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Headline Articles

Multielement and Morphological Characterization of Industrial Waste Incineration Fly Ash as Studied by ICP-AES/ICP-MS and SEM-EDS

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The leachabilities of major-to-ultratrace elements in industrial waste incineration fly ash (IWIFA) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) in order to characterize IWIFA. The leaching data of about 50 elements in the IWIFA sample could be obtained in the concentration range from mg g^{-1} to sub-μg g^{-1}, when HNO_3 and *aqua regia* were used as the leachants. In addition, morphological observations of IWIFA particles were performed by a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS) before and after the leaching treatment of the IWIFA samples. From the data for the leaching and morphological observations, the chemical states of the elements in IWIFA were elucidated as follows: (i) core materials of fly ashes were mostly composed of stable oxides of major elements such as Si, Al, Ti, and Fe; (ii) Cu, Zn, Mo, Cd, and Bi were mainly adsorbed on the surface of fly ash particles in the forms of acid soluble compounds; (iii) Mn, Co, Ni, and Pb were partly taken into the core materials of fly ash particles, and partly adsorbed on the fly ash particles; and (iv) Sb, Cr, Sn, In, and W were contained as rather stable compounds in IWIFA.

Recently, waste management has received great attention as one of the most important social issues, because an enormous amount of solid wastes is emitted from industrial activities as well as from our daily lives. In Japan, incineration is a major technology for treatment of solid wastes to reduce their volume and mass,[1] and then ca. 40% of incineration ashes are finally buried in landfills, although ca. 60% of them are recycled mainly for construction materials. However, the recycling of incineration fly ash materials, which are captured during the waste combustion process with air pollution control devices such as electrostatic precipitators and bug filters, must be conducted by persons who are very attentive to environmental management, because the materials usually contain various kinds of heavy metals at rather high concentration levels.[2]

In order to develop more appropriate incineration technologies for solid wastes from the viewpoint of environmental management strategies, scientists desire to elucidate the chemical characteristics of incineration fly ashes. So far, a number of studies on the determination of the contents of heavy metals and identification of their chemical species have been performed for coal fly ashes[2–10] and municipal solid waste incineration (MSWI) ashes.[4,8,11–19] Among such studies, most investigations have focused on the *so-called* hazardous and toxic elements, such as Hg, Cr, Cd, and Pb. However, recent studies on toxicology have revealed that most of the elements exert more or less influences on the biological systems because any element will cause toxic effects under some sufficient conditions.[20] Moreover, it should also be understood that the influences of such elements on the biological systems are synergically enhanced or suppressed under the multielement coexisting conditions. As a result, the importance of the multielement analysis is now recognized in various fields such as biological, geochemical, and environmental sciences.[21] Thus, characterization of incineration fly ashes should be performed on a multielement basis in order to evaluate their influences on the environment as well as on biological systems.

The elemental compositions of incineration fly ashes do reflect those of the original waste materials. Industrial waste incineration fly ash (IWIFA) contains various kinds of elements more abundantly than coal fly ash and MSWI ash,[22,23] because various kinds and enormous amounts of elements are used in modern industrial productions. Therefore, appropriate treatment technologies and strategies are required to prevent the environmental pollutions caused by IWIFA. On the other hand, there are great possibilities that IWIFA will become a kind of urban mining for resources of heavy metals in future, because the materials contain rare elements at rather high concentration levels. Thus, it is also desirable to evaluate the characteristics of IWIFA for the purpose of recycling the products as usable metal resources.

The present authors reported the multielement determination of major-to-ultratrace elements in the IWIFA samples[22] as well as in coal fly ash standard reference material and city waste incineration ash certified reference material. About 50 elements in the fly ash samples over the concentration range from mg g^{-1} to sub-μg g^{-1} could be determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) after alkali fusion using $LiBO_2$. It was found that various kinds of elements, especially chalcophile elements including hazardous and toxic ones, were enriched in IWIFA, since they are widely used in industrial products and materials. The present authors also investigated the leaching behaviors of major-to-ultratrace elements in the IWIFA samples, where water and HNO_3 were used as the leachants.[23]

In the present study, *aqua regia* was used as a leachant. Such leaching with *aqua regia* provided some new information about the morphological structures of IWIFA. Thus, (1) the determination of total contents of major-to-ultratrace elements in IWIFA, (2) evaluation of leaching properties of the elements, and (3) morphological observation of IWIFA particles using a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDS), were performed to characterize IWIFA comprehensively.

Experimental

Instrumentation: An ICP-AES instrument (model Plasma AtomComp Mk II; Jarrell-Ash, Franklin, MA, USA) composed of a polychromator with 40 channels (detectors) was used for the simultaneous multielement determination of major and minor elements. An ICP-AES instrument (model SPS 1500V; Seiko Instruments, Chiba, Japan) with a N_2-purge type of monochromator was also used for the determination of sulfur at 180.7 nm. An ICP-MS instrument (model SPQ 8000A; Seiko Instruments) was used for the determination of trace elements. In the present ICP-MS instrument, a maximum of 30 elements (isotopes) could be determined simultaneously in one measurement, and matrix effects of major elements on the observed data were corrected by the internal standard method.[24] Since the present ICP-MS instrument was equipped with a low-resolution quadrupole-type mass spectrometer, spectral interferences were corrected by Gauss-elimination based on a procedure similar to that of Vaughan and Horlick.[25] The scanning electron microscopic experiments were performed on a SEM instrument (model S-3000N; Hitachi, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (model EDAX Falcon; EDAX, Mahwah, NJ, USA). The operating conditions for ICP-AES, ICP-MS, and SEM-EDS instruments are summarized in Table 1.

Chemicals: The nitric acid and hydrochloric acid used were of electronics industry grade (Kanto Chemical, Tokyo, Japan). Lithium metaborate ($LiBO_2$) of ultrapure grade purchased from Spex (Metuchen, NJ, USA) was used for alkali fusion of the fly ash samples. The multielement standard solutions for standardizing the working calibration curves were prepared by mixing aliquots of 1000 μg mL^{-1} of the single-element stock solutions for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan) in 1 M HNO_3 solution. The compositions of the multielement standard solutions are shown in Table 2, where 5 and 8 groups of standard solutions were prepared for the ICP-AES and ICP-MS measurements, respectively, taking into consideration chemical stabilities and spectral interferences. Deionized water used throughout the present experiment was prepared by a Milli-Q TOC SP purification system (Nihon Millipore Kogyo, Tokyo, Japan).

Table 1. Operating Conditions for ICP-AES, ICP-MS and SEM-EDS Instruments

ICP-AES: Jarrell-Ash Plasma AtomComp Mk II	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 17 L min^{-1}
Auxiliary gas flow rate	Ar 1.0 L min^{-1}
Carrier gas flow rate	Ar 0.48 L min^{-1}
Observation height	18 mm above load coil
Nebulizer:	cross-flow type
Sample uptake rate	1.2 mL min^{-1}
Polychromator	Paschen–Runge mounting (focal length 75 cm)
Grating	2400 grooves/mm
Entrance slit width	25 μm
Exit slit width	50 μm
ICP-AES: Seiko SPS 1500 V	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 L min^{-1}
Auxiliary gas flow rate	Ar 0.5 L min^{-1}
Carrier gas flow rate	Ar 0.48 L min^{-1}
Purge gas	N_2 5 L min^{-1}
Observation height	10 mm above load coil
Nebulizer:	concentric type
Sample uptake rate	1.0 mL min^{-1}
Monochromater:	Czerny–Turner mounting (focal length 100 cm)
Grating	3600 grooves/mm
Entrance slit width	20 μm
Exit slit width	30 μm
ICP-MS: Seiko Instruments SPQ 8000 A	
Plasma conditions:	
Incident power	1.0 kW
Coolant gas flow rate	Ar 16 L min^{-1}
Auxiliary gas flow rate	Ar 1.0 L min^{-1}
Carrier gas flow rate	Ar 1.0 L min^{-1}
Sampling depth	12 mm from load coil
Nebulizer:	concentric type
Sample uptake rate	1.0 mL min^{-1}
Data acquisition:	
Dwell time	10 ms/point
Data point	3 points/peak
Number of scans	100
SEM-EDS: SEM; Hitachi S-3000N, EDS; EDAX Falcon	
Electron beam source	tungsten filament
Accelerating voltage	25 kV
Beam current	90 μA

Samples: Industrial waste incineration fly ash was collected from an electrostatic precipitator installed on a rotary kiln-type industrial waste incinerator,[22,23] by courtesy of a private waste treatment company. In this incinerator, waste oils, waste petrochemi-

Table 2. The Standard Solutions (STDs) for ICP-AES and ICP-MS Measurements[a)]

ICP-AES	(unit: μg mL^{-1})
STD 1	Na (50), K (50)
STD 2	Al (50), Si (50)
STD 3	Mg (10), P (10), Ca (10), Ti(10), V (10), Fe (10), Zn (10), Pb (10)
STD 4	Mn (1), Cu (1), Sr(1), Ba (1)
STD 5	S (72)
ICP-MS	(unit: μg mL^{-1})
STD 6[b)]	Sn (100), Sb (100)
STD 7	Cr (50), Ni (50), Co (10), Ga (10), Mo (50), Cs (10)
STD 8	Rb (50), Zr (50), Cd (5), Hf (5)
STD 9	Ge (10), As (10), In (10)
STD 10	Y (10), La (10), Ce (10), Pr (10), Nd (10), U (1)
STD 11	Sm (5), Eu (5), Gd (5), Tb (5), Dy (5), Th (5)
STD 12	Ho (1), Er (1), Tm (1), Yb (1), Lu (1), Bi (50)
STD 13[c)]	W (10)

a) The standard solutions are in 1 M HNO_3 except for STD 6 and 13, those for ICP-MS contain the internal standard elements (Rh and Re: 5 ng mL^{-1} each). The values in the parentheses are the concentrations of the elements in the standard solutions. The units of concentrations are μg mL^{-1} for ICP-AES and ng mL^{-1} for ICP-MS.

b) STD 6 is in 0.01 M HCl.

c) STD 13 is in 0.05 M HNO_3.

cal products, and waste organic solvents, as well as various kinds of industrial solid wastes were incinerated daily, and the desulfurization treatment was carried out by a NaOH solution spray method. The IWIFA sample was dried at 60 °C for 24 h and sieved through a polyethylene sieve (100-mesh; pore size 183 μm) prior to use. The IWIFA sample was homogenized by grinding with an agate mortar before decomposition.

Sample Decomposition: The IWIFA sample was decomposed in a manner similar to that used in the previous works.[22,26] After drying at 105 °C for 2 h, about 0.3 g of the sample was decomposed with about 0.9 g of $LiBO_2$ in a platinum crucible. The residue was dissolved with 7.5 mL of conc. HNO_3 and diluted with 50 mL of deionized water. The decomposed sample solution was filtrated with a 5C filter paper and diluted to 100 mL with deionized water. The filtrated sample solution was further diluted to 20 times with 1 M HNO_3, after the internal standard elements (Rh and Re; final concentration 5 ng mL^{-1} each) for correction of matrix effects in ICP-MS measurements were added.

Leaching Procedure: The IWIFA sample was subjected to the following leaching tests using deionized water, 1 M HNO_3, and 6 M *aqua regia*.

(a) Water and HNO_3 treatments: About 1 g of the IWIFA sample was weighed in a Teflon beaker (100 mL in volume), after being dried at 105 °C for 2 h. Then, 20 mL of deionized water or 1 M HNO_3 was added into the beaker as a leachant. After shaking for 3 h at room temperature, the leachate was filtered with a membrane filter (pore size 0.45 μm). The final pH values of the leachates were 9.1 and 1.0, when leached with water and 1 M HNO_3, respectively. Both of the leachates were diluted to 100 times with 1 M HNO_3 after adding the internal standard elements (Rh and Re: final concentration 5 ng mL^{-1} each).

(b) *Aqua regia* Treatment: About 1 g of the IWIFA sample in 20 mL of 6 M *aqua regia* was heated to almost boiling on a hot plate for 12 h. After cooling to room temperature, the leachate was filtered with a membrane filter (pore size 0.45 μm), and the filtrate was diluted to 100 times with 1 M HNO_3 after adding the internal standard elements (Rh and Re: final concentration 5 ng mL^{-1} each).

Results and Discussion

Determination of Major-to-Ultratrace Elements in IWIFA: Major-to-ultratrace elements in IWIFA were determined by ICP-AES and ICP-MS after alkali fusion using $LiBO_2$. The details of the analytical procedures were described elsewhere.[22] The analytical results, which were newly obtained to evaluate the leachabilities with *aqua regia* in the following experiment, are summarized in Table 3. In the present work, 51 elements in IWIFA could be determined over the concentration range from 196 mg g^{-1} of Na to 0.019 μg g^{-1} of Tm. The elemental composition of the present IWIFA sample was almost the same as that reported in the previous paper.[22] In addition, the sum (weight) of major elements (Na, S, K, Fe, P, Si, Al, Ca, Cu, Zn, and Ti) was ca. 51% in Table 3, and that of their oxides, calculated from the data in Table 3, was ca. 84%. These results suggest that quite a large amount of Cl, besides small amounts of other minor and trace elements (ca. 2–3%), was contained as anions in IWIFA, although the Cl content was not measured in the present experiment. It is noted here that the deviations of the concentrations of analyte elements in IWIFA collected on the different sampling dates were generally within ca. 10%, although such concentrations in the particles with the different particle sizes in IWIFA were significantly different from each other.[27]

As is seen in Table 3, the present IWIFA sample contained the following hazardous elements at rather high concentration levels: As 53 μg g^{-1}, Cd 17.9 μg g^{-1}, Cr 5,620 μg g^{-1}, Cu 18,900 μg g^{-1}, Pb 4,270 μg g^{-1}, Sb 413 μg g^{-1}, Sn 1,080 μg g^{-1}, and Zn 15,900 μg g^{-1}. The enrichment factors (EFs) of the elements, which indicate the degree of enrichment of the analyte elements in IWIFA as compared to those in the continental crust,[21,22] are also shown in the parentheses in Table 3. Table 3 clearly shows that the EF values of various kinds of elements, such as S, P, Cu, Zn, Cr, Pb, Ni, Sn, Mo, Sn, Mo, Sb, W, As, Bi, Cd, and In, which are widely used as composite materials in industrial products were large in the IWIFA sample, as mentioned in the previous papers.[22,27]

Leaching Behaviors of the Elements in IWIFA Sample: Table 3 also shows the release amounts of the elements from the IWIFA samples, when they were eluted with water, HNO_3 and *aqua regia*, respectively. The release amount is defined as the amount of the analyte element released from 1 g of the sample. In the water treatment, only 26 elements could be determined in the leachate, although 51 elements were determined as the total concentration in the IWIFA sample. It is noted here that heavy metals such as Cu, Zn, Ni, Mo, and Cd were significantly leached from IWIFA even by the water treatment, although major elements of IWIFA such as Fe, Si, Al, and Ti could not be detected in the water leachate. In the cases of the HNO_3 and *aqua regia* treatments, all the elements

Table 3. The Concentrations and Release Amounts of Major-to-Ultratrace Elements in IWIFA Sample

Element$^{a)}$	Concentration$^{b)}$ /μg g^{-1}		Release amount$^{c)}$/μm		
			Water	HNO_3	*aqua regia*
Na†	196000	(32)	180000 ± 2000	190000 ± 2000	190000 ± 1000
S†	91200	(510)	88900 ± 700	88100 ± 900	87600 ± 900
K†	46000	(8.4)	38100 ± 800	38900 ± 6500	42700 ± 500
Fe†	42600	(3.8)	n. d.$^{d)}$	3100 ± 110	35600 ± 800
P†	25900	(130)	1300 ± 100	23100 ± 1200	21400 ± 200
Si†	20900	(0.28)	n. d.	5210 ± 280	125 ± 22
Al†	20500	(1.0)	n. d.	5540 ± 250	15600 ± 400
Ca†	19000	(1.9)	3460 ± 20	15900 ± 600	17300 ± 2100
Cu†	18900	(2900)	359 ± 17	16900 ± 200	19200 ± 200
Zn†	15900	(950)	2300 ± 40	9910 ± 290	14900 ± 100
Ti†	11300	(11)	n. d.	244 ± 14	167 ± 67
Cr	5620	(170)	2.0 ± 0.2	128 ± 2	1820 ± 10
Pb†	4270	(1100)	7.29 ± 0.04	1030 ± 190	4490 ± 40
Ni	3590	(250)	291 ± 6	1100 ± 2	2800 ± 90
Mg†	2900	(0.51)	245 ± 36	1060 ± 310	2490 ± 20
Ba†	2230	(15)	4.28 ± 0.30	26.0 ± 0.7	20.1 ± 5.6
Sn	1080	(1800)	0.21 ± 0.04	36.1 ± 1.2	656 ± 9
Mo	1060	(3700)	322 ± 10	740 ± 59	1010 ± 10
Mn†	682	(3.7)	29 ± 1	182 ± 5	551 ± 9
Co	493	(80)	20.9 ± 0.4	163 ± 1	391 ± 6
Sb	413	(5300)	1.20 ± 0.06	23.1 ± 0.6	261 ± 1
V†	250	(10)	32 ± 9	99 ± 46	193 ± 1
Sr†	130	(1.5)	6 ± 0	67 ± 3	92 ± 7
W	94.8	(370)	11.7 ± 0.7	25.5 ± 0.4	59.1 ± 1.7
Zr	91.9	(1.8)	n. d.	1.53 ± 0.03	0.40 ± 0.08
As	53	(120)	2 ± 0.3	39 ± 0.4	37 ± 0.1
Ce	35	(2.3)	n. d.	11.3 ± 0.5	17.7 ± 4.1
Bi	24.1	(1100)	n. d.	16.6 ± 0.03	22.2 ± 0.4
La	22.7	(2.9)	n. d.	4.96 ± 0.15	6.17 ± 1.24
Y	22.5	(3.6)	n. d.	8.22 ± 0.17	18.0 ± 3.4
Cd	17.9	(700)	7.11 ± 0.19	14.5 ± 0.1	16.7 ± 0.3
Cs	17.8	(20)	5.48 ± 0.02	13.6 ± 0.04	16.9 ± 0.1
Rb	16.5	(0.82)	12.0 ± 0.1	13.9 ± 0.1	16.5 ± 0.1
Nd	7.01	(1.0)	n. d.	3.37 ± 0.09	4.71 ± 1.17
Ga	5.63	(1.5)	n. d.	1.23 ± 0.03	4.38 ± 0.12
Ge	3.71	(10)	0.11 ± 0.01	0.94 ± 0.01	2.16 ± 0.11
In	2.75	(210)	0.006 ± 0.002	1.38 ± 0.02	2.37 ± 0.03
Pr	2.22	(1.3)	n. d.	1.03 ± 0.03	1.48 ± 0.37
Hf	1.47	(1.2)	n. d.	0.030 ± 0.001	0.006 ± 0.001
Eu	1.4	(4.2)	n. d.	0.543 ± 0.012	1.11 ± 0.29
Th	0.718	(0.33)	n. d.	0.039 ± 0.004	0.134 ± 0.027
Sm	0.67	(0.39)	n. d.	0.37 ± 0.01	0.48 ± 0.12
Gd	0.39	(0.38)	n. d.	0.19 ± 0.02	0.25 ± 0.05
U	0.340	(0.78)	n. d.	0.142 ± 0.008	0.254 ± 0.012
Dy	0.277	(0.28)	n. d.	0.160 ± 0.015	0.240 ± 0.054
Tb	0.218	(1.3)	n. d.	0.091 ± 0.002	0.129 ± 0.035
Er	0.181	(0.33)	n. d.	0.086 ± 0.003	0.111 ± 0.020
Yb	0.147	(0.29)	n. d.	0.063 ± 0.005	0.084 ± 0.018
Ho	0.046	(0.22)	n. d.	0.023 ± 0.0004	0.031 ± 0.006
Lu	0.0209	(0.23)	n. d.	0.0090 ± 0.0003	0.0128 ± 0.0013
Tm	0.019	(0.25)	n. d.	0.008 ± 0.001	0.011 ± 0.002

a) The elements with † were determined by ICP-AES and others by ICP-MS.

b) Values in the parentheses are enrichment factors of the elements.

c) Release amount of analyte element from 1 g of the sample. Mean ± SD ($n = 3$).

d) Not detected.

determined in the IWIFA sample could be detected in the leachates. As is seen in Table 3, the release amounts of the el-

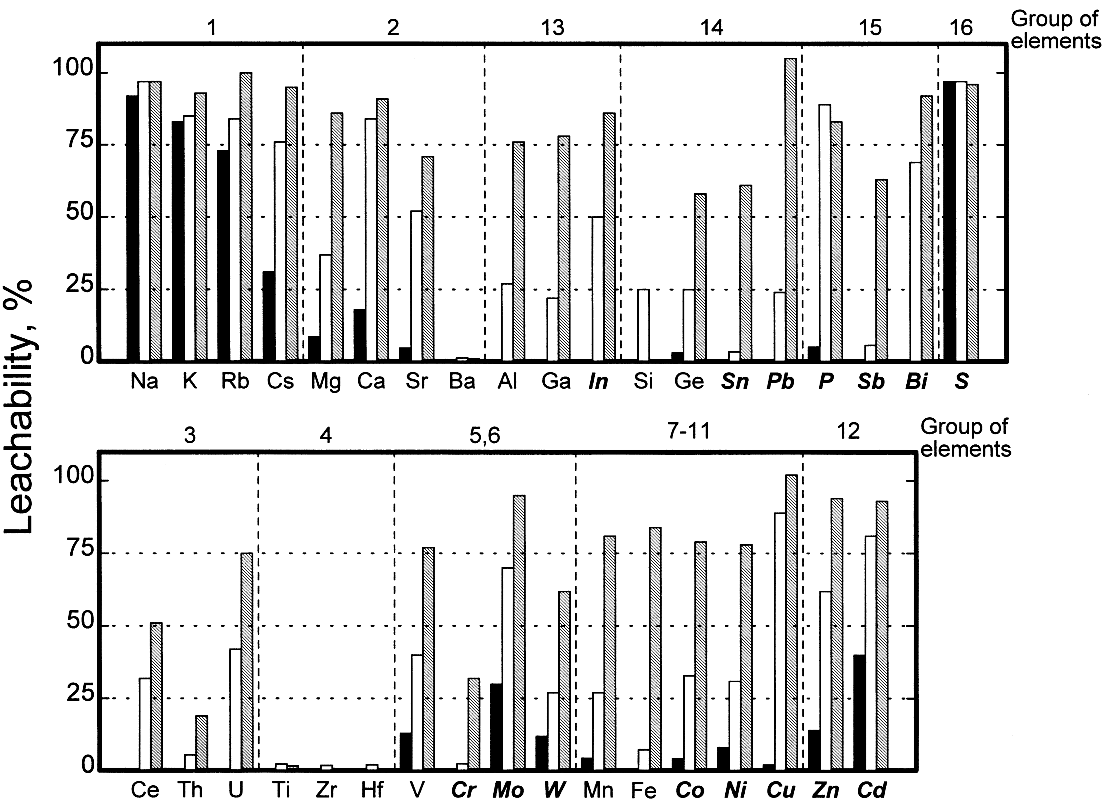

Fig. 1. Leachabilities of elements in IWIFA sample.
■: water treatment, □: HNO_3 treatment, ▨: *aqua regia* treatment.

ements generally increased in the following order of leachants; water < HNO_3 < *aqua regia*. More than 80% of total contents of the elements in IWIFA were leached with *aqua regia*, which provided the most severe leaching condition in the present experiment.

In order to understand leaching behaviors more clearly, we estimated the leachabilities (%) of analyte elements, where the leachability was defined as the ratio of the release amount of each element to its total content. The results are summarized in Fig. 1. As the leachabilities obtained by the water and HNO_3 treatments in the present experiment were almost the same as those in the previous work,[23] the leachabilities in the *aqua regia* treatment will mainly be discussed hereafter. In Fig. 1, Ce was shown as a representative of rare earth elements (REEs; Y and lanthanides), because the leaching behaviors of REEs were quite similar to each other and Ce provided the highest concentration among REEs in the IWIFA sample. Since the leachabilities of the elements may reflect their chemical properties, the elements are arranged in order of the groups in the periodic table. Furthermore, the elements with large EF values were found to provide relatively large leachabilities in the previous work,[23] and so the elements with the EF values larger than 100 are shown by bold-italic font.

Alkali metals (Na, K, Rb, and Cs) and S exhibited large leachabilities, even when the IWIFA sample was leached with water. These results suggest that most of these elements existed in the forms of water-soluble salts such as chlorides and sulfates, which might be formed during the desulfurization process of exhaust gas. The elements in Groups 12 and 15 (Zn, Cd, P, Sb, and Bi), which were highly enriched in the IWIFA sample, were leached by more than 60% and 80% of their total contents with HNO_3 and *aqua regia*, respectively, from the IWIFA sample, except for Sb. Antimony provided the lower leachabilities, which were ca. 5% and ca. 60% in the HNO_3 and *aqua regia* treatments, respectively. These results indicate that Zn, Cd, and Bi in IWIFA were mostly in the acid-soluble forms, maybe chlorides, while Sb was contained as rather stable oxides. The leaching behaviors of the elements in Groups 13 (Al, Ga, and In) and 14 (Si, Ge, Sn, and Pb) were similar to each other except for Si; they were dissolved more than 50% with *aqua regia*, although they were not dissolved very much with water. The relatively low solubilities of these elements may indicate that they were in the oxide forms. It is noted here that the leaching behaviors of REEs and U were similar to that of Al, when IWIFA was leached with *aqua regia* as well as with water and HNO_3. These results indicate that most of these elements may co-exist as oxides with major lithophile elements in IWIFA.

As is seen in Fig. 1, Ti, Zr, and Hf in Group 4 were not much leached from IWIFA even with *aqua regia*. Among them, Ti provided a relatively large EF value in the present IWIFA sample (EF = 11), which may reflect its wide usage as TiO_2, for example, in white pigment of paints, ceramics, medicines, and so on. Moreover, it is well known that TiO_2 is not dissolved by mineral acids except for sulfuric acid. These results indicate that Ti exists mostly as TiO_2 in IWIFA. Since Zr and Hf were hard to dissolve with any leachant, they may also exist as extremely stable oxides like Ti.

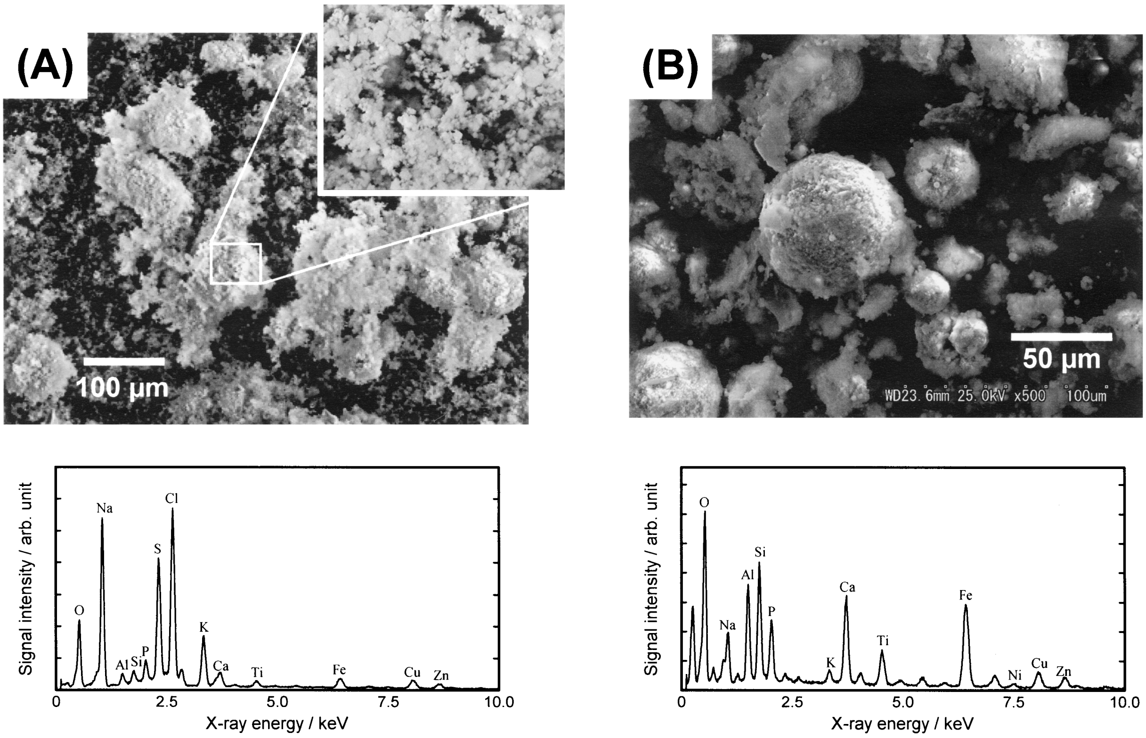

Fig. 2. Scanning electron micrographs and corresponding EDS spectra of IWIFA sample. (A): non-leached sample, (B): water-leached sample.

The leachabilities of Groups 7–11 elements with *aqua regia* were more than 75%. On the contrary, their leachabilities in the HNO_3 treatment were different from one another: ca. 25% for Mn, Co, and Ni, 5% for Fe, and 90% for Cu. These results indicate that Fe mostly existed as stable oxides inside core materials of IWIFA, while other elements were present as the acid-soluble deposits on the surfaces of fly ash particles. The elements in Groups 5 and 6 except for Cr provided relatively large leachabilities particularly in the *aqua regia* treatment. These results suggest that these elements existed as oxoanion forms in IWIFA. Kirby and Rimstidt[15] reported that Cr was present in the phases resistant to chemical weathering, when MSWI ash was treated by a sequential extraction technique. This fact may support the observation for Cr in the present work.

Various metallic elements are significantly enriched in IWIFA, and also heavy metals such as Cu, Zn, Ni, Mn, Co, Cd, and so on are markedly leached even with water and diluted HNO_3. These results suggest that most heavy metals may pollute underground water and river/lake water, when IWIFA is exposed to rain and snow for a long time. Such pollution of the aquatic environment may give some serious influences on the biological systems such as plants, planktons, fishes, and shells. Thus, IWIFA in the landfill sites should be carefully managed to minimize the environmental pollution due to heavy metals. Hence, further study on the environmental and biological influences of heavy metals in IWIFA is really expected from the viewpoints of risk assessments.

Morphological Characterization of Industrial Waste Incineration Fly Ash by SEM-EDS: The morphological structures of the particles in IWIFA were observed by a scanning electron microscope (SEM), and their elemental compositions were semi-quantitatively analyzed by an energy dispersive X-ray spectrometer (EDS) before and after leaching. Figure 2 shows the scanning electron micrographs and the corresponding EDS spectra for the non-leached and water-leached IWIFA samples. It can clearly be seen in Fig. 2(A) that small particles deposited on the surfaces of IWIFA particles. It is also seen in the EDS spectrum that such small particles mainly consisted of O, Na, S, Cl, and K, while Al, Si, P, Ca, Ti, Fe, Cu, and Zn were also slightly observed as the small X-ray peaks. These results indicate that the small particles covering fly ash particles were composed of water-soluble salts such as NaCl, Na_2SO_4, KCl, and K_2SO_4, which were formed during the desulfurization process of exhaust gas and aggregated together on ash particles. Such aggregations of salts in MSWI fly ash were also reported in other papers.[16,18]

Figure 2(B) depicts the water-leached IWIFA sample, where small particles on the surfaces, observed in Fig. 2(A), almost disappeared on the SEM micrograph. It is clearly seen in Fig. 2(B) that the fly ash particles are in various shapes and sizes. The main particles observed in Fig. 2(B) were found to consist of O, Al, Si, P, Ca, Ti, and Fe, while the signals corresponding to Na, K, S, and Cl substantially decreased on the X-ray spectrum. These facts suggest that ash particles were composed of oxides of Al, Si, Ca, Ti, and Fe, which belong to lithophile and siderophile elements. Besides the major lithophile and siderophile elements, Cu and Zn belonging to chalcophile elements were also detected in the water-leached fly ash samples as well as in the non-leached ones. These observations reflect that they were preferentially condensed on the surfaces of ash particles; this resulted in their enrichments in the IWIFA sample.

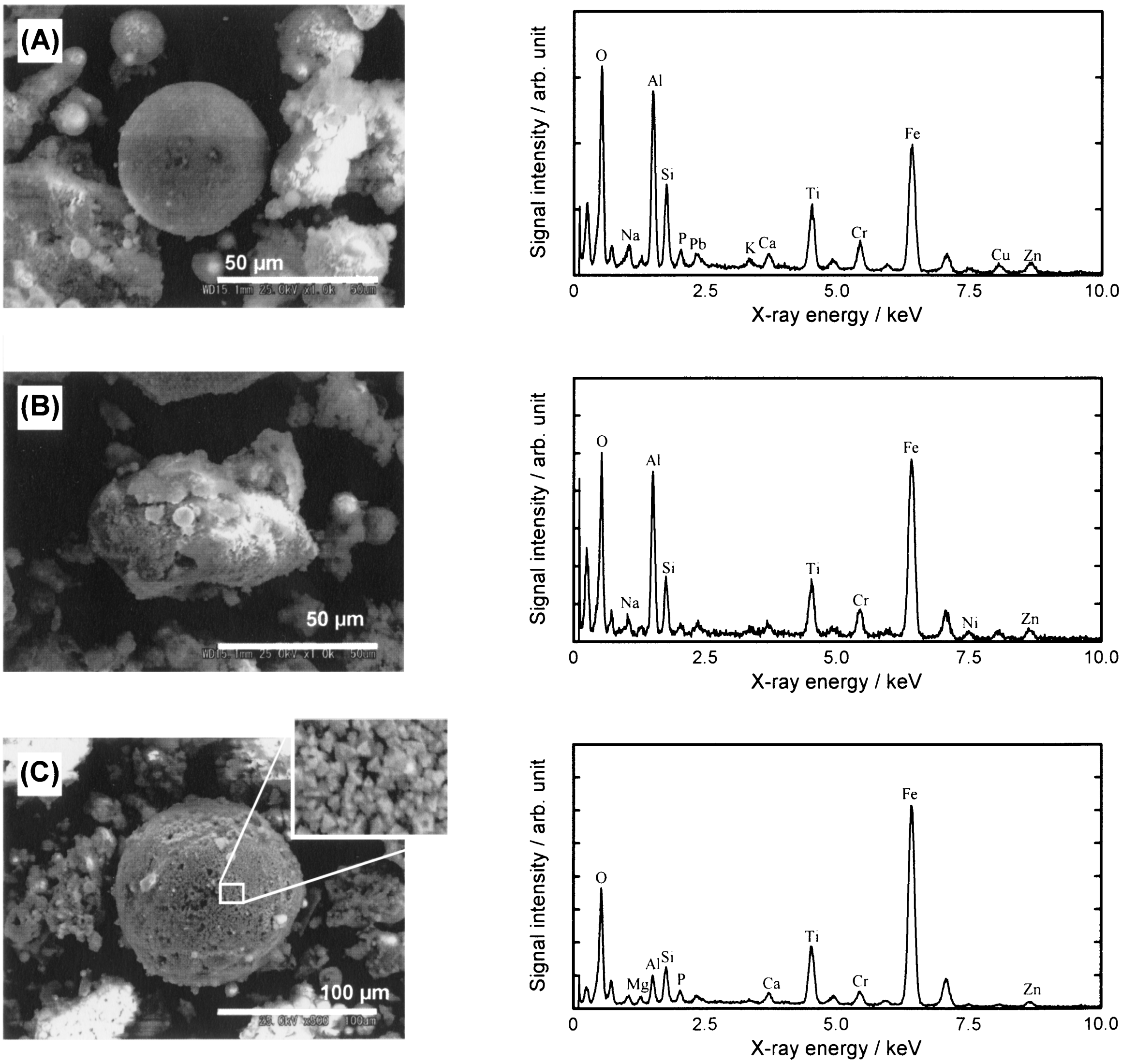

Fig. 3. Scanning electron micrographs and corresponding EDS spectra of HNO_3-leached IWIFA sample. There were spherical (a) and non-spherical (b) particles. Some particles showed interlocking crystalline structures (c).

Figure 3 shows SEM micrographs and the corresponding EDS spectra of IWIFA particles after they were leached with HNO_3. It is noted that some spherical and non-spherical particles in different sizes were observed in the SEM micrographs. The spherical particles seen in Fig. 3(A) were very often observed in the HNO_3-leached sample. As is seen in the EDS spectra, these particles provided the relatively large peaks of O, Al, Si, Ti and Fe, together with the small peaks of P, Ca, Cu, and Zn. According to the leaching behaviors with HNO_3 mentioned earlier, P, Ca, Cu, and Zn were leached by 84%, 89%, 89%, and 62% of their total contents, respectively. These results indicate that P, Ca, Cu, and Zn existed in the acid-soluble forms on the surfaces of fly ash particles. Figure 3(B) shows a non-spherical particle in the HNO_3-leached sample, whose major and minor components were almost the same as those of spherical ones (Fig. 3(A)). In the expanded micrograph of Fig. 3(C), it is seen that some particles were covered with crystal-like grains, which were dominantly composed of Fe and O. The surface structures of this type of particles were very similar to those of the acid-extracted residues of ferromagnetic coal fly ash particles reported by Warren and Dudas.[6] From the results of EDS analysis, thus, main components of the fly ash particles leached with HNO_3 were considered to be oxides of major elements such as Si, Al, Fe, and Ti.

Figure 4 shows SEM micrographs of the ash particles treated with *aqua regia*. The spherical particles were mainly observed in the *aqua regia*-leached sample, although their surfaces were not so smooth, compared to those of the HNO_3-leached sample shown in Fig. 3. It was found from the results of EDS analysis that fly ash particles in the *aqua regia*-leached samples were dominantly composed of Si, Ti, and O, although those in the HNO_3-leached samples were mainly composed of Al, Fe, Si, Ti, and O. Iron was a major component of the HNO_3-leached sample, but it was just slightly observed in IWIFA after the *aqua regia* treatment. These results indicate that Fe in IWIFA particles was finally leached out with *aqua regia*. These observations are consistent with the leaching behaviors of Fe shown in Fig. 1; the leachability of Fe with *aqua*

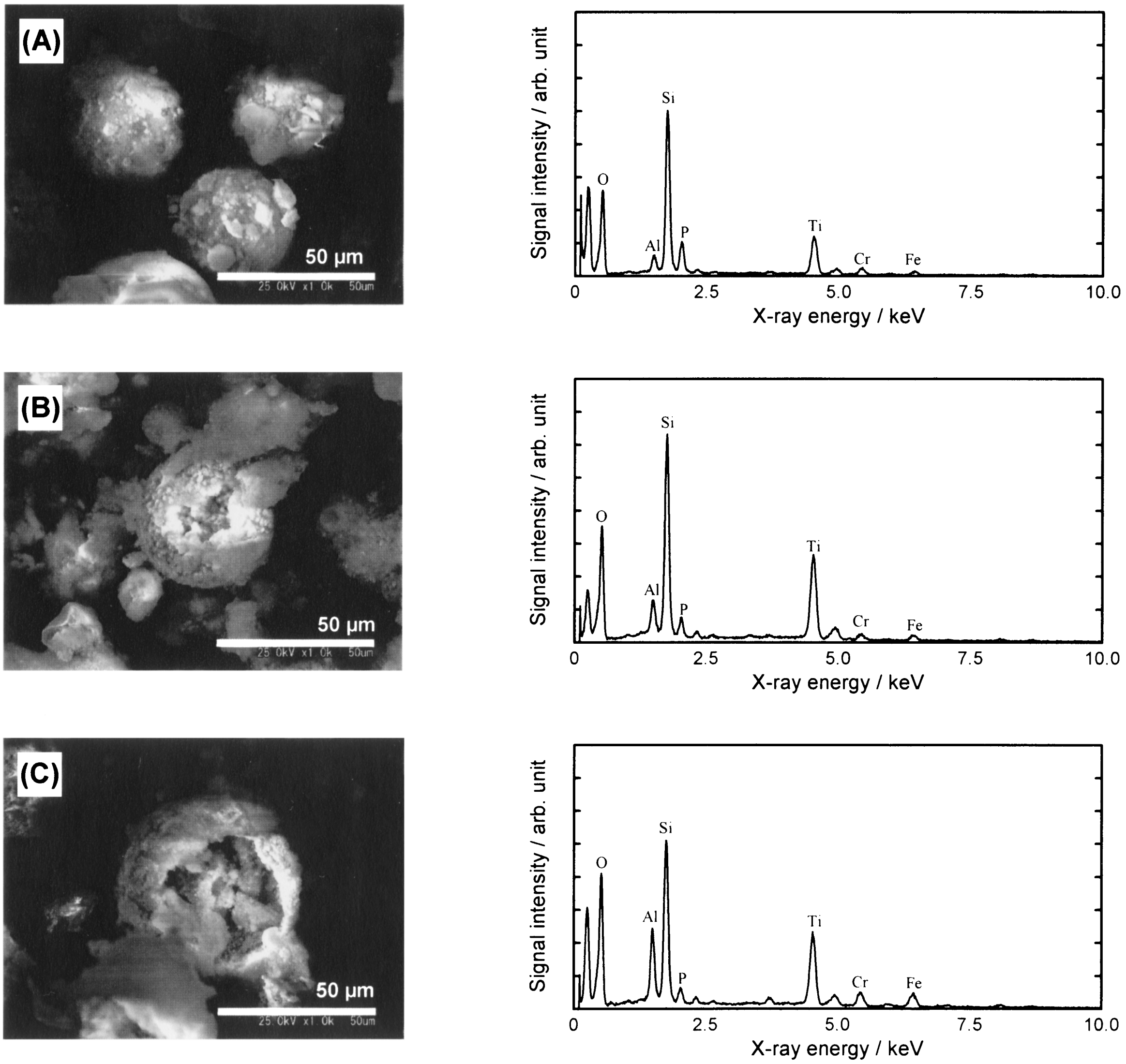

Fig. 4. Scanning electron micrographs and corresponding EDS spectra of *aqua regia*-leached IWIFA sample.

regia was ca. 80%, although that with HNO_3 was less than 5%. It is noted here that Cr was still detected in fly ash particles of the *aqua regia*-leached sample.

The micrograph in Fig. 5 shows a typical spherical particle with some cracks on its surface after the *aqua regia* treatment. The EDS spectra for the surface (the position marked as 1) and the inside (the position marked as 2) of the particle are also shown in Fig. 5. It should be noted here that only Si was observed on the particle surface, while various transition metals (Ti, Cr, Fe, and Zn) were detected inside the particle. These results indicate that the main composition of the particle with a hollow structure was SiO_2, which was packed with some transition elements. Such a hollow structure can explain the results for the leaching experiments; most elements in IWIFA were not completely leached even with *aqua regia*, because the elements inside the hollow particles of IWIFA could not be extracted with any leachant. These results indicate that IWIFA particles can keep various kinds of elements inside them for a long time, and thus great attention should be paid to utilization of fly ashes from the viewpoint of environmental protection.

Conclusion

Industrial waste incineration fly ash was comprehensively characterized by means of multielement composition analysis, leaching behavior investigations, and morphological observation. The leaching behaviors of more than 50 elements in IWIFA were investigated by using acidic leachants such as HNO_3 and *aqua regia*. Morphological observations performed by SEM-EDS revealed the particle structures and elemental compositions of the IWIFA samples before and after leaching treatments. With those analytical results, the chemical characteristics of IWIFA were discussed. The core materials of IWIFA particles mostly consisted of the stable oxides of major elements such as Si, Al, Ti, and Fe, which belong to the lithophile and siderophile elements of the geological chemical classification. The other lithophile elements at the minor and trace concentration levels co-existed as oxides with major elements. On the other hand, although the chalcophile and some trace siderophile elements were abundantly enriched in IWIFA sample, they provided particular distributions in IWIFA particles as

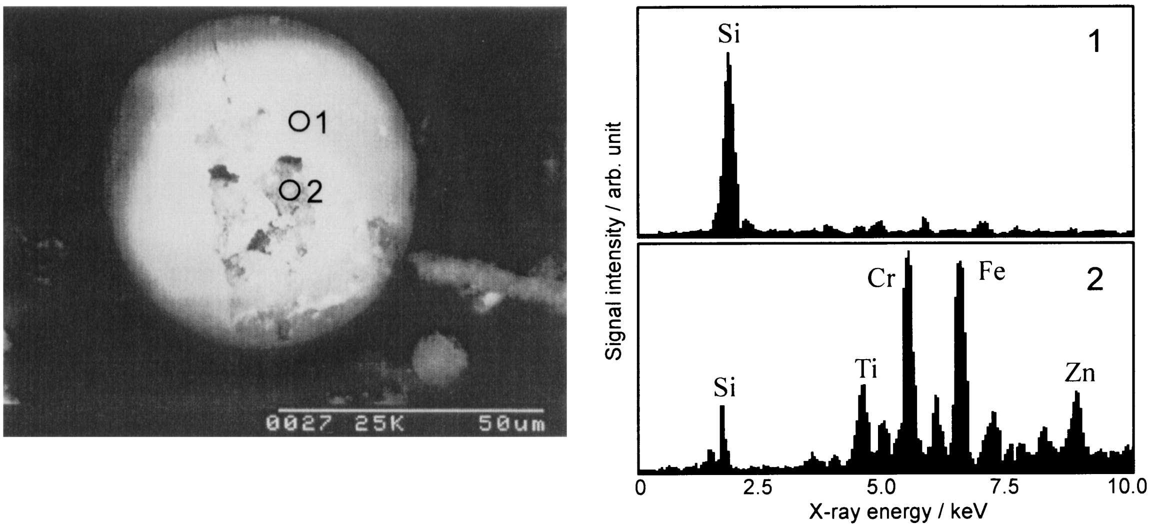

Fig. 5. Scanning electron micrograph and corresponding EDS spectra of a spherical particle in IWIFA after the *aqua regia* treatment.
1. Surface of the particle. 2. Inside of the particle observed through a crack.

follows: Cu, Zn, Mo, Cd, and Bi were mostly adsorbed on the surface of fly ash particles, Mn, Co, Ni, and Pb were partly taken into core materials and partly adsorbed on the surface of fly ash particles, and Sb, Cr, Sn, In, and W were contained as rather stable compounds. Moreover, IWIFA particles with hollow structures were found to contain various kinds of elements inside them even after severe leaching treatments. In conclusion, these characterizations for IWIFA may provide useful information for prevention of the environmental pollution caused by IWIFA as well as for recycling it as some construction materials.

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