Extractability of Metals in Municipal Solid Wastes Fly Ash Using Supercritical CO₂ Containing Cyanex 302

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The extraction of lead from fly ash produced during the thermal treatment of municipal solid wastes was studied using supercritical carbon dioxide (SC-CO₂) and Cyanex 302 (bis(2,4,4-trimethylpentyl)monophosphinic acid). The extraction of lead from the fly ash was carried out in a 5 cm³ internal volume reaction vessel under static extraction conditions at 323 K, and 24 MPa for 1 h. The extraction efficiencies of lead ranged from 4% to the total extraction under the conditions of 0.05 g fly ash with 2 cm³ Cyanex 302. There was a linear relationship between the extraction efficiencies of lead using the SC-CO₂ + Cyanex 302 and using a water-based method described by JLT13.

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Introduction

The potential environmental pollution caused by heavy metals leached from waste landfill has been one of the serious problems in many countries around the world. In Japan, a leachability test stipulated by the Ministry of the Environment Government of Japan (JLT13) must be carried out for wastes before landfill disposal. The test is categorized as a batch test like the Availability Test (NEN 7341) in the Netherlands and the Toxicity Characteristic Leaching Procedure (TCLP) in the USA. It requires 6 h for the leaching of any heavy metals from the wastes. Moreover, the leachate solutions should be treated as laboratory wastes because they mostly contain heavy metals.

Wai *et al.* found in 1991 that supercritical carbon dioxide (SC-CO₂) could extract not only organic compounds, but also metals with the aid of ligands.¹ Supercritical fluid extraction (SFE) with CO₂ can minimize secondary wastes since the solvent changes to gaseous CO₂ by depressurization. There are now many researchers who extract metals from various materials.²⁻⁶

To test the heavy metal leachability from wastes in a shorter time with little waste generation, we propose applying the SFE to the leaching test. Using SC-CO₂ as a solvent for leaching can reduce the generation of waste liquid containing heavy metals. Moreover, the high diffusivity of SC-CO₂ may enable the test time required to be shorter than the ordinary leaching test with aqueous solution. In this study, real samples of fly ash discharged from waste thermal treatments in Japan were used as the waste samples, and lead was chosen as the target heavy metal since lead is well-known to be one of the toxic heavy metals, and its content is relatively high in fly ash. As for the SFE of fly ash, Kersch *et al.* studied the removal of heavy metals from fly ash and simulated ash.^{7,8} They found that Cyanex 302 (bis(2,4,4-trimethylpentyl)monophosphinic acid) was effective as a ligand to extract lead with SC-CO₂.⁸ We

employed Cyanex 302 as a ligand, and compared the extractability of lead with Cyanex 302 and SC-CO₂ with the leachability by the JLT13 process for 6 samples of fly ash.

Experimental

Fly ash and ligand

Six fly ash samples were employed in this study. In recent years, a melting treatment has been proposed and used for stabilizing the ash discharged from municipal solid waste incineration (MSWI). Its high temperature (~1800 K) is able to melt the ash and decompose any dioxins present. Most heavy metals in the ash are fixed in the stable slag formed by the melting treatment. However, this melting process discharges fly ash, whose heavy metal content is higher than that of the MSWI fly ash.⁹ Samples 1 through 3 were discharged from the melting processes of the real MSWI fly ash, and Sample 4 was discharged from the automobile shredder dust process in Japan. Samples 5 and 6 were MSWI fly ashes. The elemental contents of the samples which were measured by commercial laboratories (Tokai Technology Center, Unichemy Co., Ltd.) are shown in Table 1. All samples contain lead in relatively high concentrations of 0.13–2.0 wt%. In particular, the higher content is confirmed in the fly ash from the melting processes (Samples 1 to 4) than in the incineration fly ash (Samples 5 and 6). For the ligand, Cyanex 302 was purchased from Fluka (Switzerland).

SC-CO₂ extraction

Extraction under static conditions. A schematic diagram of the experimental apparatus is shown in Fig. 1. A 2 cm³ ligand and 0.05 g of sample were placed in reaction vessels ((7) in Fig. 1) and (8), respectively. The total volume of vessels (7) and (8) was approximately 5 cm³. A 7 cm³ of tri-*n*-butylphosphate (TBP, Wako, Japan), whose amount was 26×10^{-3} mol corresponding to approximately 5 times that of the ligand, was placed in a 60 cm³ mixing vessel (6). Pressurized CO₂ (99.9%)

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Table 1 Elemental content (wt%) of employed fly ash

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Pb	1.8	1.6	1.9	2.0	0.26	0.13
Zn	3.7	2.0	6.7	2.8	0.8	1.04
Cu	0.11	0.27	0.36	0.38	0.04	0.05
Fe	0.56	0.08	0.3	1.12	N.M. ^c	N.M. ^c
Si	4.49	0.12	13.7	3.74	6.66	6.7
Al	0.83	0.04	3.3	0.79	3.32	4.44
Ca	21.9	13	3.8	19.4	26.4	17.1
Na	7.27	16.6	0.59	5.42	N.M. ^c	N.M. ^c
K	6.06	7.7	0.7	6.9	N.M. ^c	N.M. ^c
S	0.43	N.M. ^c	1.2	0.4	1.49	1.89
Cl	34	26.8	16.2	22	16.3	19.6
Treatment process	Melting	Melting	Melting	Melting	Incineration	Incineration
Feed-treated	MSWI fly ash ^a	MSWI fly ash ^a	MSWI fly ash ^a	Automobile shredder dust	MSW ^b	MSW ^b

a. MSWI fly ash, municipal solid waste incineration fly ash. b. MSW, Municipal solid wastes. c. N.M., Not measured.

Fig. 1 Experimental apparatus for extraction by SC-CO₂.

at 24 MPa was introduced from a cylinder by a syringe pump (260D; ISCO, USA) cooled at 278 K into the reaction vessel (7) to dissolve the ligand; then the valve were opened between vessels (7) and (8). The valve remained open during a static extraction for 1 h. Then, the mixture of SC-CO₂ and TBP was introduced through the mixing vessel (6) at 2 cm³ min⁻¹, and 24 MPa for 1.5 h. The TBP is completely miscible in SC-CO₂ at greater than 11 MPa, 323 K.¹⁰⁻¹² We used TBP as a washing diluent to collect the extract. The extract was collected in the collection vessel (10). The temperatures of the reaction vessels (7, 8) and the mixing vessel (6) were kept at 323 K throughout the experiment using water baths (5, 9).

Extraction under flowing conditions. A 0.5 g sample was placed in reaction vessels (7) and (8). Pressurized CO₂ and Cyanex 302 at 24 MPa were pumped into the reaction vessel at 1.8 and 0.17 cm³ min⁻¹, respectively. Under this condition, the ligand was miscible with SC-CO₂ in the vessels. The extract was collected in the collection vessel (10) every 30 min. The temperature of the reaction vessels was kept at 323 K throughout the experiment.

Extraction efficiency. To calculate the extraction efficiency, we subjected the extracts to a back-extraction using 3 mol dm⁻³ HNO₃. The lead concentrations in the back-extracts were measured by ICP-AES (ICPS-7000; Shimadzu, Japan). The extraction efficiency was determined as follows:

$$E = N_e/N_0 \times 100 \quad (1)$$

where E is the extraction efficiency in %, and N_e and N_0 are the

Table 2 Extracted amount of lead and extraction efficiency by SFE

Sample No.	Extracted amount/mg	Extraction efficiency, %
1	0.47	52
2	0.26	32
3	0.03	4
4	0.63	63
5	0.10	80
6	0.07	113

amounts of lead in the extract and in the original fly ash in mg, respectively.

Leachability test

The leachability test was carried out at 10% scale of JLT13 as follows: 5 g samples were added to 50 cm³ of water, then vertically shaken in a vessel at a 5 cm amplitude and at 200 rpm for 6 h. The solution was filtered through a filter with a mean pore diameter of 1 μm. The lead concentration in the leachate solutions was measured by ICP-AES.

Results and Discussion

Extraction of lead with SC-CO₂

The extracted amount and extraction efficiencies of lead for all six samples of fly ash are shown in Table 2. The extraction efficiencies of lead from the fly ash discharged from the melting process (Samples 1 to 4) seemed to be relatively low compared with those from the incineration fly ash (Samples 5 and 6). We found that the fly ash samples differed from one another regarding the extraction efficiency. This means that there was no relationship between the amounts of the extracted lead and their contents in the fly ash. When the extraction experiment was repeated for Sample 1, lead was extracted with an error of 4%.

Figure 2 shows the result of the extraction of lead from Sample 1 using the Cyanex 302 flowing condition. We collected the extract every 30 min, however, the extraction of lead was almost finished during the first collecting period. The extraction efficiency was 57%, which was similar to the efficiency obtained under the static conditions shown in Table

Table 3 Leachability of lead by JLT13

Sample No.	Leachate concentration/ mg dm ⁻³	Leaching fraction, %
1	490	27
2	530	32
3	31	1.7
4	910	46
5	70	27
6	48	37

2. This means that the extraction with Cyanex 302 and SC-CO₂ rapidly occurred within 30 min. The remainder might exist in the slaggy matrix formed by the high temperature melting process since no extraction occurred after 30 min. The consumption of Cyanex 302 within the 30 min was calculated for a 5.1 cm³ amount. For Sample 1, the 5.1 cm³ Cyanex 302 seemed to be sufficient to extract lead from 0.5 g ash.

Relation of leachability of heavy metals and extractability

Table 3 shows the leachability of lead for all six samples of fly ash. The lead concentrations in the leachate and leaching fraction differed from one another similar to the previously mentioned extraction above. The error of 3% was found in the lead leaching fraction by the repeated tests of Sample 1.

In Fig. 3, the lead amount extracted with Cyanex 302 and SC-CO₂ shown in Table 3 was plotted *versus* the leachate concentration shown in Table 2. Although the data in both Tables 2 and 3 have some errors, the extractability of lead seemed to be proportional to the leachabilities of those from the fly ash. The leachable lead with water seems to be extractable by SF-CO₂. Kersch *et al.* compared the metal extractability from a real sample of coal fly ash and a simulated fly ash which was prepared by mixing sand with solutions containing metals and then dried.⁸ Based on their results, the extraction efficiency of metals from coal fly ash was lower than that from the simulated fly ash. They postulated that the reason for the lower extraction efficiency was that most of the metals in the fly ash were bound in the glass matrix and were not extracted by the SC-CO₂. Our samples were not coal fly ash but fly ash discharged from the MSW treatment processes, but there seems to be a similarity in the characteristics of the fly ash and the metal extractability. For environmental safety, the behavior of the leachable metals contained on the surface of the ash, and not in the glass matrix, is important. Although the relation shown in Fig. 3 should be improved to gain a quantitative understanding, we considered that the leachable metal amount might be estimated by the extractability with SC-CO₂. It means that there is some possibility of applying the SFE to the leaching test. In addition, further comparisons of the leachability and extractability are necessary for other elements, other fly ash or wastes for the application.

Conclusions

In order to confirm the applicability of the SFE to the heavy metal leaching test, the SFE was carried out for six samples of fly ash using SC-CO₂ and Cyanex 302. Cyanex 302 was effective for extracting lead from the fly ash, however, the extraction efficiencies differed with each sample of the fly ash. There is a proportional relationship between the lead amounts extracted from the fly ash and the leachability of the fly ash.

Fig. 2 Change in extraction efficiency of lead from Sample 1 with time.

Fig. 3 Relation between the leachability and the extractability of lead in fly ash.

This implies that there is the possibility of applying the SFE to the leaching test.

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