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Thermal Treatment of Heavy Metal in Incinerator Fly Ashes

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Fly ash discharged from an incinerator has been considered as hazardous wastes due to their leaching of various toxic inorganic and organic substances (Eighmy *et al.*, 1995; Johnson *et al.*, 1995; Kida *et al.*, 1996). It has been measured that some heavy metals in fly ash frequently exceed their regulatory toxicity characteristics leachability procedure (TCLP) limits. Those that meet the regulatory TCLP limits still have a great tendency to contaminate the soil-underground water system in the long run, because the alkalinity of fly ash will be continuously neutralized by the infiltrated water which is weakly acidic due to acid rain or/and absorption of CO_2 from the atmosphere. The fly ash in landfill will eventually reach a state of $pH<7.0$. Thus it is desirable to immobilize heavy metals in fly ash by various means before they are disposed of. Thermal treatment has been emerging as a promising technique to immobilize or react heavy metals with inorganic constituents, such as SiO_2, Al_2O_3, bentonite, kaolinite, etc. (Wei, 1995; Wei, 1996; Wei *et al.*, 2001). The reaction products via thermal treatment are more resistant to acid leaching tests, such as TCLP, than their original forms are.

Most fly ash discharged from a municipal solid waste incinerator is rich in calcium compounds (i.e., $Ca(OH)_2$, CaO, $CaCl_2$) because CaO or $Ca(OH)_2$ is often sprayed into the boiler-cooled flue gas stream to react HCl into $CaCl_2$ that is then collected by a bag house or an electrostatic precipitator. In order to meet the stringent HCl emission limit such as $\leqq$40ppm in stack gases of an incinerator, spraying of CaO or $Ca(OH)_2$ in excessive amounts (i.e. at a Ca/Cl mole ratio much greater than their stoichiometric ratio, 0.5) is necessary. This leaves a considerable quantity of CaO or $Ca(OH)_2$ un-spent, that will accompany the reaction product $CaCl_2$ as the major constituents of fly ash. The CaO or $Ca(OH)_2$ is sprayed into the flue gas duct at a place located downstream from the heat-extraction boiler; therefore they do not experience the high-temperature environment in the incineration chamber. They have the potential of forming calcium aluminum silicates to immobilize heavy metals if the fly ash collected by an air pollution control device is further thermally treated. Frequently, NaOH and/or KOH are mixed with CaO or $Ca(OH)_2$ and sprayed into the boil-cooled flue gas to enhance the reaction with HCl to form NaCl and/or KCl to reduce dioxin formation. Therefore, fly ash discharged from such an incinerator system may also be rich in content of NaCl and KCl, both of which can promote sintering of fly ash during further thermal treatment due to

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their low melting point. Numerous studies have been devoted to the leaching properties, speciation, acid neutralizing capacity, and mineralogical aspects of incinerator fly ash (Kida *et al.*, 1996; Steenari and Lindqvist, 1999; Shimaoka and Hanashima, 1996); however, none so far has ever tried to link the leaching properties of fly ash with the chemical reactions of heavy metals that occur in the high-temperature incinerator chamber. A better understanding of such chemical reactions that form heavy metal compounds in fly ash will provide more information to help develop better incineration techniques to reduce the leaching percentage of heavy metals to a non-hazardous level.

This study focus on two parts: (i) linking the leaching properties of heavy metals in fly ash discharged from various municipal waste incinerators with their formation reactions in the incineration chamber; and (ii) explaining the sintering phenomenon of fly ash, that is observed with the scanning electron microscope (SEM) technique, based on the information on Cl and Ca contents in fly ash.

MATERIALS AND METHODS

Four fly ash samples were collected from the ash discharges of air pollution control devices of various municipal waste incinerators with an incinerating capacity greater than 700 tons/day. They are all designed by well-recognized companies in the world, and have been serving for less than 5 years. The major chemical composition of the fly ashes is depicted in Table 1. Their Ca+Na+K content is 25.9%−39.7%, and 31.4%−50.2% if both Si and Al contents are included with Ca+Na+K. All fly ashes are rich in chloride (5%−21.4% Cl content) because the incinerated refuses contain a considerable percentage of polyvinyl chloride.

The dried (at 105℃, 3−5days) fly ash samples were electrically heated for 1 hour at 300, 500, and 900℃. All the dried and heated samples were leach-tested according to the glacial acetic acid-based TCLP method (U.S. EPA SW-846 Method 1311, TCLP) after their morphologies were studied with a SEM. The TCLP leachates were digested in a microwave oven, and the content of Cu, Pb, Zn, and Cr measured with a flame atomic absorbency spectrometer (FAAS). The respective method detection limits were 0.30 mg Cu/kg, 0.60 mg Pb/kg, 0.13 mg Zn/kg, and 0.15 mg Cr/kg. The procedure from TCLP leaching for each sample was carried out in triplicates, and each TCLP extract was measured three times for the concentration of heavy metals.

It is a well-known fact that Cl content in fly ash can affect both the solubility and volatility of metals (Wey *et al.*, 1996). Metal chlorides are usually more soluble in weak acid and more volatile than their oxides are. Here, we correlate Cl content with the leaching percentage of heavy metals from fly ash. The correlation coefficients are used to propose possible reaction routes for the formation of heavy metal chlorides in an incinerator chamber. Cl and Ca contents in fly ash are used as indices to explain the sintering results observed by SEM.

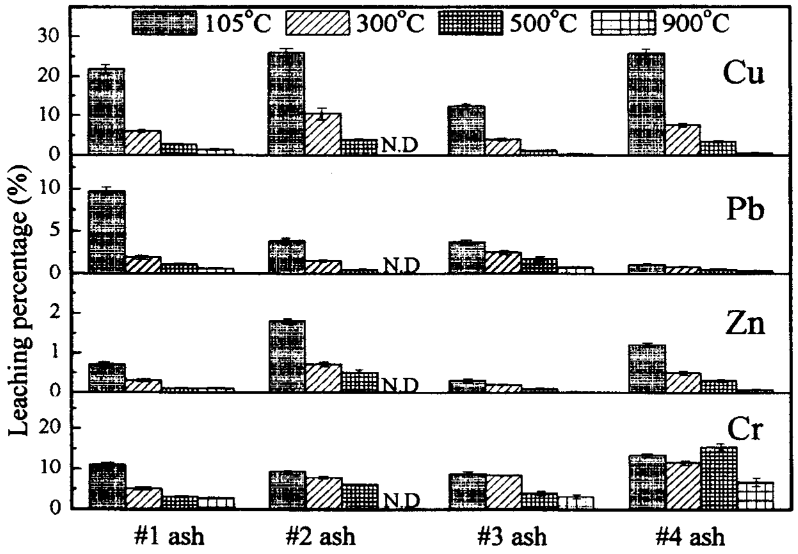


Figure 1. Leaching percentage of heavy metals from #1 – #4 fly ashes after thermal treatment from 105 – 900℃.

RESULTS AND DISCUSSION

Figure 1 shows the effect of treatment temperature (105, 300, 500, and 900℃) on the leaching percentage (error bar represents standard deviation) of Cu, Pb, Zn, and Cr from fly ash, respectively. They indicate that thermal treatment of fly ash can very effectively reduce the leaching of Cu, Pb, Zn, but not Cr.

Figure 1 also indicates that all the heavy metals can be more fully immobilized with a greater temperature, except for Cr in #4 ash. Table 2 shows the leaching percentages of Cu, Pb, Zn, and Cr from various dried fly ashes. All correlations between the leaching percentages of any two heavy metals (i.e., data of any two rows in Table 2) are rather poor except that between Cu and Zn. The correlation coefficients are: $r_{Pb\text{-}Cu} = -0.14$, $r_{Pb\text{-}Cr} = -0.23$, $r_{Cu\text{-}Cr} = +0.55$, $r_{Pb\text{-}Zn} = -0.31$, $r_{Cr\text{-}Zn} = +0.15$, and $r_{Cu\text{-}Zn} = +0.88$. This implies that when one fly ash is holding "A" heavy metal tightly and "B" heavy metal loosely, another fly ash may hold "A" loosely and "B" tightly despite the similarity among the fly ash samples. The above phenomenon may be attributed to the variety of heavy metal speciation in fly ash, and to the intrinsic complexity of chemical properties of fly ash. There are many difficult-to-resolve factors that affect the leaching behavior of heavy metals.

We believe that the fractions of Cu, Pb, and Zn that are leached by TCLP are mostly in chloride form because CuO, PbO, and ZnO are insoluble in weak acids. Thus the leaching percentages of Cu, Pb, and Zn shown in Table 1 can be regarded as being the percentages of their chloride form in fly ashes. For Cr, the fraction leached is mostly in hexavalent oxyanion form (Lee *et al.*, 1995; Rinehart *et al.*, 1997; Spanos *et al.*, 1995) because chromium chloride, unlike $CuCl_2$, $PbCl_2$, and $ZnCl_2$, is only very slowly soluble in weak acids. We suggest that the percentage of the chloride form of heavy metals in any fly ash is always in a decreasing order of Cu>Pb>Zn as observed in Table 2.

In order to explain the experimental observation, two possible routes based on thermodynamics are proposed and compared to each other. Note that the temperature in an incineration chamber is as high as 850 – 1050℃, therefore the reaction kinetics is rather fast and the activation energy barrier is easy to overcome. The first route is formation of chlorides of heavy metals via reactions of metal oxides with HCl in the incinerator chamber:

rx 1 $CuO+2HCl_{(g)} \rightarrow CuCl_2+H_2O_{(g)}$ $\Delta G = -20.7$ kcal/mole
rx 2 $PbO+2HCl_{(g)} \rightarrow PbCl_2+H_2O_{(g)}$ $\Delta G = -38.9$ kcal/mole
rx 3 $ZnO+2HCl_{(g)} \rightarrow ZnCl_2+H_2O_{(g)}$ $\Delta G = -21.3$ kcal/mole

According to the Gibbs free energy change, reaction 2 is more favored than reactions 1 and 3, and the percentage of heavy metal chloride in fly ash should be in a decreasing order of Pb>Zn>Cu. However, this is inconsistent with our experimental observation of Cu>Pb>Zn shown in Table 2. The second possible route is that chlorides are formed via the reaction of metals with HCl:

rx 4 $Cu+2HCl_{(g)} \rightarrow CuCl_2+H_2$ $\Delta G = -123.1$ kcal/mole
rx 5 $Pb+2HCl_{(g)} \rightarrow PbCl_2+H_2$ $\Delta G = -68.0$ kcal/mole
rx 6 $Zn+2HCl_{(g)} \rightarrow ZnCl_2+H_2$ $\Delta G = -64.4$ kcal/mole

The Gibbs free energy change indicates that rxs 4 – 6 can proceed more spontaneously than rxs 1 – 3, and that rx 4 is more favored than rxs 5 and 6. Therefore, the percentage of heavy metal chlorides in fly ash is predicted to be in a decreasing order of Cu>Pb>Zn. This prediction is consistent with our experimental observation presented in Table 2.

Table 2 also presents the correlation coefficients between the leaching percentage of each heavy metal and Cl content in fly ash. The correlation coefficients ($\gamma_{H.M\text{-}Cl}$) are 0.999 for Cu, –0.098 for Pb, 0.885 for Zn, and 0.509 for Cr, respectively. As mentioned above, the fractions leached are most probably in chloride form. Thus the 0.999 correlation coefficient for Cu implies that formation of $CuCl_2$ in the incineration chamber is directly proportional to HCl vapor pressure that is rapidly formed in the incineration chamber, and it is then mostly converted into $CaCl_2$, KCl, and NaCl when the flue gas stream enters the sprayer. It should be noted that heavy metal chlorides only represent quite a small portion of chloride salt in fly ash which mainly consists of $CaCl_2$, KCl, and NaCl due to the great percentage of Ca, K, and Na (see Table 1). A fairly acceptable correlation coefficient, $\gamma_{H.M\text{-}Cl} = +0.885$, for Zn implies that the formation of $ZnCl_2$ in the incinerator chamber is also roughly proportional to HCl vapor pressure. Contrarily, $\gamma_{H.M\text{-}Cl}$ for Pb is –0.098, which means that there is no good correlation for Pb at all. This is probably due to the various valence states of Pb and the formation of Pb_3O_4 which is thermodynamically more stable than $PbCl_2$. Note that it is unlikely for compounds, such as Cu_3O_4 or Zn_3O_4 to form. The poor correlation between Cr leaching percentage and Cl content ($\gamma_{\text{H.M-Cl}} = +0.509$) is explainable by the fact that the major leached Cr species is CrO_4^{2-}. Unlike the high solubility of $PbCl_2$, $CuCl_2$, and $ZnCl_2$ in water or weak acids, $CrCl_3$ is almost insoluble.

Table1. Major composition and properties of various fly ash samples

element	#1 fly ash	#2 fly ash	#3 fly ash	#4 fly ash
Ca (%)[a]	24.8	16.6	17.1	11.3
Si (%)[a]	2.5	2.4	13.0	3.9
Al (%)[a]	1.6	0.50	6.2	1.6
Na (%)[a]	10.6	9.5	9.6	9.9
K (%)[a]	4.3	3.0	4.3	4.7
Ti (%)[a]	0.20	0.93	1.1	0.36
P (%)[a]	0.50	0.30	2.3	0.8
Mg (%)[a]	0.59	0.91	0.27	1.08
Fe (%)[a]	0.86	0.49	1.76	0.99
Pb (ppm)[b]	1140	1620	1010	2300
Zn (ppm)[b]	5610	6920	8620	16210
Cu (ppm)[b]	887	833	1022	942
Cr (ppm)[b]	390	679	880	290
C (%)[c]	2.28	2.13	0.70	1.63
H (%)[c]	1.53	3.12	0.40	3.06
S (%)[c]	1.28	1.47	3.30	3.00
Cl (%)[c]	16.4	21.4	5.0	20.1
PH	11.6	11.3	9.9	10.4
LOI (%)[d]	14.2	13.9	5.5	13.6
BET (m^2/g)[e]	7.60	5.28	1.46	3.64

[a]: measured by inductively coupled plasma technique.

[b]: measured by an FAAS.

[c]: measured by an elemental analyzer.

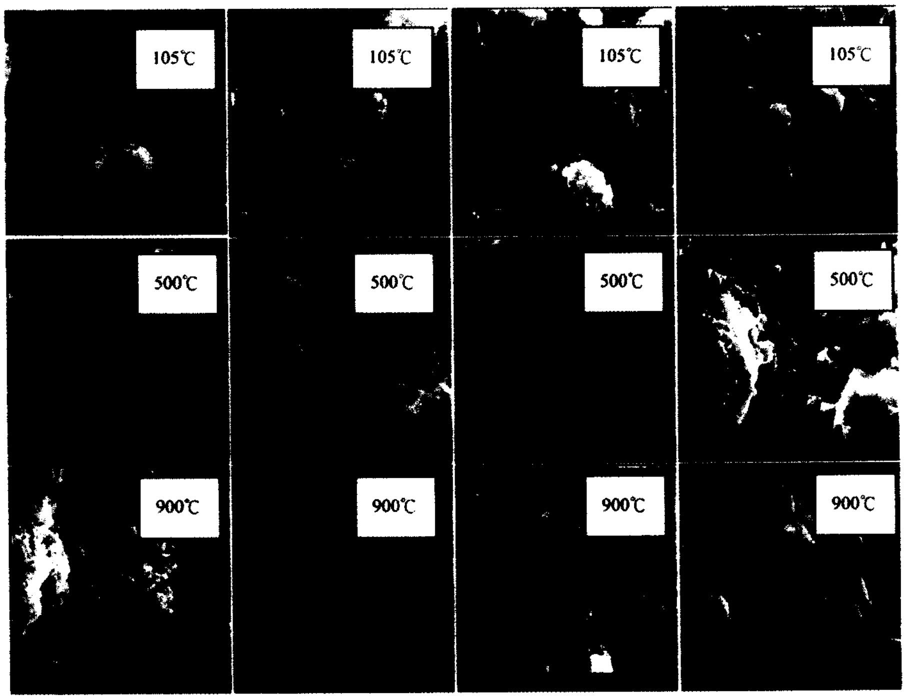
[d]: loss on ignition (LOI), weight loss after heating at 1000℃ for 1 hour.

[e]: Brunauer-Emmett-Teller (BET) surface area, measured by a BET micrometer.

Table2. Leaching percentage of heavy metals from various dried fly ashes, and correlation coefficients between each heavy metal and Cl content*

heavy metal	leaching percentage (%)				$\gamma^{*}_{\text{H.M.-Cl}}$
	#1 ash	#2 ash	#3 ash	#4 ash	
Cu	21.8	26.0	12.4	25.7	+0.999
Pb	9.3	3.7	3.7	1.1	-0.098
Zn	0.72	1.8	0.29	1.2	+0.885
Cr	11.0	9.2	8.8	13.4	+0.509

*: Cl contents are: 16.4% (#1 ash), 21.4% (#2 ash), 5.0% (#3 ash), and 20.1% (#4 ash).



#1 ash **#2 ash** **#3 ash** **#4 ash**

Figure2. Morphology of incinerator fly ashes treated at different temperatures.

Figures 2 are SEM images of each fly ash that was thermally treated at different temperatures. SEM photos of #2 and #4 fly ashes show that a considerable sintering phenomenon occurs after both samples are thermally treated at 900℃ for 1 hour. It is unusual to observe that #2 fly ash is sintered into a needle-like appearance, while #4 is into a pellet-like one. The considerable sintering of #2 and #4 fly ashes may be interpreted by the factor of their relatively higher Cl content (see Table 1). Many researchers have recognized that $CaCl_2$, KCl, and NaCl would enhance sintering due to their relatively low melting point (≤800℃).

Furthermore, although #1 fly ash also contains a considerable amount of Cl (16.4%), however, due to an over-addition of $Ca(OH)_2$ a lot of CaO that has a melting point of 2570℃ was left un-reacted in the collected fly ash, causing hindrance of sintering. It is thus suggested that to make sintering an easier process, the spray of $Ca(OH)_2$ into the flue gas stream of a waste incinerator to react with HCl should be kept at a minimum level.

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