



MINTEQ modeling for evaluating the leaching behavior of heavy metals in MSWI fly ash

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Abstract

At present, all kinds of municipal solid waste incineration (MSWI) fly ash stabilization technology has been reported and successfully applied in many countries. However, leaching procedures are very different that the technologies lack uniform standard, and it is even impossible to predict the long-term stabilization. Geochemical model can explain the environmental stabilization based on chemical phase and thermodynamic crystal structure, and it is also able to guide the development of environment-friendly stabilization technology and choosing of chemical agents. Both experiment analysis and geochemical modeling were used to study the correlation between leaching behavior of MSWI fly ash and variation of pH. Dissolution/precipitation mechanism was applied in the simulation. The result indicated that the pH-dependent leaching behavior predicted by Visual MINTEQ is well in agreement with the result of pH-dependent test. pH value of leachate can significantly change the leaching behavior of MSWI fly ash. The leaching behavior of heavy metals for Pb and Cd is controlled by dissolution/precipitation mechanism, whereas for Zn and Ni, it is effected by surface adsorption reaction over a special extent of pH value.

Key words: MINTEQ model; incinerator fly ash; stabilization mechanism

Introduction

In 2005, the amount of municipal solid waste incinerator (MSWI) fly ash achieved 2.37×10^8 kg generated in China. As fly ash is one of the hazardous waste including both heavy metals and dioxins (Xu *et al.*, 2007; Jiang *et al.*, 2004), fly ash stabilization technology attracted wide attention. At present, fly ash stabilization products are evaluated following the various toxicity leaching procedures, but few experiments can completely describe the fly ash leaching behavior (Jing *et al.*, 2004). The existing research results (Eighmy *et al.*, 1997) indicated that although the whole influence factors of stabilization were just system liquid-solid ratio (L/S, V/W), pH, ion strength, the existing forms of heavy metals, and reaction time, the stabilization evaluation results may be different when following the different toxic leaching method and its correlative standard because the different modeling simulating situation was used in different countries in the toxicity leaching experiment (e.g., different pH of leachant, liquid-solid ratio, leaching time, and other parameters).

Meanwhile, it is proved that the nationally common methods just as toxicity characteristic leaching procedure (TCLP) is limited by system chemical environment, so it can only reflect rapid washing processes of surface phase and soluble phase (Wan, 2006). When acid neutraliza-

tion capacity (ANC) of fly ash is high, the stabilization evaluation will be a failure. Therefore, it is necessary to find a more scientific method for the evaluation of fly ash stabilization mechanism and products stabilization.

The simulation research of heavy metals leaching behavior based on geochemical model has been commonly developed currently in America, Canada, and Denmark (Fernández-Olmo *et al.*, 2007). The model of MINTEQ A2, Visual MINTEQ, ORCHESTRA, PHREEQE, and SOLTEQ (Batchelor, 1998; van Herck *et al.*, 2000; Park and Batchelor, 1999, 2002) were commonly applied to describe heavy metal leaching behavior in the field of soil, waste water, and solid waste. Visual MINTEQ model was first used in geochemical study, and then it was gradually introduced in the research of environmental science and engineering. It can be used to calculate various chemical equilibrium process including acid-base balance, dissolution-precipitation balance, redox balance, and adsorption balance. The software contains powerful equilibrium constants database, which can be modified.

At present, the model was applied to simulate and predict incineration residue stabilization and stability of treated residue (Eighmy *et al.*, 1995; Meima, 1998). MINTEQ model was used to simulate carbonation process and the form of product on MSWI fly ash carbonation technology study (Meima and van der Weijden, 2002); and it was also applied to simulate heavy metal leaching behavior and transfer behavior of solidified/stabilized fly ash (Li *et*

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al., 2001). According to chemical equilibrium simulation of leaching process, the stabilization mechanism of fly ash was clearly investigated, and long-term stabilization was predicted with the characteristic of treated fly ash, too.

There is little report about the study on model simulation of fly ash stabilization technology in China. With the emission standard of the incineration flue gas being strict step by step, more CaO was added in the incineration plants for incineration flue gas processing. Thus, the fly ash is high alkaline with high content of CaO. At the same time, there occurred error in the result of normal fly ash leaching experiment because of high ANC of fly ash. Therefore, it is very meaningful in China to develop the research on simulation and prediction of MSWI fly ash stabilization according to different character because it is helpful for research and design of stabilization agent and determination of fly ash stability. In this study, both Visual MINTEQ model and lab-experiment were used for the study on simulation and prediction of MSWI fly ash leaching behavior and stabilization mechanism.

1 Materials and methods

1.1 Samples

The MSWI fly ash used in this investigation was sampled from a large-scale municipal solid waste incineration plant in Shenzhen, China. The plant is equipped with reciprocating grates, and the treatment capacity of the plant is approximately 1,000 tons/d. The time of sampling is from 5th to 8th in March, 2006.

1.2 Experiments and methods

1.2.1 pH-dependent experiment

The pH-dependent leaching behavior of the MSWI fly ash was investigated using pH-dependent test. Seven single batch extractions were performed in parallel. A series of leachants with pH value 1, 3, 5, 7, 9, 11, and 13 were prepared by HNO₃ and NaOH separately. After tumbling for 24 h at the L/S ratio of 10, the equilibrium pH and heavy metal concentration were measured. The Cl⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻, and S²⁻ were analyzed by AgNO₃ titration, BaSO₄ gravimetric analysis, H⁺ titration, ammonium molybdate spectrophotometry, and Methylene Blue spectrophotometry, respectively.

1.2.2 Sequential leaching test

According to Tessier's method (Tessier *et al.*, 1979), heavy metal can be classified into five operationally defined fractions in MSWI fly ash (Table 1). Five gram of fly ash sample was prepared. The heavy metal concentration of leachate was analyzed using ICP-MS (IRIS Intrepid IIXSP, Thermo Electron, USA).

1.2.3 X-ray fluorescence test

As a kind of heterogeneous material, fly ash is composed of compounds with calcium, silicon, and aluminum. The element of fly ash was analyzed using X-ray fluorescence (XRF) (Type 1700, Shimadzu, Japan).

After the sample was dried at 105°C, the sample was analyzed using XRF. Technical indexes are as follows: wavelength scanning crystal analysis, power 4 kW; inde-

Table 1 Sequential leaching test experiment procedure

Chemical form	Extraction condition	Function
Exchangeable	Five gram (dry weight) of sample from batch test was shaken for 1 h at room temperature with 100 ml of 1 mol/L NaAc (pH 8.12).	Exchangeable heavy metal occurs nonspecific adsorption on solid surface by diffusion process and outer complexation, thereby they can be extracted by ion exchange from the samples.
Bound to carbonates	The residual from exchangeable fraction was shaken for 5 h at room temperature with 100 ml of 1 mol/L NaAc adjusted to pH 5.0 with HAc.	Heavy metal exists in carbonate in the form of precipitation and coprecipitation. HOAc-NaOAc is most common extractant at pH 5. Therefore, this is the best reagent that extracts heavy metal of carbonate forms.
Bound to iron and manganese oxides	The residual from bound to carbonate fraction was added with 100 ml of 0.04 mol/L NH ₂ OH-HCl in 25% (V/V) HAc. The mixture was heated to 96 ± 3°C for 5 h with occasional agitation.	Heavy metal is strongly adsorbed in iron and manganese oxides. The most characteristic of heavy metal is the lower stability under the reductive condition.
Bound to organic matter	The residual from bound to metal oxide fraction was added with 15 ml of 0.02 mol/L HNO ₃ and 25 ml of 30% H ₂ O ₂ adjusted to pH 2 with HNO ₃ , and the mixture was heated to 85 ± 2°C for 2 h with occasional agitation. A second 15 ml aliquot of 30% H ₂ O ₂ then added, and the sample was heated again to 85 ± 2°C (pH 2 with HNO ₃) was for 3 h with intermittent agitation. After cooling, 25 ml of 3.2 mol/L NH ₄ Ac in 20% (V/V) HNO ₃ was added and the sample was diluted to 100 ml and agitated continuously for 30 min.	Heavy metal exists in organic form of samples. The function of extractant is the oxidation of organic compounds and the extraction of organic compounds.
Residual	The sample 0.2 g (dry weight) from bound to organic matter fraction was digested with 1 ml of HNO ₃ (70%), 3 ml of HCl (37%), 1 ml of H ₂ O ₂ (30%), and 3 ml HF (48%) in Teflon FA vessel using microwave heating. The digested sample was diluted to 100 ml with deionized distilled water.	Residual is an important phase of the heavy metal in the samples, and it generally exist samples, and it generally exists in primary, secondary, and other minerals.

pendent drive system for angle of θ –20; reproducibility of goniometer position: $\theta < 0.001$.

1.2.4 Leaching modeling

MINTEQ is an equilibrium speciation model that can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. The model is useful for calculating the equilibrium mass distribution among dissolved species, adsorbed species, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressures. The leaching were usually solubility controlled and dependent on precipitation/dissolution/complexation equilibrium, which may be estimated based on these equilibrium reactions.

Input mass concentration for each component (Ca^{2+} , Al^{3+} , Pb^{2+} , etc.) is based on the initial concentration of pH-dependent experiment. Visual MINTEQ was run for predicting pH dependent leaching behavior and stabilization process with addition of chemical agent in the absence of surface complexation reactions. According to the information referenced (Eighmy *et al.*, 1997; Fernández-Olmo *et al.*, 2007), the species was supplied, and the thermodynamical parameter of some compounds was modified in the database. The likelihood of solid solution formation during dissolution and reprecipitation required further modification to MINTEQA2 to use idealized solid solutions as possible controlling solids. A simplistic zero heat of mixing and ideal site substitution model was assumed.

2 Results and discussion

2.1 Initial concentration of MSWI fly ash

The content of various elements from the result of XRF test was used as total amount of the element, and the initial concentration (C_i , mg/L) was calculated as the following equation:

$$C_i = 10^5 \times \left(\frac{m_e}{m_{fa}} \times 100\% \right) \times \left(\frac{m_{ee}}{m_e} \times 100\% \right)$$

where, m_e (mg) is the quality of the element, m_{fa} (mg) is the quality of the fly ash; m_{ee} (mg) is the quality of the exchangeable element.

The elemental initial concentrations of MSWI fly ash are listed in Table 2.

Table 2 Initial elemental concentration of MSWI fly ash (unit: mg/L)

Element	Concentration (mg/L)	Element	Concentration (mg/L)
Cl^-	24,160	PO_4^{3-}	813.38
SO_4^{2-}	13,486	AsO_4^{3-}	4.57
Mg^{2+}	770	Al^{3+}	1,902
Ca^{2+}	11,950	Fe^{3+}	625
Zn^{2+}	171	Cr^{3+}	12.96
Cd^{2+}	0.18	Mn^{2+}	35.98
Cu^{2+}	45.46	Pb^{2+}	10
Ni^{2+}	3.8		

2.2 Leaching behavior of MSWI fly ash at various pH values

The experimental result was obtained by pH-dependent test, and the experiment result and simulation result are shown in Fig.1.

It can be observed from Fig.1 that leaching toxicity concentration of heavy metal in fly ash increased to maximum at $\text{pH} < 8$; when pH increased to more than 8, leachability of heavy metal was relatively low, but heavy metal dissolved again at $\text{pH} > 13$. It can be concluded that pH value played an important role in leaching behavior of MSWI fly ash. Meanwhile, the result was obtained by phase composition from leaching modeling.

Cd: the dissolution/precipitation modeling result showed that CdCl^+ and $\text{CdCl}_2(\text{aq})$ were the main form of Cd in the solution at acid, neutral, and weak basic condition (pH 0–9), accounting for about 98% of total dissolved forms; CdOH^+ , $\text{Cd}(\text{OH})_2(\text{aq})$, $\text{Cd}(\text{OH})_3^-$, and $\text{Cd}(\text{OH})_4^{2-}$ were the main form of Cd in the solution at basic condition (pH 10–14), and the percentage of them was higher when pH value was higher, the percentage of $\text{Cd}(\text{OH})_4^{2-}$ was up to 64.35% at pH 14. Cd was precipitated mainly as the form of $\text{Cd}_4(\text{OH})_6\text{SO}_4$ at pH 9–12, and Cd was precipitated mainly as $\text{Cd}(\text{OH})_2$ at pH 12–14. Over pH 14, $\text{Cd}(\text{OH})_2$ started to dissolve, as well as Cd leaching, again. Correlation of the results between experiment and modeling showed that there was a relatively great error at pH 10–12, which can be explained by the absence of adsorption (surface complexation) in modeling process.

Pb: the results of dissolution/precipitation simulation are in concordance with the experiment analysis. PbCl^+ and $\text{PbCl}_2(\text{aq})$ were formed on acid and neutral condition (pH 0–5), up to 75% of total dissolved forms; over 99% of Pb was precipitated as PbPO_4Cl at pH 5–8; Pb existed mainly as $\text{Pb}(\text{OH})_2$ at basic condition (pH 8–13), meanwhile, $\text{Pb}(\text{OH})_2$ can be dissolved and the concentration of Pb^{2+} increased over pH 14.

Zn: the results of dissolution/precipitation simulation are in concordance with the experiment analysis without considering adsorption (surface complexation). So it can be concluded that leaching behavior of Zn is determined by dissolution/precipitation mechanism.

Zn element existed in the solution mainly as the forms of Zn^{2+} and ZnCl^+ , up to 80% of total dissolved forms on acid and neutral condition (pH 0–6); and it existed in the solution mainly as the forms of ZnSiO_3 , ZnOH^+ , $\text{Zn}(\text{OH})_2(\text{aq})$, $\text{Zn}(\text{OH})_3^-$, and $\text{Zn}(\text{OH})_4^{2-}$ at basic condition (pH 7–13); the percentage of $\text{Zn}(\text{OH})_2$ decreased over pH 14.

Ni: The modeling results are well in accordance with the experimental results. Ni was precipitated mainly as $\text{Ni}(\text{OH})_2$ at pH 7–14, but when pH was at 4–8, the line of experiment result was lower than that of modeling, which may be because of surface adsorption reaction at the range of pH value.

Ca: Ca existed in the solution mainly as the forms of Ca^{2+} and CaCl^+ at pH 0–12, achieving 98% of total dissolved forms; and it existed in the solution mainly as

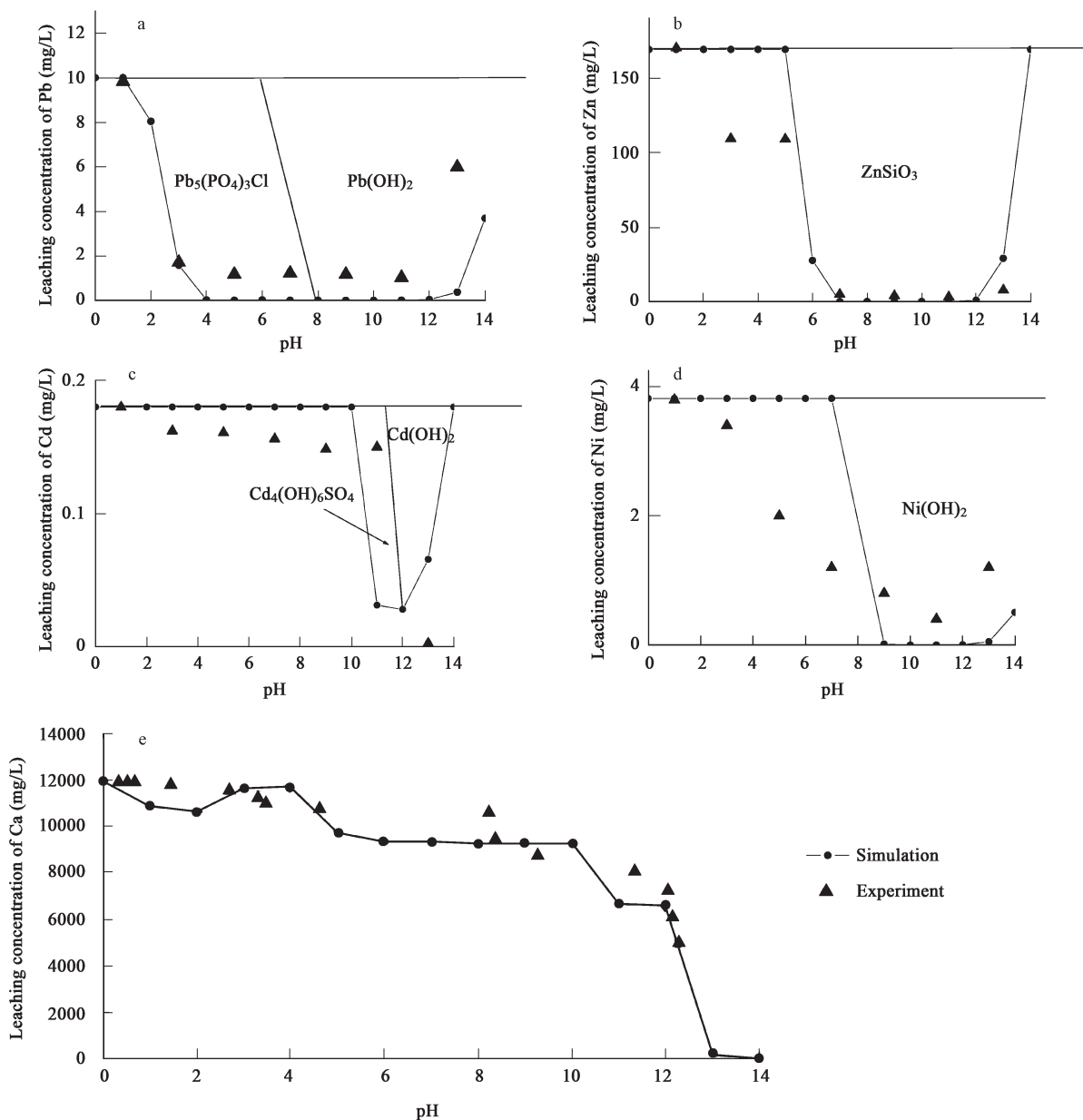


Fig. 1 Comparison between MINTEQ modeling result and experiment result. (a) leaching concentration of Pb; (b) leaching concentration of Zn; (c) leaching concentration of Cd; (d) leaching concentration of Ni; (e) leaching concentration of Ca.

the form of $CaOH^+$ at strong basic condition (pH 12–13); the percentage of $Ca(OH)_2$ was higher, as well as pH value was higher. The percentage of $CaOH^+$ was 79.74% at pH 14. Meanwhile, Ca could form a little of $CaSO_4 \cdot 2H_2O$ at pH 0–14, and it could form a little $Ca_2PO_4(OH)$. Ca was precipitated as much of $Ca_6Al_2(SO_4)_3 12(OH) \cdot 26H_2O$ (Ettringite) at pH 11–13; $Ca(OH)_2$ was the controlling solid of Ca at pH 13–14.

2.3 Modeling on leachate composition of MSWI fly ash with different stabilization agents

MSWI fly ash was stabilized by the addition of 10% phosphate. The pH value of fly ash leachate was set at 12.4 according to experiment test. The main production of stabilization process was simulated by Visual MINTEQ with dissolution/precipitation mechanism, which is shown in Table 3.

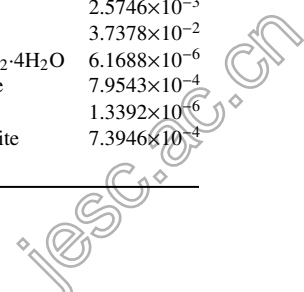
Meanwhile, the result on the percentage of various

ions indicated that 95.821% of Pb was performed as $Pb_5(PO_4)_3OH$, which can prove good stability of the production.

MSWI fly ash was stabilized by addition of 10% CO_2 (calculated by carbonate). The pH value of fly ash leachate

Table 3 Main precipitation produced by MSWI fly ash stabilization with phosphate

Precipitation	Equilibrium concentration (mol/L)	Precipitation	Equilibrium concentration (mol/L)
$Pb_5(PO_4)_3OH$	1.9920×10^{-2}	Ettringite	3.4694×10^{-3}
Hematite	7.7659×10^{-3}	Zincite	2.5746×10^{-3}
Calcite	2.1658×10^{-2}	Diaspore	3.7378×10^{-2}
Brucite	2.1388×10^{-2}	$Ca_3(AsO_4)_2 \cdot 4H_2O$	6.1688×10^{-6}
Portlandite	9.4944×10^{-2}	Pyrochroite	7.9543×10^{-4}
$Pb(OH)_2$	4.8239×10^{-5}	$Cd(OH)_2$	1.3392×10^{-6}
Cr_2O_3 (crystal)	2.9243×10^{-5}	Cupric ferrite	7.3946×10^{-4}
$Ni(OH)_2$ (crystal)	6.4584×10^{-5}		



was set at 11.2 according to previous experience. The main production of stabilization process was simulated by Visual MINTEQ with dissolution/precipitation mechanism, which is shown in Table 4.

Table 4 Main precipitation produced by MSWI fly ash stabilization with CO₂

Precipitation	Equilibrium concentration (mol/L)	Precipitation	Equilibrium concentration (mol/L)
Ca ₅ (PO ₄) ₃ OH	6.667×10 ¹	Ettringite	3.3333×10 ²
Hematite	4.2800×10 ²	Zincite	1.7000×10 ²
Calcite	1.6126×10 ⁻¹	Diaspore	5.3333×10 ²
Brucite	5.1999×10 ²	Ca ₃ (AsO ₄) ₂ ·4H ₂ O	1.000
Portlandite	8.5084	Pyrochroite	4.3999×10 ¹
Pb(OH) ₂	1.0000×10 ¹	Cd(OH) ₂	1.7996×10 ⁻¹
Cr ₂ O ₃ (crystal)	2.5500	Cupric ferrite	4.7000×10 ¹
Ni(OH) ₂ (crystal)	3.8000		

Meanwhile, the result on the percentage of various ions indicated that 59.957% of Pb was performed as Pb(OH)₂ and 28.999% of Pb was as the compounds of PbOH⁺, but there was no carbonate.

The stabilization products of MSWI fly ash can be clearly known with Visual MINTEQ modeling. Therefore, the effect for the stabilization processing can be evaluated according to the species and their percentage of the stabilization products, meanwhile, the long-term stability of productions can also be predicted according to the structure of productions.

3 Conclusions

The pH-dependent leaching behavior predicted by Visual MINTEQ is well in agreement with the result of pH-dependent test. The result indicates that pH value of leachate can significantly change the leaching behavior of MSWI fly ash. The leaching behavior of heavy metals for Pb and Cd is controlled by dissolution/precipitation mechanism but that of heavy metals for Zn and Ni is effected by surface adsorption reaction over a special extent of pH value.

Only the dissolution/precipitation model was applied for leaching behavior stimulation by Visual MINTEQ in this work, but for some heavy metals, both dissolution/precipitation reaction and surface adsorption reaction will occur in leaching process. It will be further proved in the future work. At the same time, the effect for stabilization processing can be evaluated according to the species and their percentage of the stabilization products, and the long-term stability of productions can also be predicted according to the structure of productions. This technology can clearly show the mechanism of MSWI fly ash stabilization, and it also has a great help for the choosing of MSWI fly ash stabilization agents.

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