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## Water extraction with CO<sub>2</sub> bubbling as pretreatment of melting-furnace fly ash for metal recovery

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**Abstract** In Japan, melting-furnace fly ash (MFA) generated from ash melting and gasification/melting plants is considered an “urban mine” due to its high metal content. This study aimed to develop a novel approach to pretreating MFA for metal recovery. Water extraction with CO<sub>2</sub> bubbling was investigated because MFA mainly consists of water-soluble salts containing elements such as Cl, Ca, Na, and K. Instead of acid addition, CO<sub>2</sub> bubbling was applied to maintain the optimal pH for minimizing the release of target metal elements and maximizing the removal of undesirable elements during water extraction. The results revealed that CO<sub>2</sub> bubbling effectively decreased the release of Pb, Zn, and Cd into the treatment water. This was mainly due to coprecipitation with CaCO<sub>3</sub>, which was primarily formed by the reaction of Ca<sup>2+</sup> from the MFA with CO<sub>3</sub><sup>2-</sup> from the CO<sub>2</sub> gas. The bubbling process also helped accelerate the removal of Cl from MFA. Furthermore, the study showed that it is possible to lower the water-to-solid ratio to 5 with only a slight reduction in water extraction effect. Finally, approximately four times the concentration of target metals (rare metals and Cu, Pb, and Zn) was achieved by removing 90% of Cl, 70%–90% of Na and K, and 30%–40% of Ca through water extraction with CO<sub>2</sub> bubbling, resulting in a concentration of target metals that was nearly equal to that of ore.

**Key words** Melting-furnace fly ash (MFA) · Water extraction · CO<sub>2</sub> bubbling · Metals

### Introduction

Melting technologies for treating solid waste in Japan were developed to overcome dioxin problems and a short-

age of landfill sites. Waste melting has not yet been successfully implemented in Europe and other countries, but, recently, EU directives and national policies have focused on decreasing landfilling and increasing incineration with energy recovery. Asian countries including Korea also plan to increase incineration as a part of municipal solid waste (MSW) management. Thus, in view of the fact that the utilization and safe disposal of incineration residues will become a major problem, melting technology may become more commonplace in other countries to recover resources and detoxify incineration residues in the near future.

The types of melting furnaces presently being used in Japan can be roughly divided into two main categories: ash melting that treats MSW incineration residues (bottom ash and fly ash) and gasification/melting that directly melts MSW. As of 2005, 153 ash melting and gasification/melting plants were in operation, accounting for about 10% of all incineration plants. In both types of plants, the primary products are molten slag and melting-furnace fly ash (MFA). Approximately 0.2 million tons of MFA and 0.5 million tons of molten slag are generated annually.

Considerable attention is given to MFA in Japan in terms of resource recovery and environmental impact. MFA is classified as a specially controlled waste due to its high content of toxic heavy metals and it must be solidified and stabilized with cement, chemical agents, or both prior to landfilling to prevent the leaching of toxic metals to the environment.<sup>1</sup> However, the high metal content of MFA makes it a candidate for resource recovery. According to a report from the Japan Waste Research Foundation,<sup>2</sup> MFA contains 0.75%–31.6% of Zn, 0.29%–13.8% of Pb, and 0.10%–2.75% of Cu. Jung and Osako<sup>3</sup> found that not only Zn and Pb but also rare metals such as Ag, Bi, Ga, Ge, In, Pd, Sb, Sn, Te, and Tl are highly concentrated in MFA, which is nearly equal in quality to crude ore. These rare metals have become increasingly important in modern high-technology industries, but these resources are extremely unevenly distributed around the world and their supply fluctuates widely according to the management policy of the resource's country.<sup>4</sup> It is therefore important to diversify

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the sources of rare metals to support a stable supply from the viewpoint of resource security.

This study focuses on MFA as an “urban mine” for rare metals as well as for Zn, Pb, and Cu. However, MFA contains a significant amount of undesirable elements, such as salt components including Cl, which hinder the nonferrous metal smelting process.<sup>5-7</sup> In addition, the metal content is not high enough to feed it as a resource straight into the nonferrous metal smelting process. Thus, pretreatment is required to remove undesirable elements and to improve the concentration of target rare metals. Up to now, various studies have been conducted on MFA pretreatment processes – selective extraction and concentration by chemical agents, e.g., H<sub>2</sub>SO<sub>4</sub>, HCl, NaOH, and NaHS, and volatilization and concentration for highly volatile metals such as Pb and Zn.<sup>5,7-14</sup> Several patents for metal resource recovery methods using extraction and concentration with chemical agents<sup>15-17</sup> and volatilization/concentration by thermal processing<sup>18,19</sup> have been granted by the Japan Patent Office. Most of the pretreatment methods, however, are complex and require the use of chemical agents, thermal energy, or both. Generally, less energy consumption and low cost are desirable at the pretreatment stage. From this standpoint, water extraction is the most practical and the simplest method compared to the other methods. However, previous reports have indicated that water extraction has its limits in satisfying the standards of the nonferrous smelting process.

Our preliminary study revealed that most of the salts in MFA were easily leached, regardless of the pH level, and Cu, Pb, Zn, and rare metal elements except for Tl showed the lowest release rates at pH 9–10.<sup>20</sup> This means that water extraction controlled at pH 9–10 could be an effective and practical pretreatment method for recovery of Cu, Pb, Zn, and rare metals from MFA. We therefore aimed to develop a novel pretreatment method using water extraction. To control pH, CO<sub>2</sub> bubbling was applied instead of adding acid during water extraction. The bubbling process was expected to accelerate the removal rate of soluble salts by promoting effective contact between MFA and water. The effect of CO<sub>2</sub> bubbling on the removal of undesirable elements and concentration of target metal elements in the residue was investigated. The effect of the ratio of water to solid (L/S) on water extraction was also studied to find the optimal ratio for minimizing the generation of wastewater without reducing the effect of water extraction.

## Experimental

### Materials

The MFA used in this study was collected from plasma- and surface-melting furnaces, which made up about 75% of the existing ash melting plants in 2005.<sup>2</sup> Table 1 shows the detailed composition of the MFA. In general, MFA from ash melting plants contains a higher metal content compared to that from gasification/melting plants.

**Table 1.** Detailed composition of MFA used in the study

Element	Content in MFA*	
	Plant A	Plant B
Target rare metal elements		
Ag	230	34
Bi	43	45
Ga	38	68
Ge	12	4.8
In	14	13
Pd	10	18
Sb	660	280
Sn	2200	1800
Te	2.0	12
Tl	2.8	2.5
Other elements		
As	10	10
B	380	350
Ca	84000	150000
Cd	370	670
Cl	340000	330000
Cr	12	67
Cu	3500	5700
Fe	3700	14100
K	150000	120000
Mg	1700	2000
Mn	60	1100
Na	110000	130000
Pb	26000	23000
Se	1.6	2.1
Zn	83000	100000

All data are milligrams per kilogram

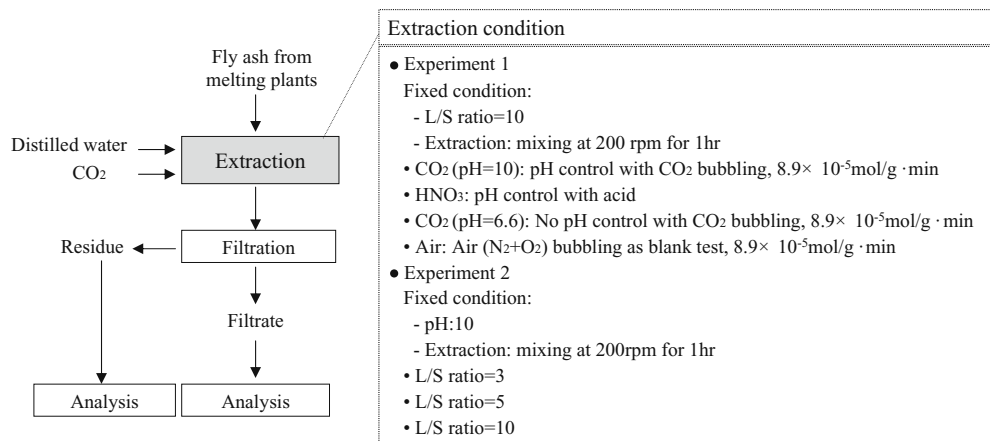
\*MFA: melting furnace fly ash

In both types of MFA, there is a remarkably high content of Na, Ca, K, and Cl, which make up about 70% of MFA. This implies that the removal of these elements is significant in terms of improving the concentration of target metal elements for recovery. Pb and Zn are included in MFA at about 2% and 10%, respectively. The ratio of total target rare metal elements in MFA is 0.2%–0.4%.

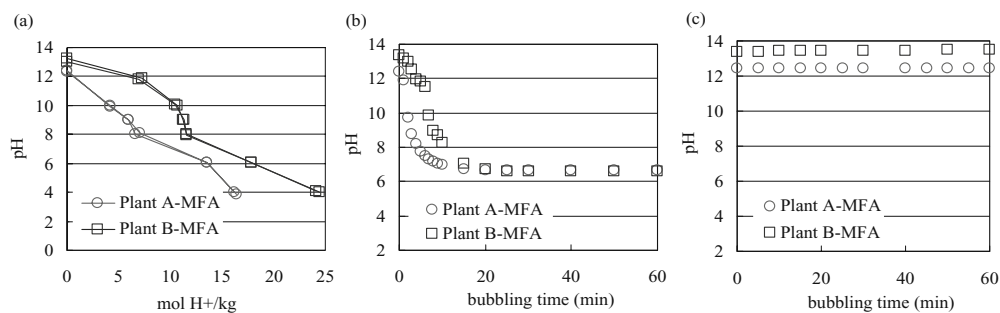
### Experimental conditions

Two experiments were conducted to investigate the effect of water extraction with CO<sub>2</sub> bubbling on the removal of undesirable elements and on the concentration of target metal elements. In the first experiment, we examined the influence of CO<sub>2</sub> bubbling on the water extraction. The experiment was conducted under four conditions as explained in Fig. 1 (experiment 1). The pH was controlled at 10 during water extraction, which was determined by the results of a previous study.<sup>20</sup> The L/S ratio was fixed at 10 (distilled water 250 ml/MFA 25 g) and extraction was conducted by mixing at 200 rpm for 1 h. In the CO<sub>2</sub> (pH = 10) test, pH was controlled by intermittent pure CO<sub>2</sub> bubbling, while in the HNO<sub>3</sub> test, HNO<sub>3</sub> was used to adjust the pH. In the CO<sub>2</sub> (pH = 6.6) test, pH was not controlled and pure CO<sub>2</sub> bubbling was continued for 1 h. Water extraction with

**Fig. 1.** Experimental flow and water extraction conditions. L/S, liquid (water) to solid ratio



**Fig. 2.** Change in pH on HNO<sub>3</sub> addition (a), CO<sub>2</sub> bubbling at  $8.9 \times 10^{-5}$  mol/g·min (b), and air bubbling at  $8.9 \times 10^{-5}$  mol/g·min (c). MFA, melting-furnace fly ash



air (N<sub>2</sub>+O<sub>2</sub>) bubbling was also carried out as a blank test for CO<sub>2</sub> bubbling, which was designed to examine the effect of the bubbling process on the leaching of salt components and the concentration of metal elements. In the second experiment, we examined the influence of the L/S ratio on water extraction. The amount of distilled water was fixed at 250 ml and the amount of MFA was increased from 25 g to 83.3 g (L/S ratio: 3, 5, and 10). The pH was controlled at 10 by CO<sub>2</sub> bubbling. Duplicate experiments were conducted for all tests.

#### Analytical method

After water extraction, the liquid was filtered using a membrane filter with a 0.45- $\mu$ m pore size and then it was divided into two solutions. One sample was for Cl analysis and the other was for metal elemental analysis. Cl was measured by ion chromatography, and the concentrations of metal elements – Ag, Bi, Ca, Cu, Ga, Ge, Na, In, K, Pb, Pd, Sb, Sn, Te, Tl, and Zn – were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES) (Seiko, Vista-PRO) and/or inductively coupled plasma–mass spectrometry (ICP–MS) (Agilent, 7500C) after acidifying with suprapure HNO<sub>3</sub> to pH < 2. The water washing residues were analyzed by X-ray diffractometer (Rigaku, RINT Ultima+) to investigate the change in mineral phase.

## Results and discussion

### pH control with HNO<sub>3</sub> addition, CO<sub>2</sub> bubbling, and air bubbling

To estimate the amount of acid required to decrease the pH of MFA to 10, which is the optimal pH for water extraction as determined in a previous study,<sup>20</sup> the acid neutralization capacity (ANC) was calculated. The initial pH of MFA from Plants A and B was 12.4 and 13.2, respectively. Figure 2a provides the calculated ANC curve for MFA from Plants A and B, in which HNO<sub>3</sub> addition was calculated as mol H<sup>+</sup>/kg (dry weight sample). The amount of HNO<sub>3</sub> required to lower the pH in MFA from Plant B was much higher than that from Plant A. This was due to the high Ca content, which originated from the Ca(OH)<sub>2</sub> used in the air pollution control (APC) system in the melting plants to remove acid gases such as HCl and SO<sub>2</sub>. The Ca content in MFA from Plant B was almost twice that in the MFA from Plant A, as shown in Table 1. This reveals that excessive injection of Ca(OH)<sub>2</sub> in the APC results in a high Ca content in MFA, necessitating the addition of a considerable amount of acid for water extraction. Ideally, MFA should be produced with less Ca to facilitate metal recovery.

The change in pH on CO<sub>2</sub> bubbling and on air (N<sub>2</sub>+O<sub>2</sub>) bubbling was examined as well (Fig. 2b,c). CO<sub>2</sub> and air were

injected from the bottom at a rate of  $8.9 \times 10^{-5}$  mol/g·min. The pH in the solution with CO<sub>2</sub> bubbling was lowered to about 6.6, whereas no change occurred with air bubbling. Therefore, CO<sub>2</sub> bubbling is applicable for pH control during water extraction. The amount of CO<sub>2</sub> required to lower the pH in MFA from Plant B was much more than that required for MFA from Plant A due to the high ANC.

#### Effect of CO<sub>2</sub> bubbling on water extraction

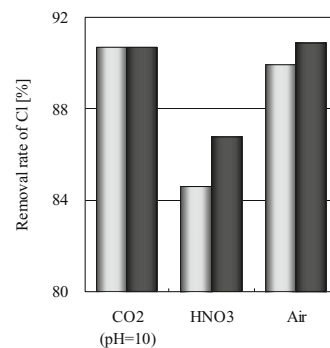
As explained in the previous section, water extraction is the most practical and efficient method of pretreating MFA for metal recovery because most of the undesirable elements in MFA are water soluble. To maximize the concentration rate of target metal elements in the residue, pH was controlled at 10, which is the optimal pH for minimizing the release of metal elements such as Cu, Pb, Zn, Ag, Bi, In, Ga, Ge, Pd, Sb, Sn, and Te.<sup>20</sup> The effect of CO<sub>2</sub> bubbling on the removal of undesirable elements and the concentration of target metals was investigated.

#### Effect of CO<sub>2</sub> bubbling on removal of salt components (Cl, Ca, Na, and K)

MFA mainly consists of Cl, Ca, Na, and K, which made up about 70% of the MFA used in this study. Generally, Cl causes corrosion of nonferrous smelting equipment as well as volatilization and loss of target metals as chlorides during the smelting process. Thus, the Cl content in feedstock is strictly regulated, and nonferrous metal smelting plants prefer less than 0.2% Cl in the feedstock. The removal of these components, including Cl, is essential if MFA is to be used as feedstock in nonferrous smelting.

The effect of CO<sub>2</sub> bubbling during water extraction on the removal of Cl, Ca, Na, and K was investigated. Figure 3 illustrates the Cl removal rate under CO<sub>2</sub> (pH = 10), HNO<sub>3</sub>, and air tests. The removal rate of Cl during water extraction with CO<sub>2</sub> bubbling increased by about 10% compared to that in water extraction with the addition of HNO<sub>3</sub>. It was hypothesized that the carbonation process decomposes barely water-soluble chlorides such as PbCl<sub>2</sub>·PbO, ZnO·ZnCl<sub>2</sub>, and Friedel's salt (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCl<sub>2</sub>·10H<sub>2</sub>O), which results in an increased Cl removal rate.<sup>21,22</sup> However, the above barely water-soluble chlorides might also be decomposed by acid, i.e., HNO<sub>3</sub>, added for pH control in the HNO<sub>3</sub> test. So, it would be difficult to conclude that the carbonation process by CO<sub>2</sub> bubbling accelerated the removal of Cl in this study. As shown in Fig. 3, the removal rate with air bubbling was higher than that for HNO<sub>3</sub> addition and was almost the same as that for CO<sub>2</sub> bubbling. Therefore, the acceleration of Cl removal might be due to the effective contact of MFA with water promoted by the mechanical bubbling process. Further study is required to clarify the mechanism.

As for Na and K removal, no difference was found between CO<sub>2</sub> (pH = 10), HNO<sub>3</sub>, and air tests, and 70%–90% of these components were removed. On the other hand, the



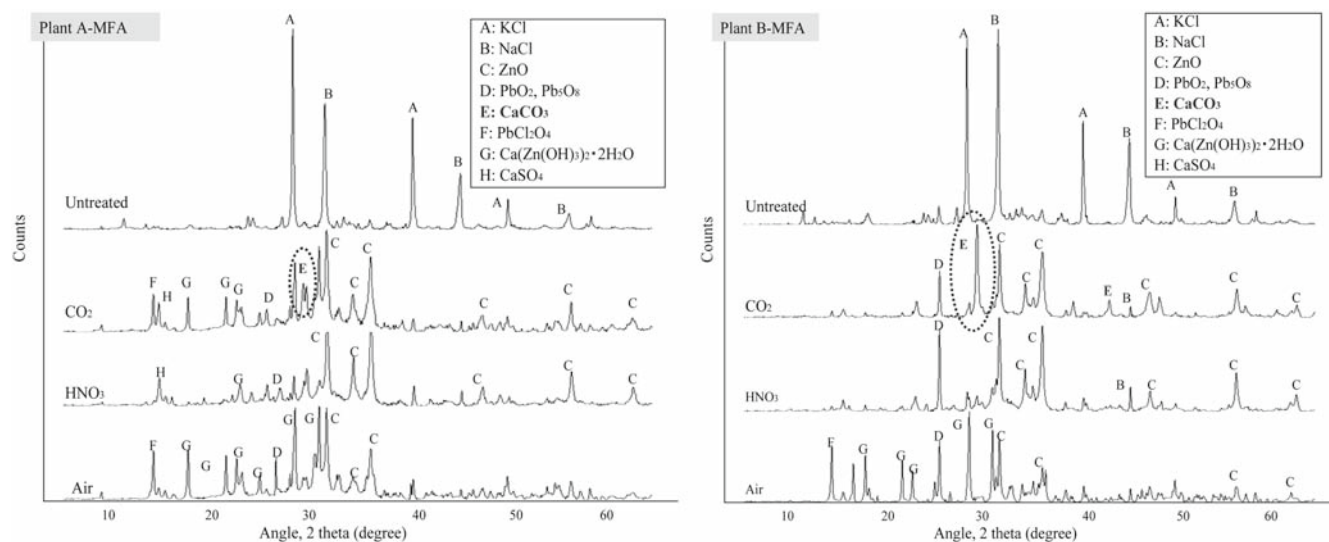
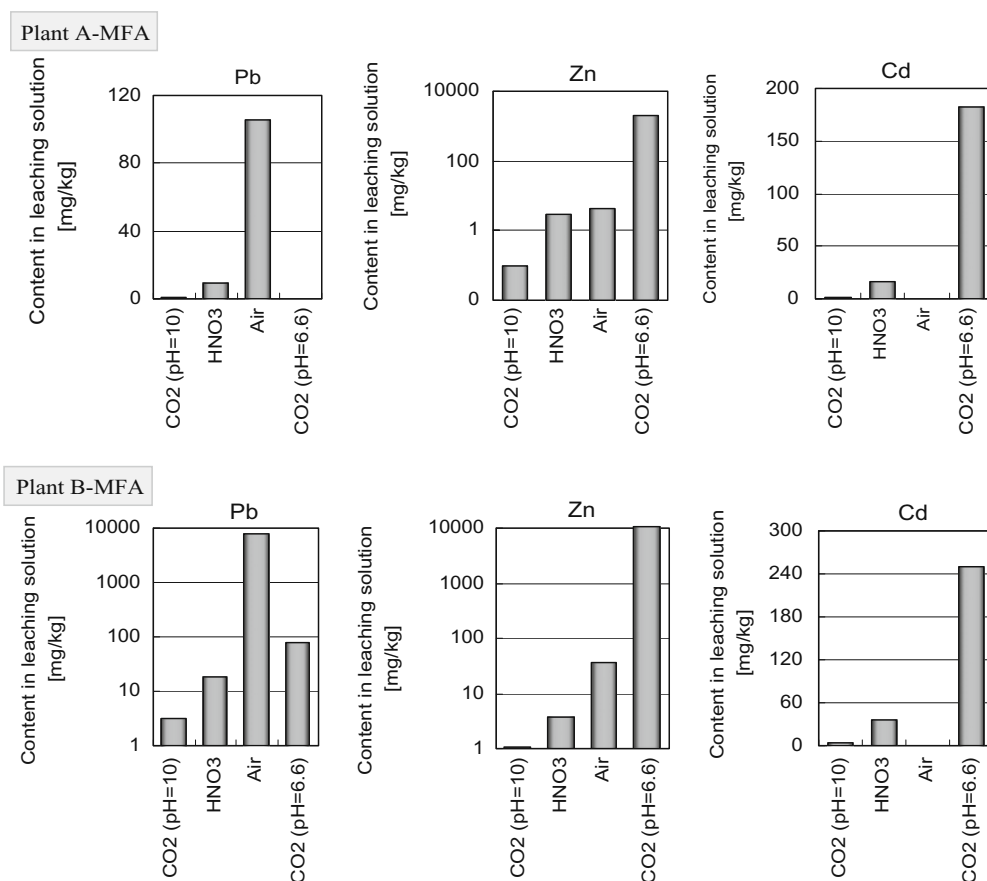
**Fig. 3.** Effect of CO<sub>2</sub> bubbling on Cl removal. *Light bars*, Plant A-MFA; *dark bars*, Plant B-MFA

Ca removal rate decreased by about 17% in the CO<sub>2</sub> (pH = 10) test compared to that in the HNO<sub>3</sub> test; only 30%–40% removal was achieved. This is due to the formation and precipitation of CaCO<sub>3</sub> resulting from the reaction of CO<sub>3</sub><sup>2-</sup> from CO<sub>2</sub> gas with Ca<sup>2+</sup> from MFA. This was clarified by investigating the mineral phase in water extraction residues using X-ray diffractometry, which is explained in more detail in the next section.

#### Effect of CO<sub>2</sub> bubbling on leaching of metal elements

Ideally, target metals should not be released, i.e., they should be concentrated in the water extraction residues from the viewpoint of resource recovery and minimization of environmental impact. Figure 4 shows the Pb, Zn, and Cd content in the leaching solution for the different test conditions. As explained in Fig. 1, pH was controlled at 10 in both the CO<sub>2</sub> (pH = 10) and HNO<sub>3</sub> tests by CO<sub>2</sub> bubbling and HNO<sub>3</sub> addition, respectively, while pH was not controlled in the air and CO<sub>2</sub> (pH = 6.6) tests. So, the final pH in the leaching solution of the air and CO<sub>2</sub> (pH = 6.6) tests was 12–13 and 6.5–6.7, respectively (Fig. 2b,c). The test results revealed that CO<sub>2</sub> bubbling affected the leaching of Pb, Zn, and Cd. Their content in the leaching solution of the CO<sub>2</sub> (pH = 10) test was much lower than that in the HNO<sub>3</sub> and air tests. This can be explained by the mineral phase in the water extraction residues. X-ray diffractograms of the residues are shown in Fig. 5 and were used to examine the differences in the mineral phase in the water extraction residues between the CO<sub>2</sub> (pH = 10), HNO<sub>3</sub>, and air tests. The most obvious difference is the high peak for CaCO<sub>3</sub>, a result of the reaction between CO<sub>3</sub><sup>2-</sup> from CO<sub>2</sub> gas and Ca<sup>2+</sup> from MFA. In the CO<sub>2</sub> (pH = 10) test, considerable CaCO<sub>3</sub> was formed and probably coprecipitated with Pb, Zn, and Cd, which caused the decrease in leaching.<sup>23</sup> In the air and CO<sub>2</sub> (pH = 6.6) tests, Pb and Zn were leached to a greater extent. This is because both metal elements are amphoteric, showing higher solubility at high and low pH ranges. In the air test, the lower Cd leaching content was due to the leaching characteristics with pH. Cd is leached at a high concentration at a low pH range, and this decreases sharply toward

**Fig. 4.** Effect of CO<sub>2</sub> bubbling on release of metal elements



**Fig. 5.** X-ray diffractograms of water extraction residues

pH values of about 12.<sup>20</sup> The other metal elements were unaffected by CO<sub>2</sub> bubbling and the release amount was determined by their leaching characteristics.

Wastewater containing toxic elements is usually generated during water extraction and must be appropriately

treated to protect human health and the living environment. Ideally, toxic elements should not be released during water extraction. Figure 6 compares the concentration of metals in the leaching solution of CO<sub>2</sub> (pH = 10) and HNO<sub>3</sub> tests with the Japanese effluent standards for toxic substances

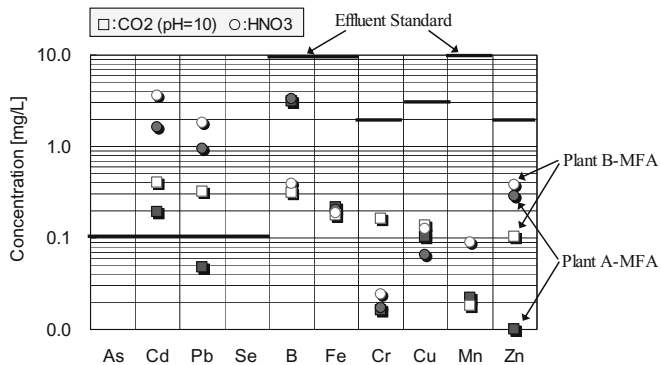
related to the protection of human health (Cd, Pb, As, Se, and B) and substances related to the protection of the living environment (Cu, Zn, Fe, Mn, and Cr). The results show that Cd and Pb exceeded the safety standards whereas As and Se were not leached during water extraction. However, as shown in Fig. 6, the concentration of Cd and Pb in the leaching solution of the CO<sub>2</sub> (pH = 10) test was much lower than that in the HNO<sub>3</sub> test. In particular, Pb in the leaching solution of the CO<sub>2</sub> (pH = 10) test satisfied the standard for MFA from Plant A. This might be due to coprecipitation with CaCO<sub>3</sub>, which was identified by X-ray diffraction anal-

ysis of water extraction residues. The influence of precipitation as metal carbonates was also expected, but it was not identified in Fig. 5.

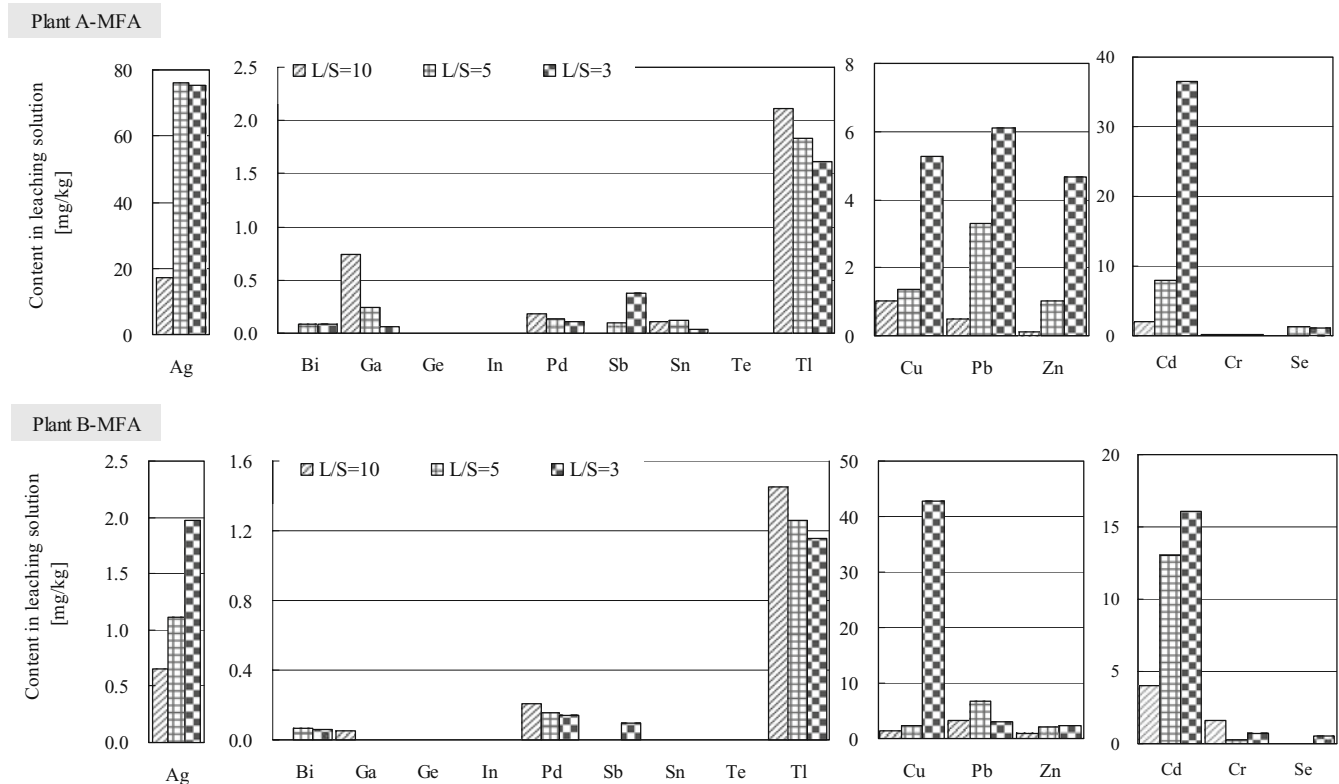
#### Effect of the ratio of water to solid (L/S) on water extraction

As it is desirable to minimize wastewater generation during water extraction, the L/S ratio should be as low as possible without reducing the effect of water extraction, because a lower L/S ratio generates less wastewater. Figure 7 shows the release of metal elements with changes in the L/S ratio. Rare metal elements except for Tl were mostly unaffected by the L/S ratio and the release amount was insignificant. Tl is highly soluble and was constantly released regardless of L/S ratio. The release of Ag, Cu, Pb, and Zn increased with decreases in the L/S ratio. This can be explained as follows. As shown in Table 1, the MFA used in the study contains highly water-soluble elements, i.e., Cl, Na, and K. Thus, their concentration in the leaching solution increased with decreases in the L/S ratio. This produced higher ionic strength in the solution, which could have resulted in the increased release of metal elements.<sup>23</sup> In addition, the high concentration of soluble salts might accelerate the formation of heavy metal-chloride complexes and the release of metal elements with soluble salts.<sup>24</sup>

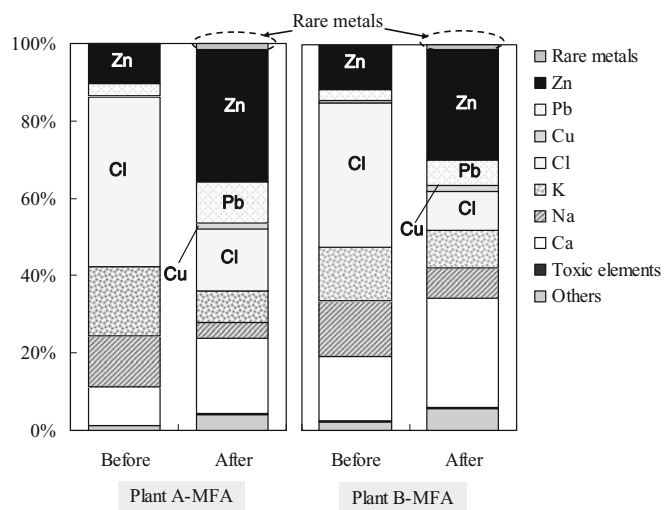
The release of metal elements such as Ag, Cu, Pb, Zn, and Cd abruptly increased at L/S = 3, as shown in Fig. 7. Thus, it can be concluded that the L/S ratio can be



**Fig. 6.** Comparison of concentration in the leaching solution of CO<sub>2</sub> (pH = 10) and HNO<sub>3</sub> tests with Japanese effluent standards related to the protection of human health (As, Cd, Pb, Se, B) and the living environment (Fe, Cr, Cu, Mn, Zn)



**Fig. 7.** Effect of the ratio of water to solids (L/S) on the release of metal elements [CO<sub>2</sub> (pH = 10)]



**Fig. 8.** Changes in composition of MFA on water extraction with CO<sub>2</sub> bubbling (pH = 10)

lowered to 5 with only a slight reduction in water extraction effect.

#### Composition change of MFA

The main objective of water extraction was not only to improve the concentration of target metal elements but also to remove undesirable elements. Figure 8 illustrates the composition change of MFA through water extraction with CO<sub>2</sub> bubbling (L/S: 10, pH: 10, extraction time: 1 h). Approximately 90% of Cl, 70%–90% of Na and K, and 30%–40% of Ca were removed, and most of the target rare metal elements and Cu, Pb, and Zn remained in the residues, achieving about four times the concentration in the original MFA. To be more exact, the content of rare metals and Cu, Pb, and Zn in the residues increased to about 1%, 2%, 9%, and 32%, respectively. About 80% of TI was released because of its high solubility, as explained in above.

About 5% of Cl still remained in the residues, although most of the Cl in MFA was removed. This achievement was not sufficient for the use of pretreated MFA in the nonferrous smelting process, and improvement of the Cl removal rate and the target metal concentration rate is required if water extraction with CO<sub>2</sub> bubbling is to be applied as the pretreatment of MFA; however, high costs and energy consumption are not desirable at the pretreatment stage. Controlling the feed ratio of pretreated MFA to that of raw ore in the smelting process is a possible means of countering the adverse effects of the remaining small amount of Cl and overcoming the deficient metal content. In this context, one smelter in Japan actually uses the water extraction method for pretreatment of MFA in the Cu smelting process. MFA is treated by mixing with water at L/S = 5 and 300 rpm for about 5 h. Then, the filtered concentrates are fed to the smelting process. Since the pH is not controlled, there is the potential for some Pb and Zn to be released due to their amphoteric leaching characteristics.

Compared to conventional water extraction, the process combined with CO<sub>2</sub> bubbling in this study is superior for the improved concentration of target metal elements and the removal of undesirable components including Cl; the bubbling process with pH control was found to be effective for Cl removal and target metal concentration.

#### Conclusion

In Japan, melting-furnace fly ash (MFA) is watched with keen interest as an “urban mine” due to its high metal content. This study aimed to develop a novel approach to pretreating MFA for metal recovery. Water extraction with CO<sub>2</sub> bubbling was investigated because MFA mainly consists of water-soluble salts containing elements such as Cl, Ca, Na, and K. Instead of acid addition, CO<sub>2</sub> bubbling was applied to maintain the optimal pH for minimizing the release of target metal elements and maximizing the removal of undesirable elements during water extraction.

It was revealed that CO<sub>2</sub> bubbling significantly decreases the release of Pb, Zn, and Cd into the treatment water. This was mainly due to coprecipitation with CaCO<sub>3</sub>, which was primarily formed by the reaction between Ca<sup>2+</sup> from MFA and CO<sub>3</sub><sup>2-</sup> from CO<sub>2</sub> gas. This was identified by investigating the mineral phase in the water extraction residues through X-ray diffractograms. Also, the bubbling process effectively accelerated the removal of Cl from MFA. The removal rate increased by about 10% compared to that for water extraction without the bubbling process. The bubbling process might promote effective contact of MFA with water and accelerate Cl removal. In the wet pretreatment of MFA, the generation of wastewater is unavoidable. Thus, it is better to lower the L/S ratio as much as possible without reducing the water extraction effect. This study shows that it is possible to lower the L/S ratio to 5 with only a slight reduction in water extraction effect.

Finally, approximately four times the concentration of rare metals and Cu, Pb, and Zn was achieved with the removal of about 90% of Cl, 70%–90% of Na and K, and 30%–40% of Ca, through water extraction with CO<sub>2</sub> bubbling. This achievement was, however, insufficient according to the criteria for feedstock for nonferrous metal smelting. For the practical application of water extraction with CO<sub>2</sub> bubbling as pretreatment of MFA for smelting, improvement of the Cl removal rate and the target metal concentration rate is required, together with strategic control of feedstock in the nonferrous metal smelting process, i.e., controlling the feed ratio of pretreated MFA to that of raw ore to prevent adverse effects from the remaining small amount of Cl and to overcome the deficient metal content in the smelting process. In addition, it would be beneficial to use the CO<sub>2</sub> present in incineration outlet gas in the proposed water extraction system. Further experiments with lower-quality CO<sub>2</sub> are required to investigate this possibility.

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