A novel process utilizing subcritical water and nitrilotriacetic acid to extract hazardous elements from MSW incinerator fly ash

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Abstract

An effective process for hazardous element extraction from municipal solid waste incinerator fly ash was developed. The key trait of the process was to extract most of the hazardous elements out of the ash but leave Ca and Si inside the residue. In the extraction process, the ash was firstly pre-washed with water, then subjected to subcritical water (SC water) treatment and nitrilotriacetic acid (NTA) extraction. SEM images indicated that SC water is strong enough to destroy the ash particles, thus greatly improving hazardous elements extraction efficiency in the subsequent NTA extraction process. The extraction percentages for Cr, As, Se, Cd and Pb under SC water+NTA treatment were around 2–6 times higher than those treated by NTA at room conditions. The preferable SC treatment temperature was 573 K and the treatment time was 3 h. The optimum NTA concentration, vibration time and liquid/solid ratio were 0.8 M, 5 h and 10:1 (ml/g), respectively. Furthermore, it was found that introduction of a suitable amount of sulfuric acid into the extraction solution could extract more than 90% of most of the hazardous elements out of the ash.

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1. Introduction

In recent years, subcritical water (SC water) has been widely applied to various processes such as organic synthesis (Holliday et al., 1998), organic extraction (Miller and Hawthorne, 1998; Yang et al., 1998; Ozela et al., 2003), decomposition of stable toxic organic wastes (Goto et al., 1997; Hashimoto et al., 2004), etc.

SC water has unique characteristics such as dramatically decreased dielectric constant, surface tension and viscosity (Miller and Hawthorne, 1998). Recent reports showed that this kind of water is able to work as a strong acid under certain conditions, especially at high density (Miyoshi et al., 2004).

SC water extraction involves oxidation and hydrolysis (Goto et al., 1997, 1998). This technique has been successfully applied to the extraction of dioxin (Hashimoto et al., 2004), pesticide (Richter et al., 2003) and PAHs (Dadkhah and Akgerman, 2002) from contaminated soils. The use of SC water for the extraction of essential oils from natural products has also been proposed (Ozela et al., 2003). Thus far, many studies

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on the application of SC water have focused on organic substances, but less information is available on inorganic waste processing. Recent report showed that SC water was effective for metal extraction from soda-lime-silicate glass, and more than 90% of Ca, Na and Co could be leached out from the glass by nitric acid after SC water treatment, and the glass was finally converted into silica (Miyoshi et al., 2004). Although SC water has many advantages and has been widely applied in various fields, to the knowledge of the authors, little information is available on the application of SC water to hazardous element extraction from waste ashes.

Extraction of heavy metals from municipal solid waste (MSW) incinerator fly ash has been greatly improved for the detoxification of this hazardous waste material in recent years. The other traditional methods, such as chelating agent stabilization, cement solidification, and melting to form slag, usually present some drawbacks, namely, a slow release of heavy metals from the treated ash.

Thus far, many extraction reagents, including mineral acids such as HCl, HNO₃, H₂SO₄, and alkaline solutions such as NaOH and aqueous NH₃, have been examined for heavy metal extraction from the ash, but they are generally not preferable since they result in extremely acidic or alkaline solution and residues which are costly for final disposal. In comparison, organic chelating reagents such as citric acid, oxalic acid, EDTA and DTPA have been found to be environmentally friendly reagents for metal extraction from fly ashes, but they are generally inefficient for heavy metal extraction with little extraction percentage (Hong et al., 2000; Janos et al., 2002). In recent years, it has been reported that NTA (nitrilotriacetic acid) has strong metal complexing properties and has been widely used industrially, e.g., used for decontamination and isotope extraction in the nuclear industry (Vohra and Davis, 1997). Previous reports indicated that NTA could effectively counteract desorption of heavy metals in Quartz-rich sediments and soils (Howard and Shu, 1996), and it could also be used as a substitute detergent for tripolyphosphate (Vohra and Davis, 1997). Nevertheless, the extraction properties of NTA on heavy metals contained in waste ashes are less understood.

In this study, we attempted to develop a highly efficient process for hazardous element extraction from MSW incinerator fly ash. The ash was pre-treated with SC water and then subjected to NTA extraction. The aims were to understand (1) the effect of SC water treatment on the properties of the ash and (2) the hazardous element extraction efficiency by NTA after SC water treatment.

2. Materials and methods

Nitrilotriacetic acid (NTA) used in this study was purchased from Aldrich in the form of Na₂HNTA, which was analytical grade. All other chemicals were purchased from Wako or Kanto Chemicals and were used as received. Incinerator fly ash (IFA) was provided by Nanyo MSW Disposal Plant in Nagoya, Japan. The ash was firstly pre-washed by distilled water for several times at a liquid/solid ratio of 20:1 (ml:g). The details of the washing process were reported in a previous study (Zhang and Itoh, in press). The pre-washed IFA was dried at 105 °C for 24 h and subjected to SC water treatment and NTA extraction. All the data reported in this study are pre-washed ash weight-based results.

In the SC water treatment experiments, 1–3 g of the pre-treated IFA and 10–15 ml of distilled water were used. The treatment temperatures varied from 423 K to 573 K, and the time varied from 1 h to 10 h. For temperatures lower than 513 K, a series of autoclaves were used, and each autoclave consists of a 50-ml Teflon interior and a stainless exterior. For temperatures higher than 513 K, platinum-coated Inconel alloy autoclaves with 50 ml capacity were employed. After SC water treatment, the autoclaves were immediately cooled using an electronic fan. The SC water-treated suspension was then transferred into 100-ml capped polyethylene bottles, and 10–15 ml of NTA solutions were added. The original NTA concentrations varied from 0.2 to 1.6 M, and the vibration time varied from 0.5 to 10 h. The final liquid-to-solid ratios (*L/S* ratios) were 10–30 (l/mg). After extraction, the suspension was filtrated using a vacuum filter. Metallic elements in the leachate were determined by ICP-AES after HNO₃ acidification. Silica in the leachate was quantified using ASTM Method D859-00 (Annual Book of ASTM Standards, 2000).

The surface morphology and composition of the residue after SC water and NTA treatment was examined by scanning electron microscope (SEM, JSM-6330F) coupled with an energy-dispersive X-ray spectrometer (EDS, JED-2140). The crystalline properties were examined by a RIGAKU X-ray diffractometer (XRD, Rint 2000) at 50 kV and 100 mA using Cu K α radiation ($\lambda=1.5418$ Å).

3. Results and discussion

3.1. Element extraction efficiency by SC water and NTA

The raw IFA was firstly pre-washed by distilled water for several times until a nearly neutral leachate was

Fig. 1. Comparison of element extraction effects by SC water and NTA from pre-washed IFA. SC water conditions: temperature=573 K, treatment time=3 h; extraction conditions: NTA concentration=0.8 M, vibration time=5 h, $L/S=10$ ml/g.

achieved. In this way, approximately 70% of Na, 80% of K, 50% of Ca, 30% of Sr and 40% of Ba were washed out from the ash. This washing process is quite important for the subsequent SC water and NTA extraction treatments. According to our preliminary study, subjecting the raw ash directly to SC water treatment could only reduce the extraction effect of hazardous elements from the ash. In this case, the solution was extremely alkaline and the metals were slightly stabilized within the ash.

Fig. 1 illustrates that SC water treatment is much more effective for element extraction from the pre-washed IFA by NTA. The extracted amounts of Cr, As, Se, Cd and Pb under SC water+NTA treatment were around 2–6 times higher than those treated by NTA at room conditions. However, no significant amounts of heavy metals were extracted from the ash after only SC water treatment, indicating that SC water could not change metals in the ash to water-soluble form, but changed them to exchangeable and organic acid-soluble forms. One interesting result from Fig. 1 is that NTA hardly extracted calcium from the pre-treated ash, e.g., only 2.2% of Ca was extracted at room conditions and 0.5% in SC water+NTA treatment. Previous study indicated that Ca exists in the forms of CaSO_4 , CaCl

(OH) and CaCl_2 (Kida et al., 1996). Part of the Ca, such as CaCl_2 , could be washed out in the water pre-washing process. In the NTA extraction process, Ca may combine with NTA to form Ca(NTA)^- and Ca(NTA)_2^{4-} complexes, which could be adsorbed onto positively charged oxides such as Al_2O_3 (Elliot and Brown, 1989), thus were retained in the residue. However, as illustrated in Fig. 1, most of the other metal–NTA complexes were transferred into the solution but not adsorbed onto the oxides. This could be attributed to the high electrostatic adsorption capability of the Ca–NTA complexes with the oxides (Elliot and Brown, 1989) and the high content of Ca in the ash.

SC water is strong enough to destroy the ash particles (Fig. 2a). It has been reported that this kind of water is capable of oxidizing organic carbon to CO_2 (Goto et al., 1997; Hashimoto et al., 2004). The loss on ignition value of the SC water treated ash reduced to 2.8% while that for the original ash was 7.2% (Zhang and Itoh, 2003), indicating that the ash contains approximately 4.4% of organic carbon. Therefore, it is proposed that the carbon was oxidized to CO_2 under SC water treatment. This process could contribute to the release of hazardous elements adsorbed on and contained in the organic material. Furthermore, this process could also

Fig. 2. SEM images of IFA after SC water and NTA treatments. (a) Original distilled water washed IFA; (b) after SC water treatment; (c) after SC water and NTA treatments. SC water conditions: temperature=573 K, treatment time=3 h; extraction conditions: NTA concentration=0.8 M, vibration time=5 h, $L/S=10$ ml/g.

produce some porous structure in the ash particle, since the BET surface area of the SW water-treated residue increased to $4.5 \text{ m}^2 \text{ g}^{-1}$, while that was $2.6 \text{ m}^2 \text{ g}^{-1}$ for the original ash. As a result, SC water molecules can diffuse into the ash particle through the porous structure and eventually create big holes in the particle (Fig. 2a). The holes in the particle are positive for the extraction of elements inside the particle.

It can also be seen from Fig. 1 that silicon is inefficiently extracted in the extraction process, e.g., approximately 6% of silicon was extracted from the pre-treated ash by NTA under room conditions, and 2% was extracted in the SC water+NTA treatment. These results are consistent with a previous report (Hong et al., 2000). However, as illustrated in Fig. 3, crystalline Na_2SiO_3 and $\text{Na}_4\text{Mg}(\text{Si}_2\text{O}_7)$ was formed after SC water+NTA treatment (Fig. 3c). It is clear that the crystals were formed in the extraction process but not in the SC water treatment process. A determination of the filtrate after SC water treatment found that 12.3% of Si originally contained in the ash sample was transferred into the solution. Therefore, it is concluded that silica contained in the ash could be partly leached out during the SC

water treatment process and react with sodium from NTA to form crystalline phases during the NTA extraction process. EDS analysis indicated that the residue after SC water+NTA treatment mainly contains Ca, Na, Si, S, etc.

3.2. Effect of SC conditions on element extraction efficiency by NTA

SC water treatment temperature is one of the key points for element extraction from the ash. Table 1 shows that at lower temperatures, such as 423 K and 453 K, only a minor effect was found for most of the element extraction; thus, it is necessary to subject the ash to higher temperature treatment, such as 573 K, so as to obtain sufficient extraction efficiency. For example, the extraction percentages of Mg, Ni and Zn increased, respectively, to 61.2%, 50.6% and 72.1 % at 573 K compared to 8.93% and 8.94 % and 39.2% at 513 K. For hazardous elements of major environmental concern, such as Cr, Se and Cd, the extraction percentages at

Fig. 3. XRD patterns of pre-treated IFA after SC water and NTA treatments. (a) Pre-washed IFA; (b) SC water treated pre-washed IFA; (c) SC water and NTA treated IFA. SC water conditions: temperature=573 K, treatment time=3 h; extraction conditions: NTA concentration=0.8 M, vibration time=5 h, $L/S=10 \text{ ml/g}$.

Table 1

Effect of SC water temperature on element extraction (%) by NTA from pre-washed IFA

	423 K	453 K	473 K	513 K	573 K
Mg	14.1	9.76	9.85	8.93	61.2
Al	0.32	0.65	1.47	3.78	8.49
K	39.5	37.8	45.6	48.9	63.3
Ca	0.25	0.36	0.34	0.40	0.53
V	61.5	58.5	62.5	58.0	83.5
Cr	10.4	10.0	11.4	9.90	45.9
Mn	0.40	0.57	0.62	0.75	46.5
Fe	6.29	6.94	7.46	6.75	29.0
Ni	10.8	8.67	9.21	8.94	50.6
Cu	57.5	61.4	63.9	62.0	83.6
Zn	47.1	43.3	45.6	39.2	72.1
As	95.2	99.3	98.4	101	98.6
Se	8.75	4.25	8.88	10.0	51.1
Sr	1.32	1.72	1.57	1.67	41.7
Cd	37.8	41.0	40.3	39.3	74.0
Pb	77.3	73.6	83.6	84.1	87.9
Si	4.29	4.95	4.43	4.14	1.86

SC water treatment time=3 h, NTA concentration=0.8 M, vibration time=5 h, L/S=10 ml/g.

573 K were, respectively, 4.64, 5.11 and 1.88 of times those at 523 K. For Pb extraction, a treatment temperature of 473 K is sufficient, i.e., by increasing the temperature from 473 K to 573 K, the extraction percentage only increased by 4.3%.

SC water treatment time is another key point that affects element extraction efficiency. According to a previous study, under hydrothermal condition, the

Table 2

Effect of SC water treatment time on element extraction (%) from pre-washed IFA

	1 h	2 h	3 h	5 h	10 h
Mg	60.2	57.5	61.2	59.5	53.7
Al	8.42	10.0	8.49	4.69	3.75
K	36.8	41.2	63.3	71.0	76.8
Ca	0.28	0.38	0.53	0.49	0.39
V	66.5	64.5	83.5	81.0	87.0
Cr	37.2	36.6	45.9	36.4	34.6
Mn	14.9	24.4	46.5	29.4	20.6
Fe	25.7	25.3	29.0	23.4	21.7
Ni	44.7	57.7	50.6	54.5	49.3
Cu	89.9	89.0	83.6	79.6	81.3
Zn	81.6	79.1	72.1	50.1	41.5
As	99.4	99.9	98.7	91.5	91.7
Se	37.2	53.0	51.1	42.9	36.5
Sr	37.3	44.2	41.7	32.8	24.0
Cd	76.5	76.9	74.0	29.0	20.1
Pb	73.6	73.1	87.9	62.5	66.7
Si	3.52	2.38	1.86	1.20	1.45

SC water temperature=573 K, NTA concentration=0.8 M, vibration time=5 h, L/S=10 ml/g.

Table 3

Effect of NTA concentration on element extraction (%) from pre-washed IFA after SC water treatment

	0.1 M	0.2 M	0.4 M	0.6 M	0.8 M
Mg	5.22	22.8	59.0	52.3	61.2
Al	1.23	1.52	6.54	9.41	8.49
K	58.8	61.8	64.1	62.8	63.3
Ca	1.67	0.21	0.37	0.23	0.53
V	24.5	58.0	41.5	44.5	83.5
Cr	6.08	17.0	37.7	43.6	45.9
Mn	6.11	18.4	28.2	39.8	46.5
Fe	7.38	19.9	25.9	26.0	29.0
Ni	34.4	34.4	36.1	30.5	50.6
Cu	51.8	52.5	64.7	68.5	83.6
Zn	35.0	58.6	70.1	52.1	72.1
As	39.6	77.7	83.0	90.2	98.6
Se	14.3	49.4	32.8	39.8	51.1
Sr	16.2	27.2	34.2	42.5	41.7
Cd	8.48	35.9	50.4	65.3	74.0
Pb	44.1	54.1	55.2	54.5	87.9
Si	10.9	7.53	8.29	3.47	1.86

SC water conditions: temperature=573 K, treatment time=3 h; extraction conditions: vibration time=5 h, L/S=10 ml/g.

metallic elements in the ash firstly follow hydrothermal leaching, and over time treatment will cause hydrothermal precipitation (Zhang and Itoh, in press). In the present study, the extracted amounts of elements changed along with the SC water treatment time, and maximum values could be reached in the treatment time sequence. As shown in Table 2, for some of the elements, including Al, Ni, Cu, Zn, As, Se, Sr and Cd, the highest extraction

Table 4

Effect of vibration time on element extraction (%) by NTA from pre-washed IFA after SC water treatment

	0.5 h	1 h	2 h	5 h	8 h	20 h
Mg	40.4	45.7	47.7	61.2	59.5	62.2
Al	3.12	3.15	6.70	8.49	4.14	2.33
K	68.7	56.8	53.3	63.3	52.6	46.0
Ca	1.32	0.88	0.71	0.53	0.37	0.21
V	72.0	68.0	65.0	83.5	72.5	73.5
Cr	29.5	31.4	31.6	45.9	39.6	41.8
Mn	50.5	46.5	44.3	46.5	32.4	27.7
Fe	14.3	17.6	19.4	29.0	27.4	30.7
Ni	27.2	32.4	35.7	50.6	49.3	58.3
Cu	55.8	58.9	56.9	83.6	71.3	78.5
Zn	68.1	68.1	67.1	72.1	71.6	71.6
As	67.1	73.6	65.6	98.6	68.4	81.6
Se	67.1	51.3	39.1	51.1	45.3	41.0
Sr	72.0	55.6	48.6	41.7	37.3	32.8
Cd	87.7	82.2	79.1	74.0	62.8	45.9
Pb	53.5	59.2	58.2	87.9	74.6	84.8
Si	8.02	5.52	2.84	1.86	1.97	1.17

SC water conditions: temperature=573 K, treatment time=3 h; extraction conditions: NTA concentration= 0.8 M, L/S=10 ml/g.

Table 5

Effect of *L/S* ratio on element extraction (%) by NTA from pre-washed IFA after SC water treatment

	<i>L/S</i> 10	<i>L/S</i> 15	<i>L/S</i> 20	<i>L/S</i> 30
Mg	61.2	68.9	61.7	66.9
Al	8.49	3.33	6.29	6.86
K	63.3	71.3	60.7	60.5
Ca	0.53	0.60	0.69	0.87
V	83.5	84.0	84.4	83.5
Cr	45.9	41.7	36.2	36.6
Mn	46.5	42.4	43.6	45.5
Fe	29.0	32.7	24.1	25.2
Ni	50.6	56.9	54.0	67.0
Cu	83.6	84.1	77.9	79.2
Zn	72.1	81.2	80.5	100
As	98.6	99.1	98.9	95.5
Se	51.1	57.5	57.0	57.3
Sr	41.7	46.9	63.3	93.8
Cd	74.0	83.3	76.5	88.6
Pb	87.9	88.9	82.6	86.8
Si	1.86	4.62	7.43	15.5

SC water conditions: temperature=573 K, treatment time=3 h; extraction conditions: NTA concentration=0.8 M, vibration time=5 h.

percentages were obtained at a treatment time of 2 h, with extraction percentages of around 10–100% (Table 2). However, for other elements, such as Mg, K, V, Cr, Mn, Fe and Pb, the maximum extraction percentages were obtained at a treatment time of 3 h with extraction percentages around 30–88%. Considering the extraction efficiency for the elements of major environmental concern such as Cr, As, Se, Cd and Pb, it is recommended that 3 h SC water treatment is the optimum time.

3.3. Optimization of element extraction conditions

It is shown in Table 3 that element extraction percentages increased with the increase of NTA concentration, e.g., the extraction amount of Cr, As,

Se, Cd, Pb increased by 7.55, 2.49, 3.57, 8.73, 1.99 times at 0.8 M compared with those extracted at 0.1 M. On the other hand, it can be seen that there were no significant differences between the extraction percentages of Al, Cr, Fe and Sr, at 0.6 M and 0.8 M, indicating the maximum extraction of these element at 0.6 M, and furthermore, maximum extraction was reached for K at 0.2 M.

The extraction kinetics was examined with the treatment time varying from 0.5 h to 20 h (Table 4). Generally, most of the extractable elements were extracted within the first 0.5 h and the maximum extraction percentages were reached within 5 h. Longer time contact of the ash with liquor conversely reduced the extraction amount of some of the elements because of the formation of metal hydroxides. The mechanism of which was explicated in a previous report (Zhang and Itoh, *in press*).

The effect of liquid/solid ratio on element extraction efficiency was examined in a range of values from 10:1 to 30:1 (Table 5). However, no significant differences were found for most elements among the four treatments. Therefore, a liquid/solid ratio of 10:1 (ml/g) is sufficient to get the maximum extraction efficiency.

3.4. Effect of sulfuric acid addition on element extraction efficiency

It can be seen from Tables 1–5 that only 8.5% of Al, 46% of Cr and 51% of Se could be extracted from the ash even at optimum conditions. Therefore, in this section, a portion of 1 M H₂SO₄ was introduced into the extraction solution so as to enhance the extraction efficiency of these elements. The percentage of sulfuric acid was 20% (v/v) of the total extraction solution. Fig. 4 illustrates that sulfuric acid addition could greatly improve the extraction efficiency of most of the

Fig. 4. Effect of sulfuric acid addition on element extraction from pre-washed IFA after subcritical water treatment. SC water conditions: temperature=573 K, treatment time=3 h; extraction conditions: NTA concentration=0.8 M, vibration time=5 h, *L/S*=10 ml/g; sulfuric acid addition percentage=20% (v/v).

elements except for Ca, Pb and Si. In this case, the extraction percentages of Al, Cr and Se were respectively enhanced to 68%, 93% and 100%. Furthermore, the extraction percentages of Mg, K, V, Cu, Zn, As, Sr, Cd and Pb were respectively improved to 86%, 83%, 95%, 100%, 98%, 100%, 84%, 98% and 92%.

Consequently, compared to other existing extraction technologies, the overall efficiency of the present process is that it is much more effective for hazardous metal extraction but leaves Ca and Si inside the residue, while traditional methods are generally preferential for Ca extraction which greatly reduces the extraction efficiencies of hazardous elements (Hong et al., 2000; Janos et al., 2002).

4. Conclusions

The dramatic effect of SC water treatment on hazardous element extraction from incinerator fly ash was well demonstrated in this work. SC water is strong enough to destroy the ash particle which greatly contributed to the extraction of hazardous elements from the ash particle. SC water could change hazardous elements contained in the ash into exchangeable and organic acid-soluble forms thus improved the extraction efficiency. To obtain sufficient extraction efficiency, the suitable SC water temperature and time are 573 K and 3 h, and the optimum NTA concentration, vibration time and *L/S* ratio are 0.8 M, 5 h and 10:1, respectively.

Following the process developed in this study, the hazardous elements of major environmental concern such as Cr, As, Se, Cd, Pb could be extracted by >90% from the ash, but Ca and Si were left inside the residue. This detoxified residue is considered to be appropriate and safe for utilization in silica fertilizer and construction material manufacture.

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