



Technical Note

Polysulfide as a novel chemical agent to solidify/stabilize lead in fly ash from municipal solid waste incineration

Yifei Sun^a, Nobuhisa Watanabe^b, Wei Qiao^c, Xingbao Gao^d, Wei Wang^d, Tianle Zhu^{a,*}^a School of Chemistry and Environment, Beihang University, Beijing, China^b Dept. of Environmental Engineering, Osaka Institute of Technology, Osaka, Japan^c College of Chemical Science and Engineering, China University of Petroleum, Beijing, China^d Department of Environmental Science and Engineering, Tsinghua University, Beijing, China

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ABSTRACT

Polysulfide was produced and tested for use as an inexpensive chemical agent for the solidification/stabilization of lead in fly ash, generating little hydrogen sulfide gas. According to the equations $S_n^{2-} \rightarrow S + S_{n-1}^{2-}$ and $S_n^{2-} + H^+ \rightarrow HS^- + S_{n-1}$, this agent was expected to achieve long-term stability of disposed Pb. The leachate concentration of Pb in fly ash after sulfide treatment showed a decrease–increase–decrease trend. We also compared Pb leaching behavior from an aging/weathering experiment to thermodynamic modeling using the database from the Geochemist's Workbench software. Thermodynamic modeling indicated the tendency that when the precipitate was formed in the order of PbO, PbCO₃·PbO, and PbCO₃, the total concentration of soluble Pb will be lowered. The leaching curve of Pb in fly ash without a lime slurry injection system was close to PbO, whose activity was initially near 1, but when leaching time increased, it shifted to that of PbCO₃·PbO, before finally ending at that of PbCO₃. However, Ca(OH)₂ sprayed on fly ash interfered with the carbonation process of Pb.

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1. Introduction

Incineration has become more widespread over the past 30 years, also in Japan, owing to its volume reduction and heat and power production. Approximately 77% of the 50 Mt of municipal solid waste (MSW) produced annually is estimated to be incinerated, 15% of intermediate disposals including thermal treatment, cement solidification, treatment with chemical agents (chelating agents) or extraction with acid or other solvents, have a final disposal of incineration, therefore approximately 92% of MSW in Japan was incinerated in 2008 (MEJ, 2006). However, incinerators produce two types of solid residue: bottom ash and fly ash. Because of high levels of soluble salts, heavy metals, and persistent organic pollutants, fly ash is generally classified as hazardous waste in the European Union (EU, 2000) and United States (EPA, 2009). Thus, intermediate treatment technology must be developed before fly ash can be sent to a landfill plant. According to the amendment in 1991 to Japan's Waste Disposal and Public Cleansing Law, for all the incinerators with a capacity equal to or greater than 5 t d⁻¹, the direct disposal of air pollution control residues is strictly prohibited unless treated by the four management strategies (Anonymous, 1993): (1) thermal treatment, including

melting calcination or vitrification (Izumikawa, 1996; Okada et al., 2007); (2) treatment with cement (Mangialardi et al., 1999); (3) treatment with a chemical agent (Eighmy et al., 1997; Zhao et al., 2002; Jiang et al., 2004); and (4) leaching with acids and other solvents (Tessier et al., 1979; Nagib and Inoue, 2000). Because thermal treatment is costly, few countries currently use this technology (Ecke et al., 2000). Although cement solidification is inexpensive, the plentiful soluble salts must be removed by an integrant washing process, which generates large amounts of wastewater, as does extraction with acid or other solvents.

Alternatively, chelating agents are widely used to immobilize contaminants. However, the cost and long-term stability of chelating agents are a major concern. Over the last 20 years, sodium sulfide has been considered to be effective because of the stability of the products and the reductive character of the sulfide ion. NaHS was applied as a chemical agent by MSW incineration (MSWI)-S in Osaka, Japan. However due to the amount of toxic hydrogen sulfide generated, sodium sulfide is not widely used over the world. On the other hand, yellowish aqueous solutions of polysulfide, are easily obtained by oxidation of hydrogen sulfide solutions at basic pH, with a reaction of hydrogen sulfide and sulfur (Kamyshny et al., 2004, 2007). In this study, we produced and tested polysulfide for use as an inexpensive chemical agent that generates only a small quantity of hydrogen sulfide gas. In addition, we predicted that the gradual generation of sulfide ion from polysulfide,

* Corresponding author. Tel.: +86 10 82317801; fax: +86 10 82314215.
E-mail address: zhutl@buaa.edu.cn (T. Zhu).

according to the equations $S_n^{2-} \rightarrow S + S_{n-1}^{2-}$ and $S_n^{2-} + H^+ \rightarrow HS^- + S_{n-1}^{2-}$ (Kamysny et al., 2006; Rickard and Luther, 2007), would achieve long-term stability of heavy metals in fly ash.

We used two types of chemical agents to treat lead in MSWI fly ash: self-made polysulfide and commercially available sodium hydrosulfide. We first measured the physical–chemical properties of density, sulfur abundance in the chemical agents, and amount of hydrogen sulfide gas generated. We then conducted post-treatment leaching tests and examined the treatment effects. Finally, to investigate the stability of the two chemical agents, we monitored leaching behavior over 124 d (aging/weathering experiment). We also compared Pb leaching behavior from the aging/weathering experiment to thermodynamic modeling using the database from the Geochemist's Workbench software (RockWare).

2. Experimental

2.1. Sulfide agents

To produce polysulfide, sulfur powder and calcium hydroxide were combined with distilled water in a pressure test tube. NaHS, commercially being utilized in practical application was supplied by MSWI-S in Osaka, Japan.

Sulfur contents and hydrogen sulfide generated by the two sulfide agents were measured. Sulfur content was measured by the gravimetric method (Otaigbe and Egiebor, 1992). The two sulfide agents were combusted in a quartz furnace and trapped by H_2O_2 . Finally, the sulfur content was determined by $BaSO_4$ formation. Hydrogen sulfide generation was measured by the detector tube method (Chung et al., 1996). The hydrogen sulfide generated by the two sulfide agents at pH 7 and pH 9 solutions connected to a hydrogen sulfide detector tube (GASTEC, Co.) (shown in Fig. 1) was measured. Hydrogen sulfide generation was calculated by:

$$H_2S \text{ generation}(\%) = \frac{\text{Amount of S in } H_2S (\mu\text{g})}{\text{Total S in reagent } (\mu\text{g})} \times 100. \quad (1)$$

2.2. Samples and leaching test

Fly ash-S and fly ash-C were collected from the flue gas treatment units (bag filters) of MSWI-S and -C in Osaka, Japan. The plants have three and four continuous stoker-type units with a treatment capacity of 240 and 870 t d⁻¹, respectively. In the flue gas treatment process, spraying of slaked lime slurry before bag filtration is conducted at MSWI-C to remove acidic gas, while MSWI-

S is not equipped with a lime slurry injection system. Both MSWIs are equipped with wet scrubber to remove acid gas. Flue gas of MSWI-S is sprayed with activated carbon to remove the residual dioxins and NO_x , while selective catalytic reactor is equipped with MSWI-C for NO_x removal.

To grasp the elemental distribution in the two types of fly ash, X-ray Fluorescence (RIX2000, Rigaku, Japan) was conducted. The element amounts in the two types of fly ash are shown in Table 1. The elements from F (9) to U (92) were normalized as 100%, and the composition of objective elements was calculated by the fundamental parameter method (Szaloki et al., 2001). Due to the lime slurry injection at MSWI-C, calcium was the most abundant element in fly ash-C. Both types of fly ash contained large amounts of chloride. The concentration of heavy metals decreased in the order of: Zn > Fe > Pb > Mg > Cu. The concentrations of the trace element Pb in fly ash-S and -C were 4700 and 1700 mg kg⁻¹, respectively, based on extraction using aqua regia and analyzed by atomic absorption spectrophotometry (AAS) (AAS-6200, Shimadzu, Japan).

Leaching tests were conducted based on the Laws and Regulations 13 governing leaching tests of Ministry of Environment in Japan. As the concentrations of heavy metals were very high in fly ash, the liquid to solid ratio was set as 50/1 mL g⁻¹. Namely, 0.8 g of each type of fly ash was combined with 40 mL of distilled water. In each leaching test, 0, 20, 100, or 200 μL of polysulfide or NaHS solution were added to the mixture of fly ash and distilled water. After vibrating for 6 h, the mixture was centrifuged at 2000 rpm for 20 min. The pH of the leachate was recorded and the Pb concentration in the leachate was analyzed periodically up to 124 d using AAS under natural aging conditions.

For disposal, the concentration of Pb in fly ash must be lower than the standard limitation value, which is 0.3 mg L⁻¹ in Japan. As a case study, Pb in fly ash was used as a target element. Stability tests of precipitate Pb from standard solution without fly ash were conducted. One hundred microliters polysulfide or NaHS was added to 10 mg L⁻¹, 40 mL of Pb standard solution. The Pb concentration in the solute was analyzed periodically up to 124 d using AAS.

2.3. Pb leaching as a function of pH and leaching test duration

A pH varying test was conducted to determine the pH dependence of leaching behavior (Van der Sloot et al., 1997). In this study, 0.8 g fly ash and a certain amount of 1 M HCl (Wako) or 1 M NaOH (Wako) were placed in a test tube with distilled water

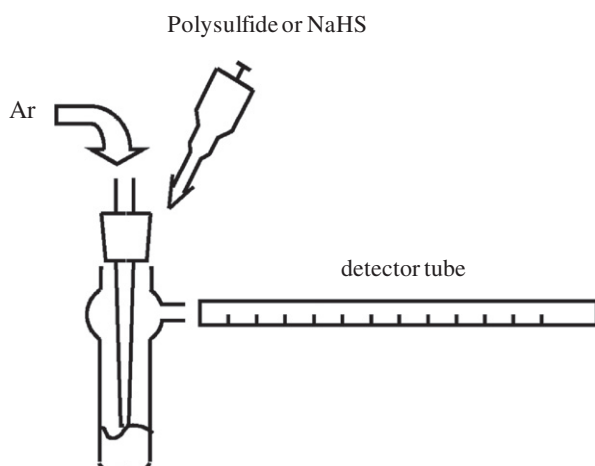


Fig. 1. Schematic diagram of hydrogen sulfide detector tube.

Table 1
Element amount by X-ray fluorescence analysis.

Element	Element amount (%)	
	Fly ash-S	Fly ash-C
Na	7.3	3.3
Mg	0.4	0.4
Al	2.0	1.8
Si	12.0	7.1
P	0.5	0.3
S	2.2	2.3
Cl	33.3	33.5
K	12.3	7.4
Ca	19.8	37.5
Ti	1.6	1.1
Fe	1.7	1.3
Cu	0.2	0.1
Zn	4.1	2.9
Br	1.1	0.4
Sr	0.1	-
Pb	1.2	0.6

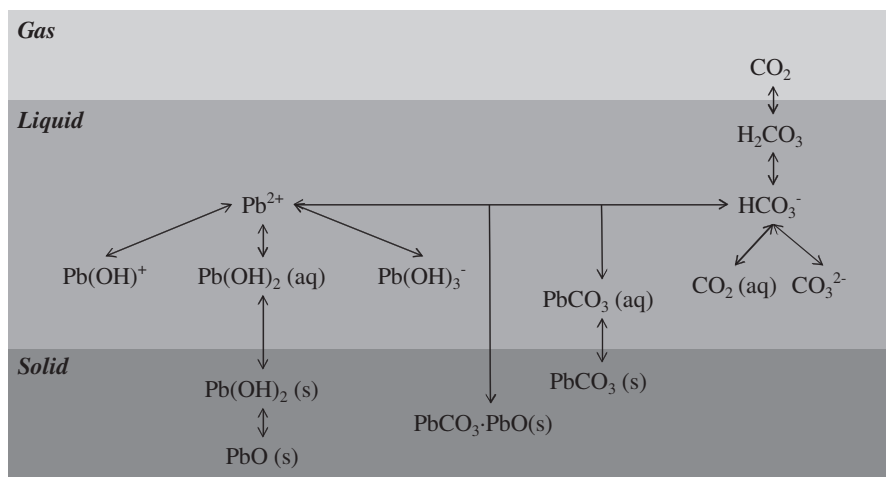


Fig. 2. Variation model of Pb species at gas–liquid–solid phase. Gas phase is an open system to air.

and brought a volume to 40 mL. After pH measurement and centrifugation at 2000 rpm for 20 min, the Pb concentration in the leachate was analyzed by AAS after 0, 5, and 11 d.

Mass action, material balances, and electroneutrality are always used to formulate a system of as many equations in the unknown equilibria (Freiser and Fernando, 1963). In this study, we propose the system shown in Fig. 2 of fewer equations solvable for reaction extents. The system is then solved for the molarities of all species shown. The thermodynamic leaching concentration of Pb was calculated when the activity (pure substances is normally taken as unity) of pure solid substance PbO, $\text{PbCO}_3 \cdot \text{PbO}$, and PbCO_3 was 1, respectively, using the Geochemist's Workbench (GWB) database.

3. Results and discussion

3.1. Properties

The properties of polysulfide and NaHS are shown in Table 2. The density of both polysulfide and NaHS was 1.1 g mL^{-1} , with a sulfur content of 0.104 and 0.099 g mL^{-1} , respectively. The amount of hydrogen sulfide gas generated was denoted by the S ratio of H_2S to polysulfide or NaHS. At pH 7, as NaHS was reacted with water, almost all of the HS^- was generated as H_2S gas within 5 min, whereas 16.6% of H_2S was generated with polysulfide in water. The reactions of NaHS at pH 7 were conducted as: $\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$, $\text{H}^+ + \text{HS}^- \rightleftharpoons \text{H}_2\text{S}$. Accompany with the generation of H_2S , reaction was continued. In addition, the polysulfide solution became clouded at pH 7, which was coincident with the reactions $\text{S}_n^{2-} \rightarrow \text{S} + \text{S}_{n-1}^{2-}$ and $\text{S}_n^{2-} + \text{H}^+ \rightarrow \text{HS}^- + \text{S}_{n-1}$, i.e., sulfur was separating out the polysulfide solution. At pH 9, 9.8% of H_2S was generated from NaHS solution, while only 0.062% of H_2S was generated from polysulfide in water. Polysulfide showed low generation ratio of H_2S at pH 9.

3.2. Leaching stability tests

The results of the leaching stability tests are shown in Fig. 3. In both types of fly ash, Pb concentrations decreased when polysulfide or NaHS were added as a chemical agent. However, Pb concentrations increased after 10 d, followed again by a decrease. The final Pb concentrations using 200 μL of the two types of chemical agents were obviously lower than without the chemical agents, which was 0.1 mg L^{-1} of fly ash-S and 1.0 mg L^{-1} of fly ash-C. Therefore, the stabilization behavior of the chemical agents was

evident. In the leaching test for fly ash-S, when 200 μL of polysulfide were used, the leaching concentration of Pb was not increased.

The observed decrease–increase–decrease pattern was more remarkable in the fly ash-C than that in the fly ash-S, whose pH value was lower than that of fly ash-C solution. As the amount of unreacted slaked lime in fly ash-C was greater than that in fly ash-S, $\text{Ca}(\text{OH})_2$ was a greater residue in fly ash-C. In this case, more CO_2 in the air was used, which reduced the opportunity of CO_2 to react with Pb^{2+} . In addition, the increased time using NaHS was earlier than that of polysulfide with fly ash-S (shown in Fig. 3a), which indicates that NaHS was consumed quickly when polysulfide was coincident with the reaction $\text{S}_n^{2-} \rightarrow \text{S} + \text{S}_{n-1}^{2-}$ and $\text{S}_n^{2-} + \text{H}^+ \rightarrow \text{HS}^- + \text{S}_{n-1}$. The precipitation of PbS occurred gradually. In fly ash-C, when more than 100 μL of the chemical agent used, the increased process reactant was generated almost at the same time of 24 d (shown in Fig. 3b).

The results of the leaching stability tests of standard solutions are shown in Fig. 3c. With polysulfide as chemical agent, Pb concentrations decreased below 0.1 mg L^{-1} before 10 d, and then increased between 10 and 20 d, after which the Pb concentration decreased again.

Samples were examined by XRD method which used XRD-6000 (Shimadzu, Japan). The used radiation was $\text{Cu K}\alpha$ ($\lambda = 0.154056 \text{ nm}$), and the samples were illuminated for 17.5 min with the step of 0.2° and speed of 4° per minute from 10° to 80° . Fig. 4 shows the XRD pattern of three fly ash samples, including raw fly ash-C, short-term polysulfide treated fly ash-C (after 5 d) and long-term polysulfide treated fly ash-C (after 30 d). PbS and S were found in Fig. 4b, in this case, lead compound in fly ash was reacted with polysulfide, the precipitate of lead sulfide and sulfur were formed. The results suggest that the precipitate of lead sulfide was formed by reactions of polysulfide with various lead compounds in fly ash. After 30 d of aging time, $\text{PbCO}_3 \cdot \text{PbO}$ was detected by XRD shown in Fig. 4c. It was believed that PbS precipitate was formed first, showing low Pb con-

Table 2
Properties of polysulfide and NaHS.

	Polysulfide	NaHS
Density (g mL^{-1})	1.10	1.12
S concentration (g mL^{-1})	0.104	0.0992
^a H_2S generation ratio (%)		
pH 9	0.062	9.8
pH 7	16.6	97.0

^a H_2S generation measured at 25°C , 101 kPa.

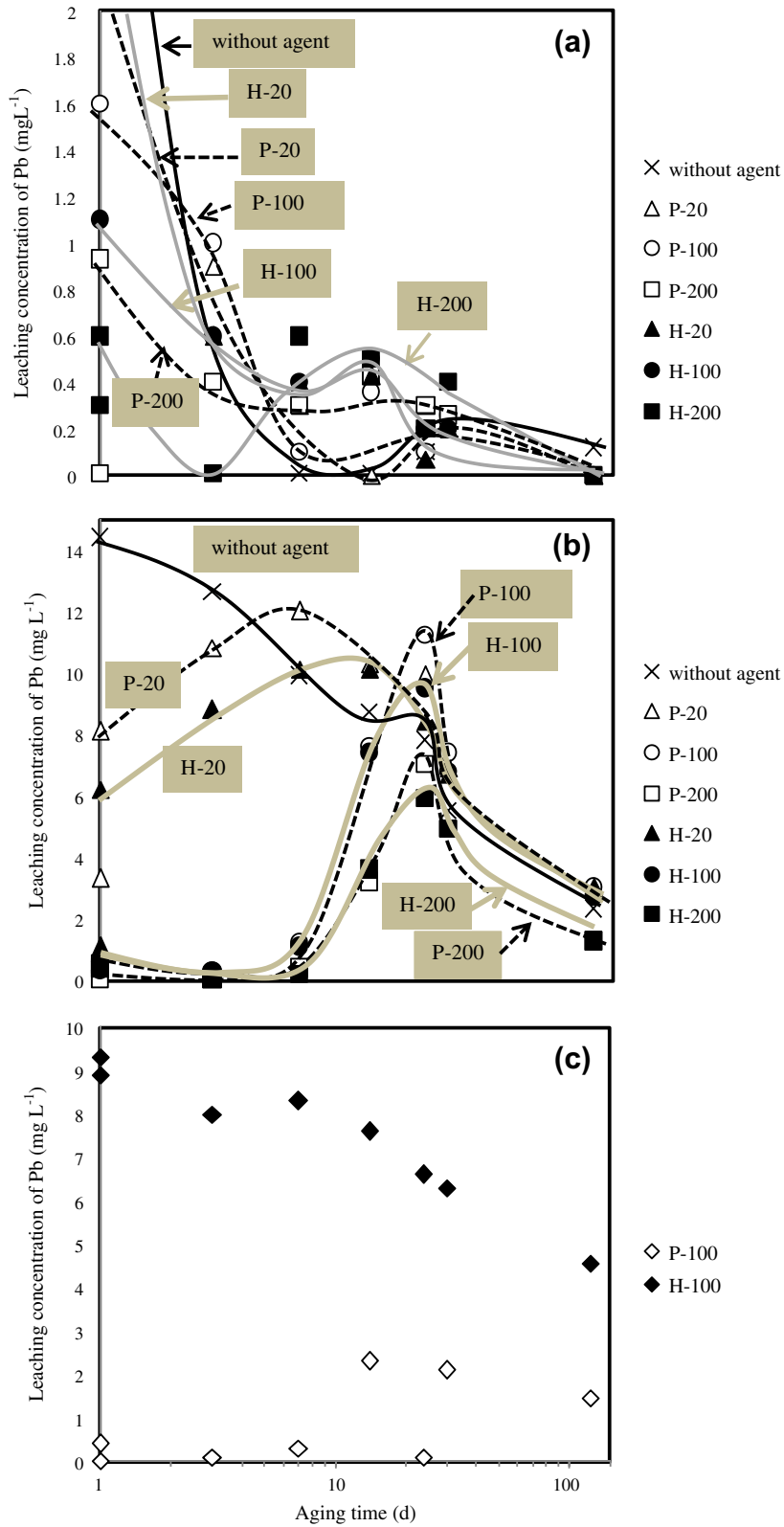


Fig. 3. Effect of aging time on the leachability of Pb from treated fly ash or standard solution by polysulfide (P) or NaHS (H). 20, 100, 200 indicate 20, 100, and 200 μ L of agent used: (a) fly ash-S; (b) fly ash-C; (c) standard solution.

centration and then a portion of PbS was oxidized to PbSO₄ in the air. PbSO₄ might be dissociated (in the acidic environment) and anion Pb²⁺ formed. Thus the Pb concentration increased with low pH and then transferred to the gas phase. Under air, CO₂

was easily dissociated to HCO₃⁻ in aqueous phase, the Pb²⁺ reacted with HCO₃⁻, and finally, a stable precipitate (PbCO₃·PbO or PbCO₃) was generated from the carbonation process resulting from exposure to air. Fig. 4c shows the formation of PbCO₃.

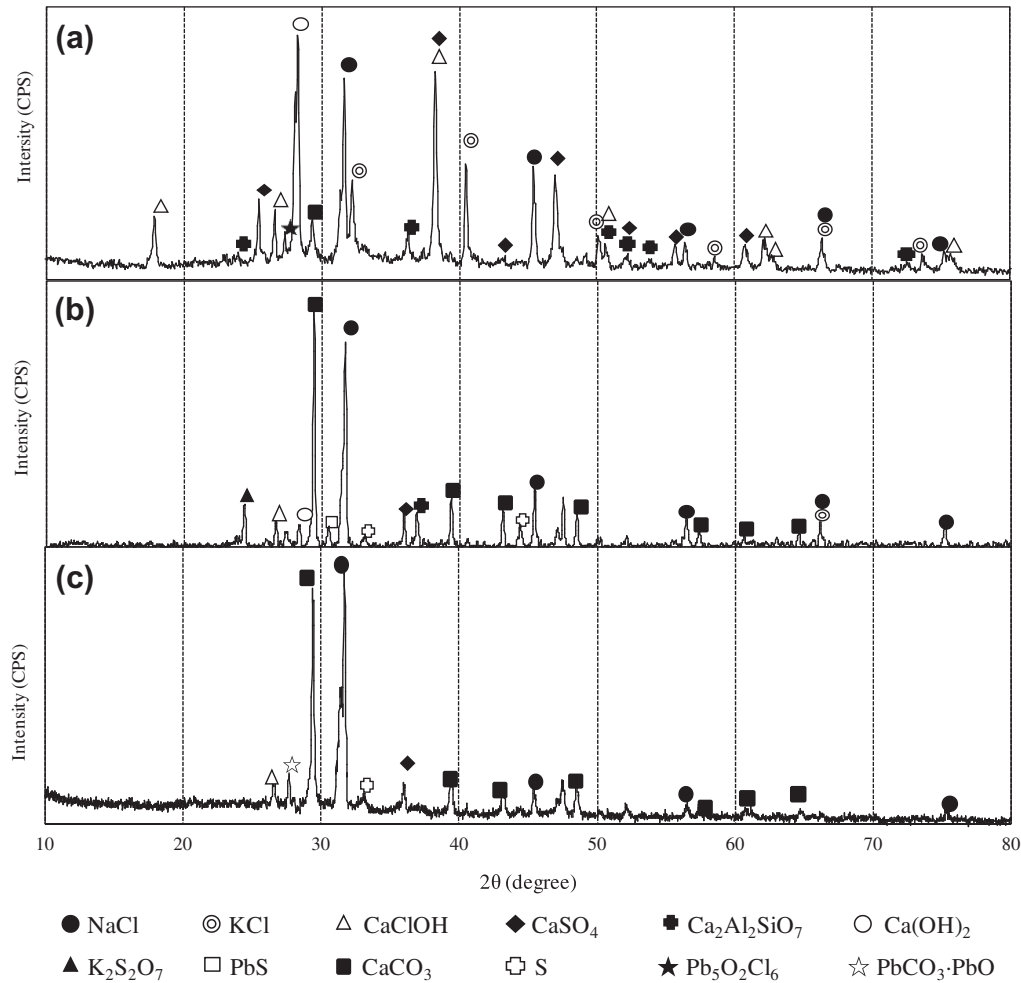
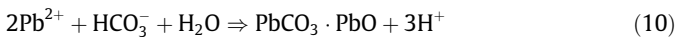
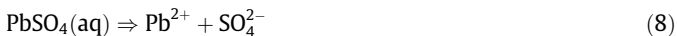


Fig. 4. XRD patterns of fly ash-C before and after polysulfide injection for 1 d. (a) Before polysulfide injection. (b) After polysulfide injection for 5 d. (c) After polysulfide injection for 30 d.

The entire sequence of reactions is shown in Eqs. (2)–(11):



Reaction	log K (25 °C, 101 kPa)
$Pb^{2+} + H_2O = PbO(s) + 2H^+$ (12)	-12.6
$Pb(OH)^+ + H^+ = Pb^{2+} + H_2O$ (13)	7.7
$Pb(OH)_2(aq) + 2H^+ = Pb^{2+} + 2H_2O$ (14)	17.1
$Pb(OH)_3^- + 3H^+ = Pb^{2+} + 3H_2O$ (15)	28.1
$CO_2(g) + H_2O = H^+ + HCO_3^-$ (16)	-7.8
$CO_2(aq) + H_2O = H^+ + HCO_3^-$ (17)	-6.3
$HCO_3^- = H^+ + CO_3^{2-}$ (18)	-10.3
$PbCO_3 \cdot PbO + 3H^+ = 2Pb^{2+} + H_2O + HCO_3^-$ (19)	9.7
$PbCO_3(s) + H^+ = Pb^{2+} + HCO_3^-$ (20)	-3.2
$PbCO_3(aq) + H^+ = Pb^{2+} + HCO_3^-$ (21)	3.7

3.3. Modeling and pH-dependent test

It is possible for Pb to form multinuclear complexes containing two or more Pb atoms. Therefore, we assumed equilibria model of various Pb ion species, which are shown in Fig. 2. The equilibria model of Pb ion almost has the same tendency with zinc ion species (Sawyer et al., 1994; Stumm and Morgan, 1996). The reaction of each step with various Pb ion species is shown in Eqs. (12)–(21), and the equilibrium constants (25 °C, 101 kPa) of each reaction (GWB database) are shown as follows.

The relationship between the logarithmic concentration of dissolved Pb and pH are shown in Fig. 5 according to the thermodynamics data given that the activity of pure solid substance PbO (s), PbCO₃·PbO (s) and PbCO₃ (s) was 1. The reactions shown in Eqs. (12), (19), or (20) were generated.

In Fig. 5, the dashed lines characterize the logarithmic concentration of Pb, Pb(OH)⁺, Pb(OH)₂, Pb(OH)₃⁻, and PbCO₃ (aq) with different pH. Summing up all soluble Pb species indicated by thick lines gave the overall solubility as a function of pH when the activ-

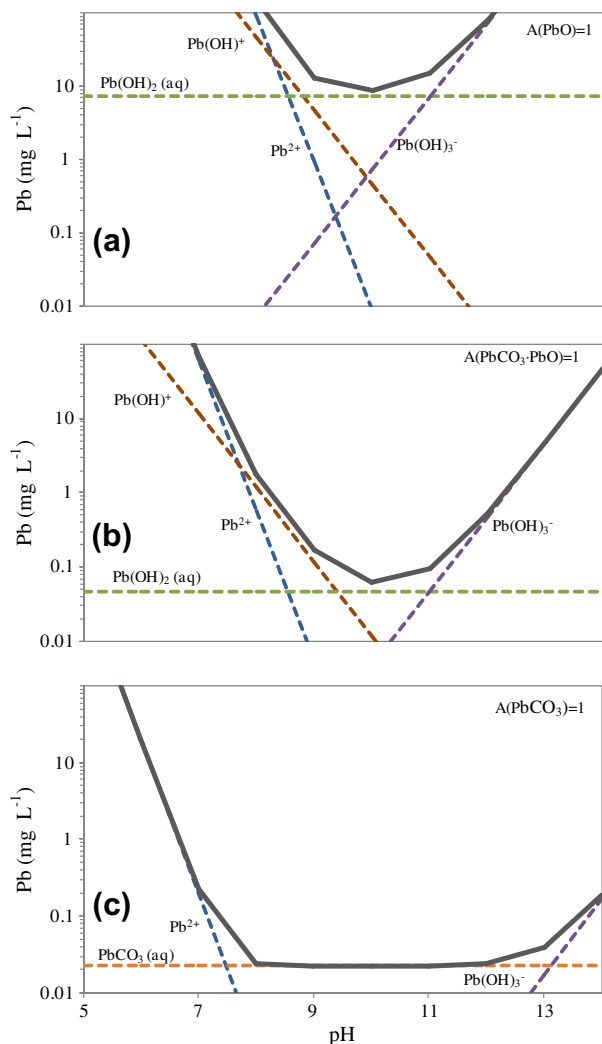


Fig. 5. Solubility of pure solid substance PbO (s), PbCO₃·PbO (s) or PbCO₃ (s) (25 °C, 101 kPa). The dashed lines show the concentration of Pb, Pb(OH)⁺, Pb(OH)₂, Pb(OH)₃⁻, PbCO₃ (aq); the thick lines show the total soluble Pb(II) concentration. (a) Activity of pure PbO (s) was 1. (b) Activity of pure PbCO₃·PbO (s) was 1. (c) Activity of pure PbCO₃ (s) was 1.

ity of pure solid substance PbO (s), PbCO₃·PbO (s) or PbCO₃ (s) was 1. Eqs. (15)–(17) show the reaction equation of CO₂ in the gas (atmosphere) and liquid phases (Miller, 2007). Partial pressure of CO₂ was assumed to be 10.1 Pa ($p_{\text{CO}_2} = 10.1 \text{ Pa}$) at 25 °C.

Although the activity of pure solid substance PbO (s), PbCO₃·PbO (s) or PbCO₃ (s) was 1, Fig. 5 illustrates that at low pH, Pb²⁺ is the predominant soluble species present, followed by Pb(OH)⁺. At very high pH, Pb(OH)₃⁻ is the predominant species. However, that concentration of total soluble Pb is the highest when reaction Eq. (11) was generated as shown in Fig. 5a, and then the total soluble concentrations of Pb were decreased accompany with the reaction Eqs. (18) or (20) generated as shown in Fig. 5b or c.

The leaching concentrations of Pb, with different leaching times and thermodynamic curves, are shown in Fig. 6. The different concentrations of Pb within 11 d showed that the carbonation process occurred somewhat faster than the chemical agent experiments. As aging/weathering time increased, the leaching concentrations of Pb decreased. The thermodynamic curves of the leaching concentrations of Pb were calculated using the GWB database when the activity of pure solid substance PbO, PbCO₃·PbO, and PbCO₃ was 1. The leaching curves of both fly ashes were most likely near that of PbCO₃·PbO under alkaline zone. Fly ash-S also had a tendency for

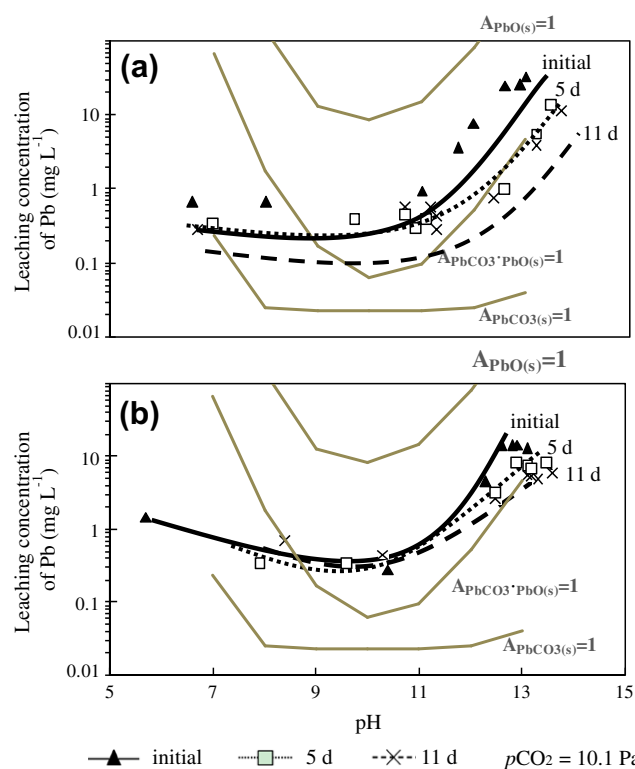


Fig. 6. Relationship between Pb leaching behavior and pH from the aging experiment and thermodynamic modeling. Black lines including solid, dotted and dashed black lines refer to experimental results, whereas gray solid lines denote the modeling results given that the activity (A) of pure solid substance PbO (s), PbCO₃·PbO (s) or PbCO₃ (s) was 1, respectively. Partial pressure of CO₂ in air was 10.1 Pa: (a) fly ash-S, (b) fly ash-C.

the leaching curve to be close to that of PbO at first, but when leaching time increased, it shifted to that of PbCO₃·PbO, before finally ending at that of PbCO₃. Compared to fly ash-C, fly ash-S without spraying of Ca(OH)₂ showed obvious carbonation effects, as Ca(OH)₂ affects Pb carbonation.

4. Conclusions

Polysulfide agent generates only a small quantity of hydrogen sulfide gas, and achieves long-term stability of disposed lead. The leaching concentration of Pb in fly ash after sulfide treatment showed a decrease–increase–decrease trend. Carbonation by CO₂ in air is a critical final step of the process. The leaching curve was close to that of PbO at first, but when leaching time increased, it shifted to that of PbCO₃·PbO, before finally ending at that of PbCO₃. However, Ca(OH)₂ sprayed on fly ash disturbed the carbonation process of Pb.

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