a TCLP end-over-end rotator to agitate for 18 h with a speed of 30 rpm.

The pH of the extractant was pre-tested by pH-meter before each TCLP experiment and the final pH after extraction was recorded before it was acidified for AA determination. The final pH of all test samples was near 11.8–12.2.

2.5. Fourier-transform infrared (FTIR) 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 was used. The sweeping range was

Table 2
Receipt of stabilization operation and TCLP data of stabilized concrete for P1 ash

Runs	Dosage amount of CAO (g/kg ash)	The used secondary chemical fixation agents	Dosage amount of second agent (g/kg ash)	(CAO + water): Ash	[Pb] (ppm)
1	–	–	–	70:100	12.4
2	4.0	–	0	70:100	5.95
3	6.0	–	0	70:100	5.54
4	8.0	–	0	70:100	5.74
5	12.0	–	0	70:100	5.42
5	0	Fume silica powder	2.0	70:100	2.7
7	0	Fume silica powder	4.0	70:100	2.3
8	0	Fume silica powder	6.0	70:100	3.1
9	0	Fume silica powder	8.0	70:100	2.8
10	0	Fume silica powder	20.0	70:100	2.9
11	0	Fume silica powder	50.0	70:100	1.4
12	0	Fume silica powder	100.0	70:100	1.1
13	0	Fume silica powder	200.0	70:100	0.6
14	0.38	Fume silica powder	24.0	70:100	4.31
15	0.38	Fume silica powder	54.0	70:100	2.41
16	0.38	Fume silica powder	104.0	70:100	1.41
17	0.38	Fume silica powder	204.0	70:100	1.46
18	0.75	Fume silica powder	30.0	70:100	3.25
19	0.75	Fume silica powder	60.0	70:100	1.96
20	0.75	Fume silica powder	110.0	70:100	1.43
21	0.75	Fume silica powder	210.0	70:100	1.25
22	0	$AlCl_3$ powder	5.0	70:100	3.8
23	0	$AlCl_3$ powder	15.0	70:100	2.9
24	0	$AlCl_3$ powder	25.0	70:100	2.2
25	0	$AlCl_3$ powder	50.0	70:100	3.2
26	0	Na_2SiO_3 powder	5.0	70:100	3.0
27	0	Na_2SiO_3 powder	15.0	70:100	2.9
28	0	Na_2SiO_3 powder	25.0	70:100	2.2
29	0	Na_2SiO_3 powder	50.0	70:100	2.4
30	0	Na_2CO_3 powder	1.0	70:100	6.4
31	0	Na_2CO_3 powder	5.0	70:100	5.6
32	0	Na_2CO_3 powder	15.0	70:100	5.2

set to be from 5° to 75°, with a scanning rate of 2°/min at room temperature.

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

3. Results

The data in Table 1 show the size distribution, major chemical compositions, and stabilization date of CAO of different fly ash. Baghouse ash from P2, P3 and P5 can be stabilized well by CAO; however, CAO cannot stabilize the ash from P1, P4, P6 and P7 plants. As indicated in Table 1, all these four ashes have a relatively higher porosity. Fig. 1 displays fixation curves of CAO for two ashes that have different porosities. Ash with a higher

Table 3
Receipt of stabilization operation and TCLP data of stabilized concrete for P4 ash

Runs	Dosage amount of CAO (g/kg ash)	The used secondary chemical fixation agents	Dosage amount of second agent (g/kg ash)	(CAO + water): ash	[Pb] (ppm)
1	–	–	–	70:100	51.78
2	1.5	–	0	70:100	44.03
3	3.0	–	0	70:100	46.76
4	9.0	–	0	70:100	38.56
5	12.0	–	0	70:100	48.66
6	0.0	Fume silica powder	10.0	70:100	48.92
7	0.0	Fume silica powder	50.0	70:100	2.01
8	0.0	Fume silica powder	90.0	70:100	0.67
9	0.6	Fume silica powder	10.0	70:100	47.9
10	0.6	Fume silica powder	50.0	70:100	6.55
11	0.6	Fume silica powder	90.0	70:100	2.14

Table 4
Receipt of stabilization operation and TCLP data of stabilized concrete for P6 ash

Runs	Dosage amount of CAO (g/kg ash)	The used secondary chemical fixation agents	Dosage amount of second agent (g/kg ash)	(CAO + water): ash	[Pb] (ppm)
1	–	–	–	70:100	4.37
2	1.5	–	0	70:100	4.85
3	3.0	–	0	70:100	4.61
4	9.0	–	0	70:100	2.97
5	12.0	–	0	70:100	5.08
6	0	Fume silica powder	15.0	70:100	2.45
7	0	Fume silica powder	30.0	70:100	2.43
8	0	Fume silica powder	90.0	70:100	1.04
9	0	Fume silica powder	120.0	70:100	0.78
10	0	$(NH_4)_2HPO_4$	15.0	70:100	2.63
11	0	$(NH_4)_2HPO_4$	30.0	70:100	2.61
12	0	$(NH_4)_2HPO_4$	90.0	70:100	2.45
13	0	$(NH_4)_2HPO_4$	120.0	70:100	1.86

Table 5
Receipt of stabilization operation and TCLP data of stabilized concrete for P7 ash

Runs	Dosage amount of CAO (g/kg ash)	The used secondary chemical fixation agents	Dosage amount of second agent (g/kg ash)	(CAO + water): ash	[Pb] (ppm)
1	–	–	–	70:100	42.60
2	0.6	–	0	70:100	16.38
3	9.0	–	0	70:100	16.24
4	12.0	–	0	70:100	16.86
5	0.0	Fume silica powder	20.0	70:100	7.86
6	0.0	Fume silica powder	60.0	70:100	1.14
7	0.0	Fume silica powder	100.0	70:100	0.92
8	0.6	Fume silica powder	10.0	70:100	10.52
9	0.6	Fume silica powder	30.0	70:100	3.87
10	0.6	Fume silica powder	50.0	70:100	1.81
11	0.6	Fume silica powder	70.0	70:100	0.90
12	0.6	Fume silica powder	90.0	70:100	0.85

porosity means it would provide a higher reactive surface to acidic extractant of a TCLP test, in addition heavy metals (lead and zinc, etc.) are bonded on the surface of ash particles or present an identical heterogeneous phase in the porous matrix. Therefore, heavy metals in high porous ashes are not easy to be fixed.
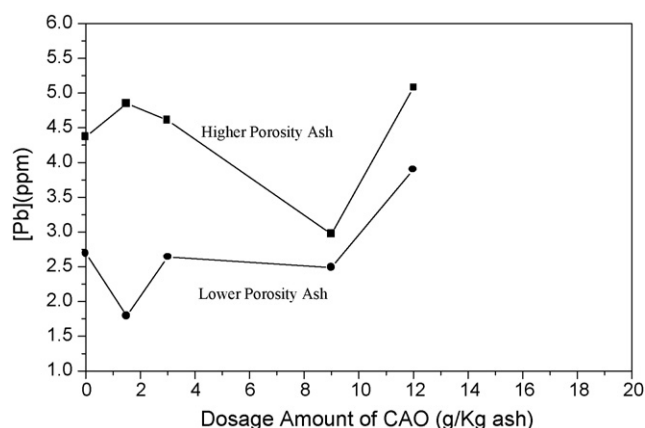

Fig. 1. Fixation curves of CAO for different porosity ashes.

3.1. Stabilization treatment of P1 ash

Table 2 summarizes the receipt of stabilization operation and TCLP data of stabilized concrete for P1 ash. The synthesized CAO solution, fume silica powder, aluminum chloride ($AlCl_3$), sodium silicate ($Na_2Si_2O_3$), and sodium carbonate (Na_2CO_3) were used as fixation agents in the ash. Proper amount of chemical fixation agents is showed as weight ratio to fly ash, and the applied weight of CAO solution was calculated from the dried CAO sample.

The results in Table 2 indicate that fume silica powder shows a good fixation efficiency, and Na_2CO_3 has the poorest fixation efficiency. Fig. 2 compares the fixation curves of fume silica alone, CAO alone and CAO + fume silica powders for lead in P1 ash to show that the incorporation of CAO with fume silica slightly reduces the fixation efficiency of lead. In this study, the optimal amount was found to be near 100 g of fume silica per 1 kg of ash.

3.2. Stabilization treatment of P4, P6 and P7 ash

Table 3 summarizes the receipt of stabilization operation and TCLP data of stabilized concrete for P4 ash. The synthesized
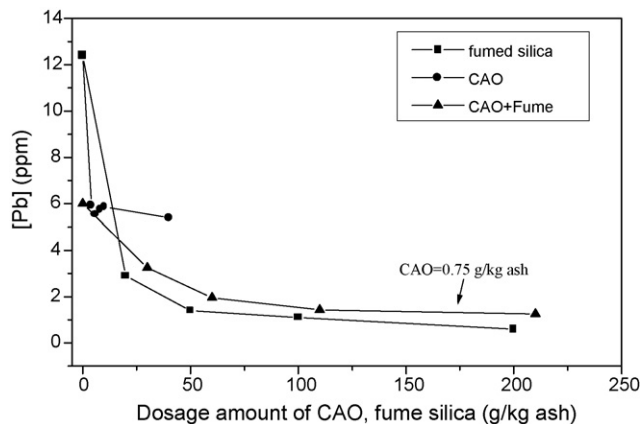
Fig. 2. Fixation curves of fume silica and CAO for P1 ash.

CAO solution and fume silica powder were used as fixation agents in the ash. Data demonstrates that fume silica powder shows higher fixation efficiency than CAO, and the fixation efficiency of in the application of fume silica powder combined with CAO was also lower than it would be by applying fume silica alone. The optimal amount was also near 100 g of fume silica per 1 kg of ash. Table 4 summarizes the receipt of stabilization operation and TCLP data of stabilized concrete for P6 ash. The synthesized CAO solution, fume silica powder and ammonia hydrogen phosphate ($(NH_4)_2HPO_4$) were used as fixation agents in the ash. Data demonstrates that fume silica powder shows higher fixation efficiency than other agents. The optimized mix amount was also near 100 g of fume silica per 1 kg of ash.

Table 5 summarizes the receipt of stabilization operation and TCLP data of stabilized concrete for P7 ash. The synthesized CAO solution and fume silica powder were used as fixation agents in the ash. Data demonstrates that fume silica powder shows higher fixation efficiency than CAO. Fig. 3 compares the fixation curves of fume silica alone, CAO alone and CAO + fume silica powders for lead in P7 ash to show that the incorporation of CAO with fume silica just slightly improves the reducing rate of the fixation efficiency of lead under low dosage amounts. The optimized mix amount is near 100 g of fume silica per 1 kg of ash.
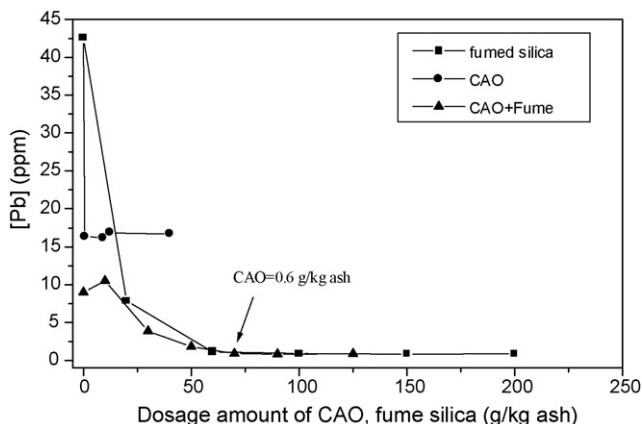

Fig. 3. Fixation curves of fume silica and CAO for P7 ash.

4. Discussions

4.1. Comparison efficiency of fume silica with other agents

For P1 and P4 ash, the fixation efficiency in the application of fume silica powder combining with CAO was slightly lower than by applying fume silica alone. This negative effect would imply a competitive reaction between inorganic polymer chains of CAO and fume silica in the ash matrix. In our previous paper [7], the authors had found that CAO could consume the OH ions in ash paste. Fume silica is a acidic matter and can be dissolved in basic catalysts, such as $NaOH_{(aq)}$ or $KOH_{(aq)}$. Therefore, the dissolution of fume silica should occur during stabilization processes of ash. But this negative effect is not observed in P7 ash (Fig. 3) because P7 ash has the highest porosity among these seven ashes.

In Table 2, the Na_2CO_3 had a poor fixation efficiency due to the carbonate ions being vastly consumed by free Ca^{2+} ions in the ash paste. In Table 4, $(NH_4)_2HPO_4$ also had a significant fixation efficiency for lead in P6 ash. $(NH_4)_2HPO_4$ also could react with Ca^{2+} and OH^- ions to form precipitates of NH_4OH, $CaHPO_4$ and $PbHPO_4$. In Table 2, $AlCl_3$ would undergo a hydrolysis process to form higher molecular weight species as does CAO, but the exothermic reaction would be inhibited by the hydration heat of active lime in ash.

In contrast, fume silica can be partially dissolved in basic water and enhanced by hydration heat of active lime in ash, and the undissolved silica core acts as a filler in the ash matrix. Therefore, fume silica has better fixation efficiency than other agents do in high porous baghouse ash. In the ash with higher porosity, CAO can diffuse into deeper pores and reacts with the alkali species rather than stay on the outside of the pore. This behavior can conduct a near positive effect on fume silica incorporation in lead stabilization.

4.2. Investigation of the fixation mechanism of fume silica

The fixation mechanism of fume silica has been investigated by a spectrum study. In order to enhance the intensity of the spectrum for observation, we added excessive amounts of fume silica in the preparation of treated ash samples. The working process of fume silica has been proposed to be that fume silica would fill into the pores on ash particles and might be dissolved in basic pore water to form insoluble lead silicate ($PbSiO_3$, etc.) precipitates on ash surface. Fig. 4 shows the XRD pattern of fresh P7 ash to observe that the lead ions in P7 ash are mainly in PbO form (2-theta = 27.9°). The patterns in Fig. 5 are XRD spectra of fume silica-treated P7 ashes under dosage amounts of (A) 20 g/kg ash, (B) 50 g/kg ash, (C) 100 g/kg ash, and (D) 200 g/kg ash, respectively. It is clear to see several new peaks at 2-theta 8.4°, 11.7°, 20.8°, 27.6°, these peaks correspond to $Ca(OH)_2$ and $PbSiO_3$ crystal phases. Fig. 6 illustrates the FT-IR spectra of several fine chemicals. The patterns in Fig. 7 illustrate the FT-IR spectra of fresh P7 ash and four fume silica-treated P7 ash samples. It is clear to observe that the peak at 1200 cm^{-1} is increased in fume silica-treated P7 ash, this peak is also attributed to $PbSiO_3$ crystals.
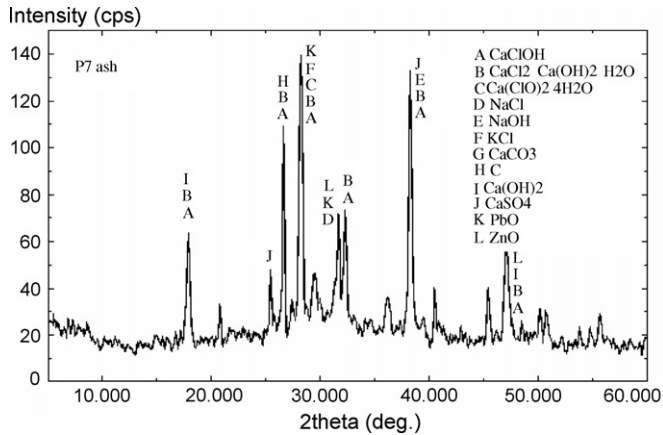
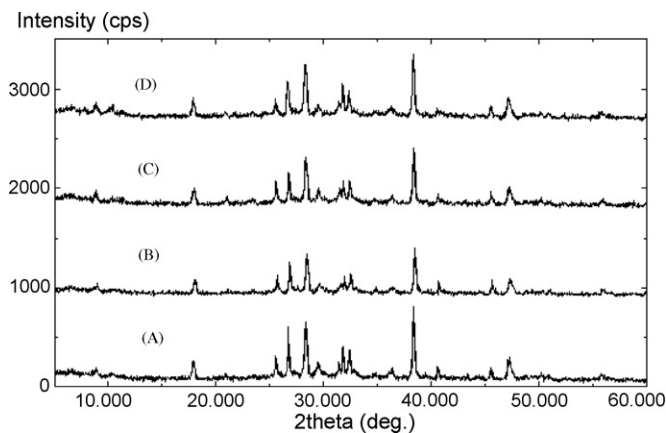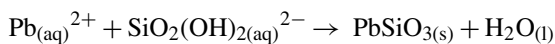Fig. 4. X-ray diffraction pattern of pure P7 ash.

Fig. 5. X-ray diffraction pattern of solidified P7 ash by various fume silica (A) 20 g/kg ash; (B) 50 g/kg ash; (C) 100 g/kg ash; (D) 200 g/kg ash.

The major fixation reaction between dissolved fume silicate and free lead ions has been proposed as following equation:

$$Pb_{(aq)}{}^{2+} + SiO_2(OH)_{2(aq)}{}^{2-} \rightarrow PbSiO_{3(s)} + H_2O_{(l)}$$

Besides, the production of cementation compounds in pores (for example, $Ca(OH)_2$) and sorption of lead ions on partially dissolved fume silicate are also possible mechanisms. But the
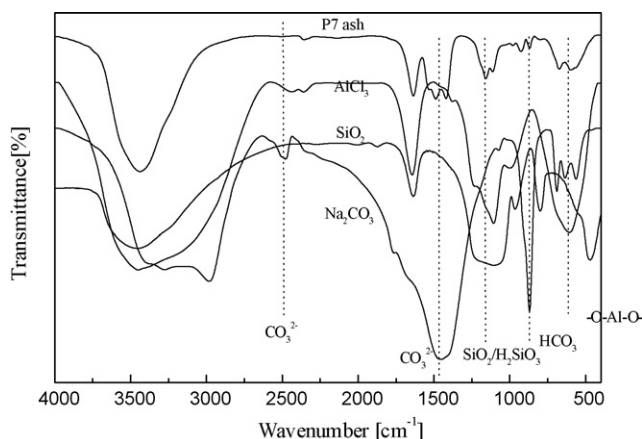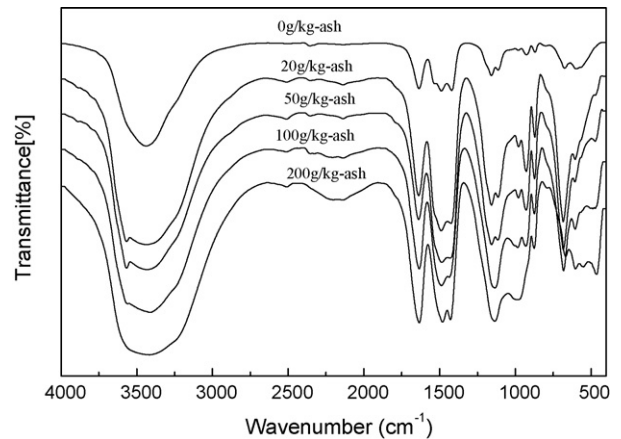

Fig. 6. FTIR spectra of P7 ash, $AlCl_3$, SiO_2 (fume silica) and Na_2CO_3.

Fig. 7. FTIR pattern of solidified P7 ash by various fume silica contents: 0 g/kg ash, 20 g/kg ash, 50 g/kg ash, 100 g/kg ash and 200 g/kg ash.

authors believe that the major fixation reaction will be the precipitation reaction between totally dissolved fume silicate and free lead ions.

5. Conclusions

In this study, we have applied fume silica (SiO_2), aluminum chloride ($AlCl_3$), sodium silicate ($Na_2Si_2O_3$), and sodium carbonate (Na_2CO_3), ammonia hydrogen phosphate ((NH_4)$_2$HPO$_4$), and colloidal aluminum oxide (CAO) as the chemical fixation agents for the lead in MSWI baghouse ash. Results indicate that fume silica powder shows good fixation efficiency for the ash with higher porosity through the major mechanism of the formation of $PbSiO_3$ precipitates. The optimized dosage amount is near 100 g of fume silica per kilogram of ash. Due to the fact that the major chemical composition of baghouse ash is almost within a certain wt% range, the application of this technique to other fly ash generated from other plants or countries is expected to be successful. To avoid the diversity in the chemical composition, an increase in the additive percentage is preferred for passing the TCLP test.

Acknowledgements

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