



# Influence of supercritical water treatment on heavy metals in medical waste incinerator fly ash

Da Bo, Fu-Shen Zhang\*, Lijuan Zhao

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

## ARTICLE INFO

### Article history:

Received 18 August 2008

Received in revised form 30 April 2009

Accepted 30 April 2009

Available online 9 May 2009

### Keywords:

Supercritical oxidation

Hazardous elements

Sequential extraction

Leachability

Waste ash

## ABSTRACT

In this work, medical waste (MW) incinerator fly ashes from different types of incinerators were subjected to supercritical water (SCW) and SCW + H<sub>2</sub>O<sub>2</sub> (SCWH) treatments. Sequential extraction experiments showed that, after SCW treatment, heavy metals in exchangeable and carbonate forms in the ashes could be transferred into other relatively stable forms, e.g., Ba and Cr into residual fraction, Cu and Pb into organic matter fraction. SCWH treatment could stabilize heavy metals in Fe–Mn oxides and residual fractions. However, the behavior of As was quite different from heavy metals, which could be leached out from residue fraction after SCW and SCWH treatments. The leached As tended to absorb onto Fe–Mn oxides and organic matters under near neutral environment, but it could react with Ca<sup>2+</sup> at lower pH, increasing the mobility of this element. Therefore, it is necessary to neutralize acidic ash to near neutral condition before subjecting it to SCW and SCWH treatments so as to effectively stabilize hazardous elements in the ash. Consequently, it is believed that SCWH treatment is an effective alternative for hazardous elements detoxification in MW fly ash.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Nowadays, incineration has been proved to be the best option for medical waste (MW) treatment as it could reduce the MW volume up to 90% and degrade the infectious materials effectively [1]. In China, especially during SARS (Severe Acute Respiratory Syndrome), numerous MW incineration plants were built to treat the highly infectious MW. Thus large amount of MW ash was generated. Recent reports have shown that this special type of ash is quite different from ashes such as municipal solid waste ash since it is enriched by toxic chemicals such as heavy metals and polycyclic aromatic hydrocarbons [2,3]. This special type of ash may cause secondary pollution to the environment if not properly treated. Currently, there are four major ways to treat the fly ash, i.e. melting treatment, chemical stabilization, cement solidification, and extraction, among which solidification is widely used because of its relatively low cost and easy operation, but there are several disadvantages in this method such as slow leaching of heavy metals from the treated ash and less effect on organic pollutants, which make it still be hazardous in the environment [4]. Therefore, detoxification of this type of fly ash is still a challenge to researchers.

In recent years, supercritical fluid technologies including supercritical fluid extraction (SFE) and supercritical water oxidation

(SCWO) have become promising approaches which have been successfully applied in the treatment of solid wastes. Recent reports showed that supercritical carbon dioxide extraction (SCCDE) was highly effective for metal extraction from coal and organic contaminants from soil and sediment [5,6]. Furthermore, for MW fly ash, supercritical carbon could extract heavy metals effectively with different entrainers and more than 90% of Cu, Pb and Zn could be extracted from fly ash by cyanex 302 [7]. Although SCCDE has been proved to be a promising method for heavy metal extraction, the incapacity of organic contaminant degradation and expensive entrainer such as Cyanex302, EDTA and NTA greatly restricted the application of these techniques.

Under supercritical water condition, organic compounds and oxygen become soluble in water. As a result, organic compounds can be effectively destructed. This technology has been proved to be environmentally friendly because no organic solvents or additives are needed during the oxidation and even highly stable aromatic compounds such as PAHs and dioxin can be degraded effectively [8,9]. Thus far, SCWO technique has been successfully applied to many kinds of wastewater and sludge treatments [10,11]. Also, some reports showed that stable and hazardous aromatic compounds which formed and absorbed on the ash particle during the combustion process could be decomposed effectively by SCWO [12]. In addition, inorganic materials such as metal salts are insoluble due to the high polarity of ions, hence the circumstance of SCWO could force these metal ions move into more stable speciation which could reduce the mobility of the metals. However, most

\* Corresponding author. Tel.: +86 10 6284 9515; fax: +86 10 6284 9515.  
E-mail address: [fszhang@rcees.ac.cn](mailto:fszhang@rcees.ac.cn) (F.-S. Zhang).

of the previous studies focused on the organic pollutants treatment using SCWO technique, while little information is available on the application of SCWO to the treatment of hazardous metals.

In this study, SCW and SCWH treatments were conducted on different types of MW fly ashes, and heavy metals (As, Ba, Cd, Cr, Cu, Pb and Zn), which were regulated by USEPA and Chinese ministry of environmental protection, are selected for examination. The objectives of this work were to: (1) compare the effect of SCW and SCWH treatments on two different kinds of MW fly ashes; (2) understand the mechanisms of heavy metal transformation under SCW and SCWH conditions; (3) investigate the potential of this technique for MW fly ash detoxification.

## 2. Materials and methods

### 2.1. Materials

Two types of fly ashes were collected. Fly ash from rotary kiln (FAR) was sampled from a large-scale MW incineration plant in Taiwan, while fly ash from pyrolysis and gasification incinerator (FAP) was obtained from a MW incineration plant in Beijing. The fly ash samples were dried at 378 K for 24 h and ground to <0.25 mm for use. Heavy metal concentrations in the raw ashes and the treated samples were analyzed by an inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer) after digesting with HNO<sub>3</sub>, HClO<sub>4</sub> and HF [13]. A scanning electron microscope (SEM, S-3000N) was employed to examine fly ash surface morphology.

### 2.2. SCW and SCWH procedures

A stainless autoclave was employed for the SCW and SCW + H<sub>2</sub>O<sub>2</sub> (SCWH) treatments. The autoclave is made of 316 L stainless alloy with 200 ml capacity. The pressure inside the autoclave changed along with the temperature change in the range of 32–42 MPa. In SCW treatment, 3 g of the ash sample and 90 ml of distilled water were mixed in the stainless autoclave, while 30 ml H<sub>2</sub>O<sub>2</sub> was added with 60 ml distilled water to keep the total volume as 90 ml in SCWH experiment. The treatment time varied from 1 h to 4 h, and the temperature was kept at 723 K. After SCW or SCWH treatments, the autoclave was immediately cooled using an electronic fan. Then the suspension was centrifuged to separate the liquid and solid, and the solid residue was dried at 378 K for further analysis.

### 2.3. Analytical method

The pH value of the treated and raw ash samples were measured by pH meter using standard method [14]. The sequential extraction procedure of metals in the ashes was performed by using the method suggested by Tessier et al. [15]. The metals were fractionated into five fractions: exchangeable (F1), bound to carbonate (F2), bound to Fe–Mn oxides (F3), bound to organic matters (F4) and residual fraction (F5). After each extraction, the separation was achieved by centrifuging at 3000 rpm for 20 min and the supernatant was filtered through 0.45 μm membranes. Heavy metals in the extraction solutions were determined by ICP-OES.

### 2.4. TCLP test

The standard method of Toxicity Characteristic Leaching Procedure (TCLP) [16] was used to determine the leachability of heavy metals in the ashes. To determine the appropriate extraction fluid for the TCLP test, a preliminary test was performed to measure the pH of the ash samples (5 g of ash samples, 96.5 ml of reagent water). If the pH was <5.0, use extraction fluid #1. If the pH was >5.0, use extraction fluid #2.

**Table 1**  
Heavy metal concentrations in raw MW fly ash samples.

	FAR	FAP
pH	3.22	5.91
Cu (g kg <sup>-1</sup> )	13.0	2.73
Pb (g kg <sup>-1</sup> )	11.8	4.34
Zn (g kg <sup>-1</sup> )	37.1	48.8
As (mg kg <sup>-1</sup> )	81.5	575
Ba (mg kg <sup>-1</sup> )	1002	1649
Cd (mg kg <sup>-1</sup> )	60.7	84.4
Cr (mg kg <sup>-1</sup> )	234	95.0

*Extraction fluid # 1:* Add 5.7 ml glacial acetic acid to 500 ml of reagent water with 64.3 ml of 1N NaOH, and dilute to a volume of 1 l. The pH of this fluid will be 4.93.

*Extraction fluid # 2:* Dilute 5.7 ml glacial acetic acid with reagent water to a volume of 1 l. The pH of this fluid will be 2.88.

About 1 g of each sample and 20 ml extraction fluid were added to a series of bottles. The bottles were shaken at 30 rpm for 18 ± 2 h. At the end of the exaction, the leachate was filtered through a glass fiber filter of 0.8 μm pore size and preserved using 2 ml of nitric acid before being analyzed by ICP-OES.

## 3. Results and discussion

### 3.1. MW fly ash characterization

Since the component of medical waste and the type of incinerator were highly affected the characteristic of MW incinerator fly ash, the samples employed in this study have quite different properties. As can be seen, FAR was much more acidic than FAP, which could be attributed to the different air pollution control devices (APCD) used in the incineration facilities. For FAR, activated carbon was injected to APCD to absorb organic compounds and acid gas, which contributed to the low pH of the ash, while for FAP a suspending solution of lime was used to neutralize the acid gas. Table 1 also shows that FAR was abundant in Cu, Pb, and Zn, with concentrations of 13.0 g/kg, 11.8 g/kg and 37.1 g/kg, respectively. Comparatively, FAP had lower heavy metal content, this ash was relatively abundant in As, Pb and Zn, with concentrations of 0.58 g/kg, 4.34 g/kg and 48.8 g/kg, respectively.

present the fractions of heavy metals analyzed by sequential chemical extraction procedure. As can be seen, in the two ashes, large ratios of Cd, Cu, Pb and Zn were associated with F1 and F2 fractions, while As and Cr were mostly bound to F5 fraction, and Ba was found existing in F4 fraction, which were consistent with an early report [2]. The large amount of heavy metals bounded to F1 and F2 fractions indicated that these heavy metals have great leaching potential into the environment.

Tables 2 and 3

### 3.2. Effects of SCW and SCWH treatments on heavy metal speciation

After SCW and SCWH treatments, about 35% of fly ash residue could be recovered. The low recovery rate was probably due to the decomposition of organic compounds and dissolution of soluble inorganic compounds such as NaCl and KCl contained in the ash. Although the solubility of inorganic compounds is rather low under SCW condition, these compounds could dissolve into water again under sub-critical condition during the cooling process. After SCW treatment, the pH value of FAR increased from 3.32 to 5.21, but only slight change was observed for FAP. This indicated that at high temperature, the absorbed acidic gas released into the solution

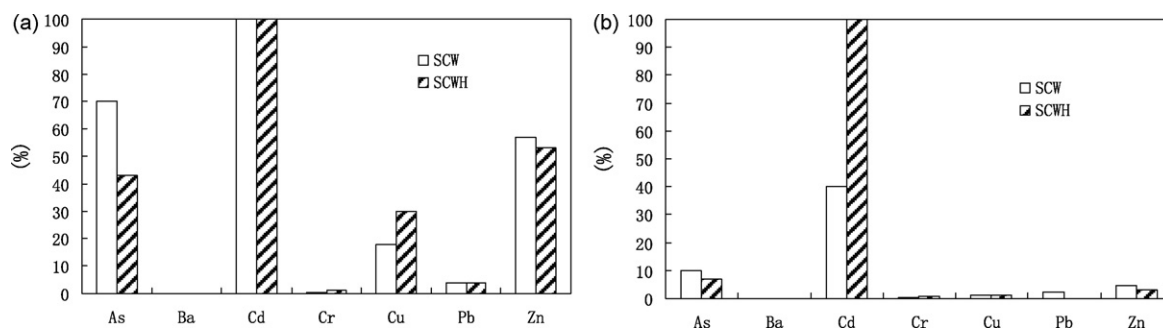


Fig. 1. Element leaching percentages from (a) FAR and (b) FAP after SCW and SCWH treatments.

along with the oxidation of the activated carbon used in the APCD system. The acidic environment could contribute to the relatively higher metal leaching rate in FAR than in FAP [17]. For example, after SCW and SCWH treatments, the leaching percentages of As, Cd and Zn from FAR were within 40–60%, 100% and 50–57%, compared to the amount of 7–10%, 40–100% and 3.2–4.7% for FAP, respectively (Fig. 1).

Tables 2 and 3 present the changes of heavy metal fractions after SCW and SCWH treatments. It can be found that heavy metals in the ashes generally transformed from F1 and F2 into F4 and F5 fractions after the treatments. This process could attribute to the significant differences of solubility between organic and inorganic compounds in SCW. Briefly, heavy metals in F1 and F2 fractions firstly dissolved into the water during the hydrothermal process, when the temperature and pressure reach the critical point (647 K, 22.1 MPa), metal ions tended to precipitate. In addition, with organic compounds dissolving into SCW, metals which bound to organic compounds were released and precipitated. As a result, a large proportions of metals such as Ba, Cr and Zn transformed into F5 fraction after SCW treatment.

It has been reported that Cu and Pb could form stable complex with organic matters [18]. These two metals tend to combine with organic matters again during the cooling process, hence they were

mainly found in F4 fraction. Comparing Tables 2 with 3, it was found that Cd and Zn performed different trends between FAR and FAP after SCW treatment, i.e. Cd could not be detected in any fractions in FAR, but 57.1 mg/kg of Cd existed in FAP and 100% of which was in F3 fraction. This could attribute to the different pHs of the solutions during SCW treatment. The acidic solution formed by acidic gas from FAR was sufficient to leach Cd into the solution, while quite amount of Cd was stable in F3 fraction in FAP at near neutral pH. Similarly, the speciation of Zn was also strongly affected by pH after SCW treatment. The result showed that the amount of F3 and F5 fractions in FAP is 78.39% and 15.98%, compared to 30.5% and 57.55% in FAR, respectively. This indicated that Zn in F3 fraction was not stable and tends to transform into F5 fraction at low pH after SCW treatment.

However, organic compounds could not be decomposed completely without additional oxidant because of the low oxidation effect of SCW. Therefore, hydrogen peroxide was added to enhance the oxidation effect of SCW. From Tables 2 and 3, it can be found that the amount of metals in F4 fraction decreased drastically whereas metals in F3 and F5 fractions increased after SCWH treatment. SEM images show that ash particle changed to porous structure (Fig. 2b and d) after SCWH treatment, demonstrating the intense oxidation effect of SCWH on organic compounds coated on ash par-

Table 2  
Effects of SCW and SCWH treatments on heavy metal fractions in FAR (%).

Element	F1			F2			F3			F4			F5		
	RA	SCW	SCWH	RA	SCW	SCWH	RA	SCW	SCWH	RA	SCW	SCWH	RA	SCW	SCWH
Ba	0.07	ND	ND	5.20	0.35	ND	0.53	ND	ND	74.7	ND	ND	19.5	99.6	100
Cd	85.0	ND	ND	7.00	ND	ND	7.00	ND	ND	ND	ND	ND	ND	ND	ND
Cr	ND	ND	ND	3.50	ND	ND	27.7	6.60	41.1	8.99	3.47	12.4	59.8	90.0	46.5
Cu	36.6	0.63	ND	17.8	0.13	2.44	33.9	0.07	36.2	8.84	89.1	19.2	4.16	10.0	47.0
Pb	47.5	0.24	9.69	15.2	2.53	16.9	18.0	15.5	0.50	17.1	68.0	20.7	2.21	13.6	52.2
Zn	67.2	2.27	6.18	10.7	4.25	4.65	18.0	30.5	19.0	1.38	5.42	6.65	2.82	57.6	63.3

ND: not detected.

Temperature = 723 K, treatment time = 4 h.

RA, raw ash; F1, exchangeable fraction; F2, carbonate fraction; F3, Fe–Mn oxide fraction; F4, organic fraction; F5, residual fraction.

Table 3  
Effects of SCW and SCWH treatments on heavy metal fractions in FAP (%).

Element	F1			F2			F3			F4			F5		
	RA	SCW	SCWH	RA	SCW	SCWH	RA	SCW	SCWH	RA	SCW	SCWH	RA	SCW	SCWH
Ba	0.42	0.17	0.26	2.53	0.27	0.38	5.24	0.09	ND	58.2	1.88	0.82	33.6	97.6	98.5
Cd	88.52	ND	ND	11.1	ND	ND	0.37	ND	ND	ND	ND	ND	ND	ND	ND
Cr	0.95	ND	ND	2.64	0.05	1.21	31.9	0.67	34.6	10.2	0.41	17.7	54.2	98.9	46.5
Cu	0.55	0.23	4.00	35.7	8.01	7.36	29.2	1.72	26.8	15.9	64.7	13.4	18.7	25.3	48.4
Pb	7.04	0.69	0.53	24.7	9.03	3.03	18.2	41.8	35.0	34.4	28.7	33.6	15.6	19.9	37.8
Zn	9.90	0.06	0.52	67.2	1.07	0.79	15.8	78.4	53.7	2.19	4.50	8.90	4.86	16.0	36.1

ND: not detected.

Temperature = 723 K, treatment time = 4 h.

RA, raw ash; F1, exchangeable fraction; F2, carbonate fraction; F3, Fe–Mn oxide fraction; F4, organic fraction; F5, residual fraction.

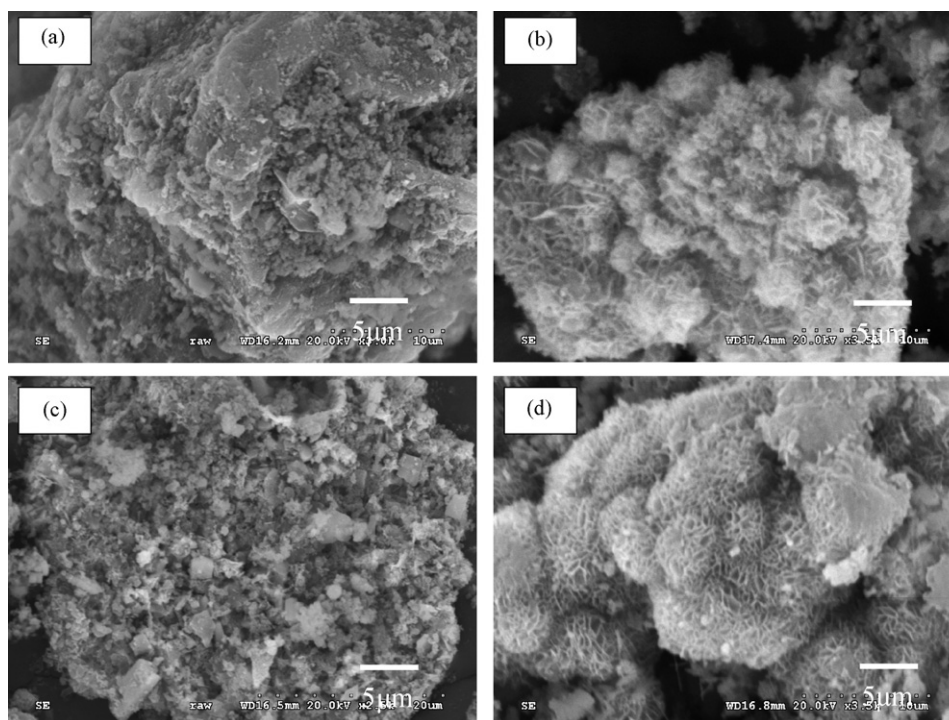


Fig. 2. SEM images of (a) raw FAR, (b) SCWH treated FAR, (c) raw FAP, and (d) SCWH treated FAP.

ticles [19]. Therefore, unlike SCW condition, heavy metals released from F1 and F2 fractions could not bind to organic matters under SCWH condition, e.g., 64.7–89.1% of Cu and 28.7–68% of Pb were found in F4 fraction in SCW treated ashes, but only 13–19% of Cu and 20–33% of Pb were in related fraction in SCWH treated ashes. Moreover, it is observed that Cd could not be detected in SCWH treated ashes, indicating that Cd released out from the ash particle into the solution under SCWH condition. It is interesting to notice that, unlike SCW treatment, after SCWH treatment, metals in F3 fraction either increased or remained unchanged, e.g., large amount of Cr remained in F3 fraction with percentages of 41% and 34% in FAR and FAP, respectively. Under SCWH condition, Fe–Mn oxides could be formed and heavy metals could be co-precipitated with Fe–Mn oxides or be oxidized to oxides. It has been reported that Fe–Mn oxides were thermodynamically stable under oxidation environment [15]. Therefore, it can be concluded that heavy metals originally in other fractions could be stabilized in this fraction under SCWH condition.

### 3.3. Effect of treatment time on heavy metal fractions

After SCW and SCWH treatments, heavy metal fractions changed greatly. Only the results of FAR are illustrated in Table 4 since similar trend was found in FAP, and moreover, F1 and F2 fractions are not presented in Table 4 since most of them changed to other forms hence it was difficult to determine these two fractions. It can be seen from Table 4 that large amount of Cu and Zn associated with F3 fraction after 1 h SCW treatment, with percentages of 57.6% and 48.2%, respectively, while after 4 h treatment, 89.1% of Cu combined to F4 fraction and 57.6% of Zn combined to F5 fraction. On the other hand, the speciation of Ba, Cr and Pb, which mainly existed in F4 and F5 fractions after SCW treatment, were less affected by the treatment time. It is well known that Fe oxide was not stable under acidic environment. Therefore, the acidic solution formed during SCW treatment could leach some metals out from F3 fraction. Consequently, more and more metals were found to be stabilized in F4 and F5 fractions along with the time.

Metallic elements were observed existing in F3 fraction after 1 h SCWH treatment, but part of F3 fraction transformed to F5 fraction along with the treatment time (Table 4). For example, the percentage of Cr in F3 fraction decreased from 71.3% to 41.1%, while Cr in F5 fraction increased from 18.2% to 46.5% with time. This could be attributed to the special oxidation property of SCWH, i.e.  $H_2O_2$  was the major oxidant within 1 h, thus metals could be easily stabilized in F3 fraction. However, with increasing treatment time,  $H_2O_2$  was exhausted, leading to the transformation of F3 to F5 fraction as illustrated in SCW section.

### 3.4. Effects of SCW and SCWH treatments on As fractions

The transformation of As fractions after SCW and SCWH treatments was quite different from heavy metals. It can be seen from

**Table 4**  
Effects of SCW and SCWH treatment time on heavy metal fractions in FAR (%).

Metal	Fraction	SCW				SCWH			
		1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h
Ba	F3	ND	ND	ND	ND	ND	ND	ND	ND
	F4	ND	2.93	2.00	ND	5.00	ND	5.56	ND
	F5	99.0	96.2	97.2	99.6	95.0	100	94.4	100
Cr	F3	4.08	3.42	10.5	6.60	71.3	48.2	44.5	41.1
	F4	1.15	2.46	4.93	3.47	10.0	10.8	7.52	12.4
	F5	94.8	95.6	84.6	90.0	18.7	41.0	50.5	46.5
Cu	F3	57.6	16.3	30.1	0.07	48.3	34.5	39.1	36.2
	F4	35.7	71.8	57.3	89.1	7.23	14.6	16.7	19.2
	F5	1.70	9.78	11.2	10.0	44.5	49.0	41.6	47.0
Pb	F3	24.7	18.2	24.8	15.5	3.19	3.52	0.40	0.50
	F4	57.6	52.8	38.3	68.0	24.1	20.8	21.5	20.7
	F5	8.78	19.7	27.1	13.6	69.9	63.1	67.1	62.2
Zn	F3	48.2	42.1	24.1	30.5	24.1	18.9	30.9	19.0
	F4	8.1	7.16	6.42	5.42	1.83	4.87	6.44	6.65
	F5	31.6	46.6	62.8	57.6	57.0	69.4	54.7	63.3

F3, Fe–Mn oxide fraction; F4, organic fraction; F5, residual fraction.

**Table 5**  
Effects of SCW and SCWH treatments on As fractions (%).

Sample	Fraction	RA	SCW				SCWH			
			1 h	2 h	3 h	4 h	1 h	2 h	3 h	4 h
FAR	F1	4.91	25.6	23.0	14.9	15.3	16.5	16.1	13.5	16.2
	F2	ND	16.0	13.5	9.17	10.7	18.2	18.5	18.0	18.2
	F3	5.94	14.4	9.10	32.3	19.6	20.2	15.0	15.8	19.4
	F4	18.5	26.1	20.3	20.1	23.0	21.5	22.7	24.5	20.7
	F5	70.6	18.2	33.3	35.9	36.4	23.6	27.7	27.4	25.5
FAP	F1	4.49	5.02	4.56	6.03	3.45	1.14	1.37	1.57	1.44
	F2	6.95	6.78	6.94	8.74	5.61	1.40	1.49	1.46	1.34
	F3	29.4	36.5	39.1	25.9	20.8	20.7	22.2	23.4	19.5
	F4	5.05	20.6	7.67	11.5	17.2	22.6	22.5	24.2	24.6
	F5	54.1	31.1	41.7	47.9	53.0	53.3	52.5	50.2	53.1

ND: not detected.

RA, raw ash; F1, exchangeable fraction; F2, carbonate fraction; F3, Fe–Mn oxide fraction; F4, organic fraction; F5, residual fraction.

**Table 6**  
TCLP results of the ash residue after SCW and SCWH treatments (mg/l).

Element	FAR			FAP			Permitted limit	
	RA	SCW	SCWH	RA	SCW	SCWH	USEPA	Chinese EPA
As	1.02	0.10	0.22	0.22	0.32	0.03	5	5
Ba	ND	ND	ND	0.11	0.03	0.05	100	100
Cd	9.79	ND	ND	3.64	0.68	ND	1	1
Cr	1.00	ND	1.80	0.03	0.02	1.80	5	5
Cu	132	29.7	33.0	2.94	3.27	3.32	–	100
Pb	73.1	14.6	3.15	19.2	2.12	0.07	5	5
Zn	485	204	59.9	601	69.7	35.0	–	100

Temperature = 723 K, treatment time = 1 h.

RA, raw ash; ND, not detected.

Table 5 that the percentage of As in F5 fraction decreased in both FAR and FAP after 1 h treatment, indicating that both treatments could leach As out from F5 fraction. However, the transformation trends of the leached As was different between FAR and FAP. For FAR, As tended to transform to other four fractions, while for FAP, only the amounts of F3 and F4 fractions of As increased. It has been reported that As mainly exist as  $\text{H}_2\text{AsO}_4^-$  at pH 2–7, which could be removed by forming  $\text{Ca}(\text{H}_2\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$  or absorbing on iron (hydr)oxide from solution [20]. Accordingly, it is supposed that the leached As in FAP in the form of  $\text{H}_2\text{AsO}_4^-$  was absorbed on Fe oxide and organic matters, which contributed to the increase of As fractions in F3 and F4. Meanwhile, in FAR, the acidic solution could destroy Fe oxide, causing As, in the form of  $\text{H}_2\text{AsO}_4^-$ , either reacted with  $\text{Ca}^{2+}$  to form calcium arsenates or be absorbed on ash particles. This process could contribute to the increase of As in F2 and F1 fractions. Therefore, it is necessary to neutralize the acidic ash to near neutral condition before subjecting it to SCW treatment. Furthermore, it can also be seen from Table 5 that the distribution of As speciation after 1 h SCWH treatment was similar to 4 h SCW treatment, and exhibited a minor change along with time. This indicates that the oxidation function could significantly accelerate the process of As transformation, and the distribution of As speciation could reach balance among the five fractions within 1 h under SCWH condition.

### 3.5. TCLP test

Table 6 presents the TCLP results. For the raw ashes, the leached amount of Cd, Cu, Pb, and Zn, which were 9.79 mg/l, 132 mg/l, 73.1 mg/l and 485 mg/l in raw FAR, while the leached amount of Cd, Pb, and Zn, which were 3.64 mg/l, 19.2 mg/l and 601 mg/l in raw FAP, respectively, greatly surpassed the permitted limits of USEPA and Chinese EPA [21], implying that both the ashes are hazardous wastes. After SCW and SCWH treatments, the leachability of the heavy metals was significantly reduced. However, it can be seen

from Table 6 that after SCW treatment, 14.6 mg/l of Pb and 204 mg/l of Zn could be leached from FAR, which still surpassed the permitted limit of the USEPA and Chinese EPA standards. But after SCWH treatment, the leaching amount of Pb and Zn remarkably decreased to 3.15 mg/l and 59.9 mg/l, respectively, lower than the permitted limit. It has been reported that metals locked with silica matrix (F5 fraction) could be hardly leached out under natural environment [22]. Therefore, compared to SCW treatment, SCWH could transform more metals to F5 fraction, which greatly reduced the leachability of heavy metals.

## 4. Conclusions

The results of this study demonstrated that SCWH treatment was an effective process for heavy metals detoxification. Leaching of heavy metals from MW fly ash could be significantly reduced to meet the USEPA and Chinese EPA permits after SCWH treatment. Sequential extraction suggested that SCW could effectively transform Ba, Cr, Cu and Pb into F4 and F5 fractions, while SCWH made these metals mainly bound to F5 fraction. More heavy metals especially Cd and Zn could be leached out or transformed to F5 fraction at lower pH since the acidic solution could destroy Fe–Mn oxide under SCW condition. On the other hand, As could be extracted from F5 fraction after SCW and SCWH treatments, and tended to absorb onto Fe oxide and organic matters under near neutral condition. Thus it is necessary to neutralize the acidic ash to near neutral condition before subjecting it to SCW and SCWH treatments so as to stabilize As in the ash. It is concluded that SCWH treatment could not only decompose hazardous organic matters but also effectively detoxify heavy metals in fly ashes.

## Acknowledgements

This research was financially supported by the National Basic Research Program (2007CB407303), the National Key Technology

R&D Program (2008BAC32B03) and National Natural Science Foundation (20777084) of China.

## References

- [1] C.O. Velzy, J. Feldman, M. Trichon, Incineration technology for managing biomedical wastes, *Waste Manag. Res.* 8 (1990) 293–298.
- [2] L.J. Zhao, F.S. Zhang, K.S. Wang, J.X. Zhu, Chemical properties of heavy metals in typical hospital waste incinerator ashes in China *Waste Management* 29 (2009) 1114–1121.
- [3] L.J. Zhao, F.S. Zhang, Z.P. Hao, H.L. Wang, Levels of polycyclic aromatic hydrocarbons in different types of hospital waste incinerator ashes, *Sci. Total Environ.* 397 (2008) 24–30.
- [4] M. Andac, F.P. Glasser, The effect of test conditions on the leaching of stabilised MSWI-fly ash in Portland cement, *Waste Manag.* 18 (1998) 309–319.
- [5] Y. Iwai, N. Okamoto, S. Ohta, Y. Arai, K. Sakanishi, Extraction of iron and calcium from low rank coal by supercritical carbon dioxide with extrainers, *J. Supercrit. Fluid.* 40 (2007) 227–231.
- [6] G. Anitescu, L.L. Tavlarides, Supercritical extraction of contaminants from soils and sediments, *J. Supercrit. Fluids* 38 (2006) 167–180.
- [7] C. Kersch, G.F. Woerlee, G.J. Witkamp, Supercritical fluid extraction of heavy metals from fly ash, *Ind. Eng. Chem. Res.* 43 (2004) 190–196.
- [8] N. Crain, A. Shanableh, E. Gloyna, Supercritical water oxidation of sludges contaminated with toxic organic chemicals, *Water Sci. Technol.* 42 (2000) 363–368.
- [9] J. Kronholm, T. Kuosmanen, K. Hartonen, M.L. Riekkola, Destruction of PAH from soil by using pressurized hot water extraction coupled with supercritical water oxidation, *Waste Manag.* 23 (2003) 253–260.
- [10] M. Goto, T. Nada, S. Kawajiri, A. Kodama, T. Hirose, Decomposition of municipal sludge by supercritical water oxidation, *J. Chem. Eng. Jpn.* 30 (1997) 813–818.
- [11] A. Shanableh, E.F. Gloyna, Supercritical water oxidation—wastewater and sludges, *Water Sci. Technol.* 23 (1991) 389–398.
- [12] T. Sako, T. Sugeta, K. Otake, M. Sato, M. Tsugumi, T. Hiaki, M.J. Hongo, Decomposition of dioxins in fly ash with supercritical water oxidation, *Chem. Eng. Jpn.* 30 (1997) 744–747.
- [13] S. Yamaguchi, Digestion method for total element analysis, in: *Soil Environment Analysis*, Japanese Society of Soil Science and Plant Nutrition, Hakuyusya, Tokyo, 1997, pp. 278–288 (In Japanese).
- [14] Ministry of environmental protection of China, Solid waste Glass – electrode test – Method of corrosivity, GB/T 15555.12, 1995.
- [15] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851.
- [16] US Environmental Protection Agency, Tests methods for evaluating solid waste, *Physical Chemical Methods*, SW-846, Method 1311, 1992.
- [17] L.C. Tan, V. Choa, J.H. Tay, The influence of pH on mobility of heavy metals from municipal solid waste incinerator fly ash, *Environ. Monit. Assess.* 44 (1997) 275–284.
- [18] D.F. Shriver, P.W. Atkins, *Inorganic Chemistry*, fourth ed., Oxford University Press, Oxford, 2006.
- [19] Z. Fang, S.K. Xu, J.A. Kozinski, Behavior of metals during combustion of industrial organic wastes in supercritical water, *Ind. Eng. Chem. Res.* 39 (2000) 4536–4542.
- [20] J.J.V. Bothe, P.W. Brown, Arsenic immobilization by calcium arsenate formation, *Environ. Sci. Technol.* 33 (1999) 3806–3811.
- [21] Ministry of environmental protection of China, Identification standards for hazardous wastes—Identification for extraction toxicity, GB/T 5085.3, 2007.
- [22] W. Calmano, J. Hong, U. Forstner, Binding and Mobilization of Heavy Metals in Contaminated Sediment Affected by pH and Redox Potential, *Water Sci. Technol.* 28 (1993) 223–235.