

COLEACHING MECHANISM OF BAGHOUSE ASH/SCRUBBER RESIDUE BINARY MIXTURES

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ABSTRACT

Leaching behavior of lead in the binary mixture of semi-dry scrubber residues (PR) and baghouse ashes (FA) collected from municipal solid waste incineration (MSWI) plants has been previously studied. In this study the leaching mechanisms were investigated to better understand how the chemical compositions affect the leaching concentration of lead from such binary mixtures. FT-IR and X-ray diffraction spectrometries of binary mixtures of FA and RP collected from two MSWI plants were examined. Results show that when the FA with high lead content is mixed with RP, the Pb leaching concentration from these two binary mixtures was reduced through two mechanisms. The first one is that lead could be re-precipitated by alumina hydrate on the RP surface, and the second one is that FA losses its active lime to increase the local pH.

INTRODUCTION

Over 90% refuse wastes in Taiwan are processed in 17 municipal solid waste incineration (MSWI) plants. The total quantity of combustion residues, such as boiler ash, scrubber ash, precipitator ash and bottom ash, is about 2000 ton d⁻¹ [1]. Heavy metal leaching of residues of incinerator air pollution controlling devices (APCDs) has been studied. Literature has also reported landfilling of such residues and solidified ash concrete behavior [2-9]. Technically the fly ash represents mixed residues collected from semi-dry scrubber (the flue gas spray dryer/absorber), electrostatic precipitator and/or baghouse. There is a relationship between chemical compositions of these residues and heavy metal leaching behavior [10-17]. In general, each residue is also a mixture of fine inorganic compound, such as Al₂O₃, SiO₂, CaO, among others.

In our previous study [1], the leaching behavior of lead was affected by chemical composition of the residue, especially free CaO. An empirical equation was proposed to describe the lead leaching behavior of the binary mixture of semi-dry scrubber residues (RP) and baghouse ashes (FA) [18]. And in the present study the leaching mechanisms were further investigated in order to better understand how the chemical compositions of these residues affect the Pb leaching from such binary mixtures.

MATERIALS AND EXPERIMENTAL METHODS

1. Sampling of Residues from Combustion Air Pollution Control Devices

The FA and RP were collected separately from two large-scale MSWI plants (over 900 ton d⁻¹) in the Northern and Southern part of Taiwan, named plant P and S, respectively. In addition, two MSWI plants with capacity about 1350 ton d⁻¹ in Western Taiwan were selected to collect the residues from the APCDs. The incinerators are mass-burn type and equipped with a cyclone, semi-dry lime scrubbing system with electrostatic precipitator. All fresh FA and RP were collected from the sampling ports and aged in a dark room under constant temperature and moisture conditions for stabilizing the hydrophilic property of RP. The boiler ash of incinerator was not sampled in this study.

2. Physical Analyses

A pH-meter (Fisher Scientific Accuement Co., USA) was used to probe the pH value of the solution. A Solar-969 atomic absorption (AA) spectrometer (Unicam Co., USA) was used to detect metal concentrations in extracts. All chemicals were purchased from

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Table 1. Basic properties of collected residues

Residues	Plant P		Plant S	
	FA	RP	FA	RP
Al ₂ O ₃ (g 100 g ⁻¹) ^a	37.93	24.61	26.33	12.0
SiO ₂ (g 100 g ⁻¹) ^a	3.91	36.68	9.26	32.20
CaO (g 100 g ⁻¹) ^a	42.60	28.16	55.21	38.45
Fe ₂ O ₃ (g 100 g ⁻¹) ^a	1.11	5.42	0.70	4.89
CaO _f (g 100 g ⁻¹) ^a	14.45	5.13	8.50	13.20
Total Pb (μg g ⁻¹) ^a	311	1615	424	3870
Acid extractable lead (μg g ⁻¹) ^b	172.8	17.0	115.2	27.8
pH	12.10	11.89	12.11	11.86
Apparent color	White-gray	Gray	Light yellow-gray	Gray

^aWet chemical analysis method.

^bBy 10 vol% of concentrated HNO₃ extraction instead of buffer solution -B in the TCLP procedure.

Alderich and used directly without any purification. All experimental methods that used in the present study are standard method adopted by Republic of China and details are given in the following.

3. Toxicity Characteristic Leaching Extraction Procedure Test

A brief for the toxicity leaching extraction procedure (TCLP) test is described below [19]. Solid waste is graded to pass the 10 mm standard sieves. The pH of used extraction buffer solution is depended on the pH of waste (ashes). If the pH of waste (ashes) is less than 5.0, the buffer solution is prepared by acetic anhydride with a pH of 2.88 (called buffer B); while if it is higher than 5.0, the buffer solution is prepared by acetic anhydride and sodium hydroxide with a pH of 4.93 (buffer A). The extraction procedure is to mix residues with a proper buffering solution under a liquid/solid ratio of 20, and following a rotation shaking with a speed of 30 rpm for 18 h. The liquid was removed through 0.45 μm glass filter filtration and the pH and metal concentration of those filtered extracts were determined.

4. pH of Ashes

10 g solid waste is mixed with 20-mL CaCl₂ standard solution (0.01 M) in a 50 mL beaker [20]. After stirring for 30 min and staying for another 30 min at room temperature, pH was measured in the supernatant of the solution at 25 °C (within 2 °C error).

5. Wet Chemical Analyzes of Ashes Composition

The levels of major components of Al₂O₃, SiO₂, CaO and Fe₂O₃ and minor components of free CaO and Ca(OH)₂ were determined based on differential wet-chemistry [1,27]. In the major component part, 0.5 g dried sample was dissolved by concentrated HCl and HNO₃ and 0.5 g NH₄Cl for several times. Parts of insoluble residues were dried and weighted which can

be attributed to the components of SiO₂, Al(OH)₃ and Fe₂O₃. The residual filtrate was reheated and NH₄NO₃ was added and the precipitate was collected after filtration. The weight of precipitate was used to calculate the percentage of NH₄OH in residues. The KMnO₄ titration with the final filtrate of the above step was used for determining the miner component. The percentage of Fe₂O₃ was determined from the titration of K₂Cr₂O₇ with a fresh sample that dissolved in concentrated HCl. The difference of weight of NH₄OH and Fe₂O₃ is the weight of Al(OH)₃.

6. Measurement of X-ray Diffraction (XRD)

The measurement was performed on XRD-6000 (Shimadzu Co., Japan) with a light source of Cu-Kα line. Sweep range is 5° to 75° with a scanning rate 2° min⁻¹ at room temperature. The data output type is ASCII and treat by personal computer to prepare the XRD spectra.

7. Measurement of Fourier-Transform Infrared Spectroscopy (FTIR)

The measurement was performed on Vector-22 FTIR (Bruker Co., USA) with a scanning range and resolution 40-4000 cm⁻¹ and 4 cm⁻¹, respectively. Solid powder sample was crushing carefully with pre-dried KBr and then pressed into a thin disc film at room temperature.

RESULTS AND DISCUSSION

The chemical compositions, apparent color, ash pH of the collected ashes have been previously studied [1] and listed in Table 1. In our previous study, the CaO-Al₂O₃-SiO₂ ternary composition grids of MSWI ashes (FA and RP) have indicated that the RP is an alumina-rich cement-like material, and FA is a Portland cement-like material [1]. Figure 1 shows the XRD patterns for the RP and FA ashes of plant P and plant S in which peaks have been assigned for the correspond-

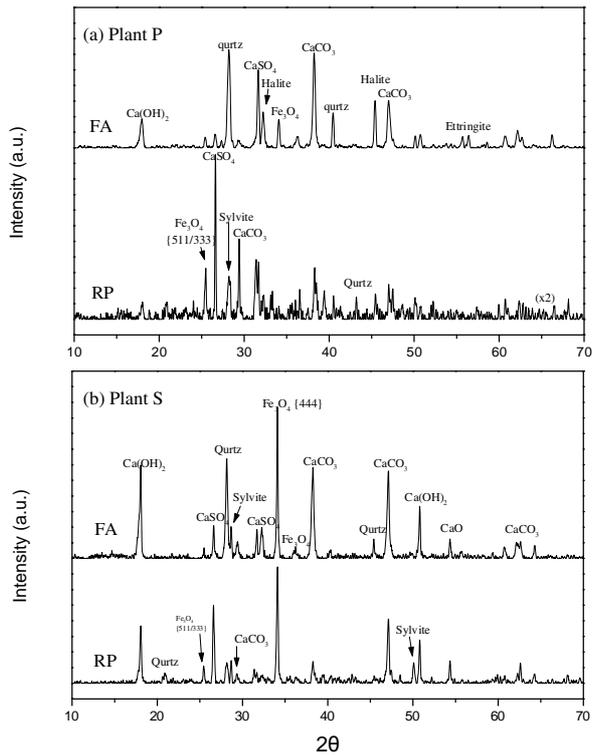


Fig. 1. X-ray diffraction patterns of residues collected from Plant P and S.

ing inorganic compounds [1,6,8]. From these results, the PR samples possess high CaCO_3 and $\text{Ca}(\text{OH})_2$ phase that produced by hydration of sprayed lime in the scrubbers (of course a higher free CaO is observed in FA samples contributed from unreacted lime). Figure 2 shows the FT-IR spectra of fresh and acid-leached ashes from plants P and S and peak assignments have been done on these spectra. After leaching, Al_2O_3 in ash might only exist in octahedral site, therefore the peaks of Al-O vibrations is absent in Fig. 2b and 2d due to its natural of infrared inactive. In Fig. 3, a blue shift was observed at the frequency of 1425 to 1475 cm^{-1} corresponding to the character absorption peak of carbonate group as the FA content increased in the binary mixtures, after TCLP leaching. This indicates that C-O bond is shortened in the mixture with a higher FA content, thus, a lower binding efficiency to metal ions could be expected. The finding of less metal binding is consistent with the TCLP leaching data shown in Table 2 and Fig. 4. Typically, the Pb leaching of the FA/RP mixture is lower as the amount of FA is decreased. However, it is noted that the Pb leaching of FA/RP mixture of Plant S in a ratio of 80/20 was higher than pure FA (Table 2). The reason(s) for this observation is unclear. Figure 4 shows the plot of lead concentration versus FA of plant S. Clearly, the leached Pb concentration is highly dependent on the FA content over 60% with insignificant Pb concentrations observed at FA < 60%.

For solidified fly ash, temperature of fly ash/ce-

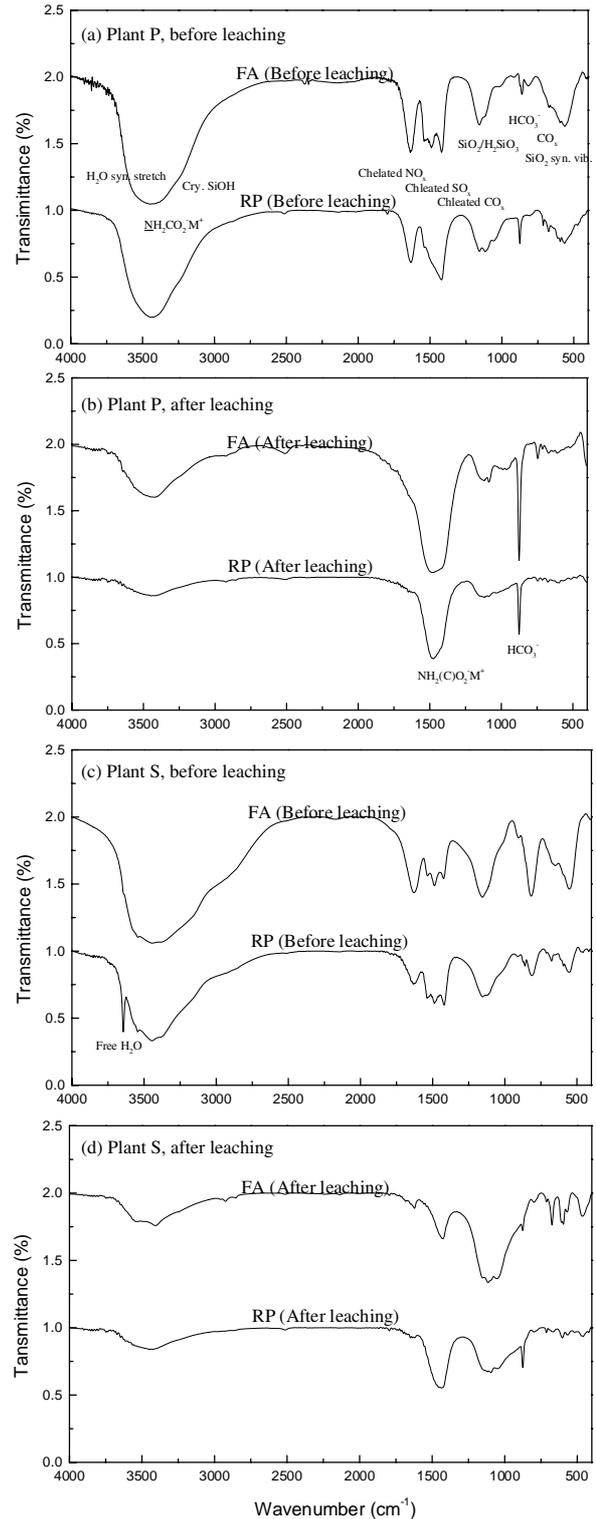


Fig. 2. FT-IR spectra of residues collected from Plant P, (a) before leaching and (b) after leaching, and Plant S, (c) before leaching and (d) after leaching.

ment paste typically rises and pH increases. The temperature of solution was controlled by a water bath regulation system. The equilibrium time was set as 10 min for each experimental temperature. Figure 5 shows plots of pH-temperature relationship for TCLP

Table 2. Pb leaching data from the TCLP test of RP/FA mixtures

Ratio of FA/RP (by weight ratio)	Plant P		Plant S	
	Residual weight (%)	Pb (ppm)	Residual weight (%)	Pb (ppm)
100/0	56	29	28	3.2
90/10	-	-	24	4.1
80/20	58	13	23	12
70/30	-	-	25	1.9
60/40	64	4.0	28	1.1
50/50	67	0.18	27	1.3
40/60	-	-	28	2.2
30/70	-	-	35	0.7
20/80	81	0.08	39	0.8
10/90	-	-	39	0.5
0/100	65	0.2	27	1.1

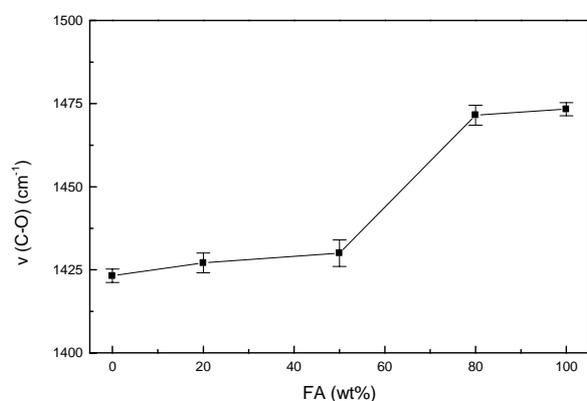


Fig. 3. Plot of the frequency of the carboxylate group vs. FA.

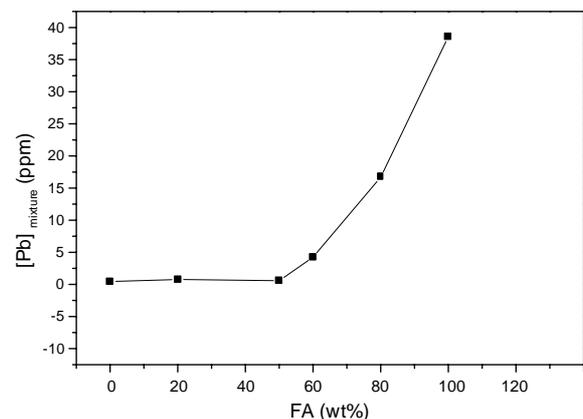


Fig. 4. Plot of lead leaching concentration versus FA of Plant S.

extracts of single RP and single FA from plant P. A linear pH decrease with temperature was observed in the FA extract with a significant transition at 55 °C observed and in the RP extract. The results of the same experiments for pure solutions of Al^{+3} , Fe^{+3} and Ca^{+2} ions made by AlCl_3 , FeCl_3 and Ca(OH)_2 are shown in Fig. 6. A similar transition was observed at 40-60 °C that is dependent on the ionic strength of so-

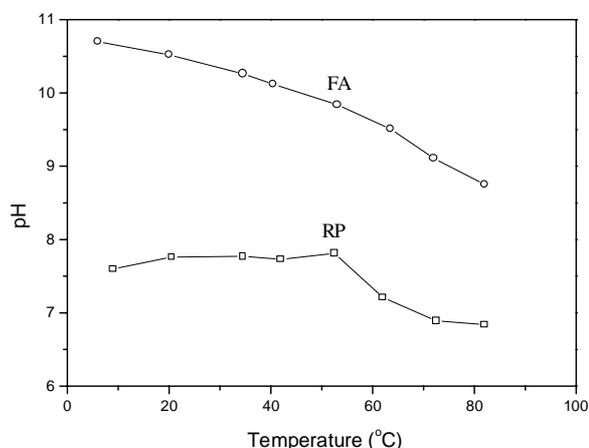
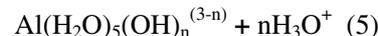
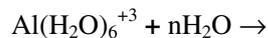
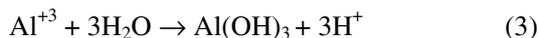
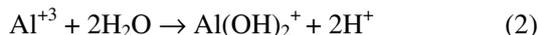
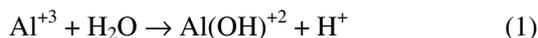


Fig. 5. Plots of pH-temperature relationship of TCLP extracts for RP and FA from plant P.

lution and maybe attributed to the dehydration reaction of ions in aqueous solution, and results have indicated that Ca^{2+} ion is the domain species in the FA extract and Al^{3+} the dominant ion species in the RP extract [22]. Therefore when the FA with high lead leaching concentration is mixed with RP, the dominated species in TCLP extracts of these binary mixtures would transfer from Ca^{+2} to Al^{+3} ion. It means that the lead ions will be re-trapped or precipitated on the ash surface due to surface complexation. The total dehydration reactions of alumina solution is as follows:



Although pH controlled leaching mechanism is well established, the mechanism proposed in this study

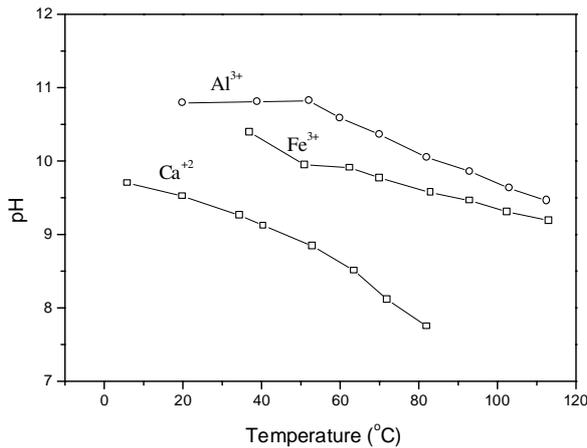


Fig. 6. Plots of pH-temperature relationship of Al^{3+} and Fe^{3+} ion aqueous solution.

should provide insightful information. If one just considers the pH controlled leaching process of lead for FA/RP mixtures, the results of Figs. 5 and 6 demonstrate that which ionic species is dominant for any given pH values of TCLP extracts of FA and RP. Bear in mind that FA is a basic ash and RP is near acidic ash. In addition, the driving force of metals leaching into acidic-extract is mainly caused from the proton ion exchange with metal ions from particulate surface. Assume that the leaching of lead from a single particulate is in equilibrium, the contribution of free CaO should not be ignored due to the fact that the RP contains more hydrated lime, CaSO_4 and lead concentration, while fly ash contains more free CaO, CaCO_3 and $\text{Ca}(\text{OH})_2$. If the FA content in the mixture is reduced, the Pb leaching concentrations will be also reduced due to decreased alkali species for lead in fly ash. And the leaching "mechanism" of lead in this paper was attributed to the alumino-silica gel due to the fact that the content of Al_2O_3 was enriched in FA and SiO_2 enriched in RP. Therefore the alumino-silica gel is easily formed in the FA/RP mixtures under acidic or basic aqueous solution.

CONCLUSIONS

This study was attempted to address the leaching mechanism of lead from the FA and RP of MSWI plants. Results shows that when the FA with high lead concentration is mixed with RP, the Pb leaching concentration from these two binary mixtures would be reduced through two mechanisms. The first is that lead could be re-precipitated on the ash surface by alumina hydrate contributing from RP, and the second is the loss of the active lime from FA.

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