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Irradiation effect on leaching behavior and form of heavy metals in fly ash of municipal solid waste incinerator

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ABSTRACT

Fly ash from a municipal solid waste incinerator (MSWI) is commonly classified as hazardous waste. High-energy electron beam irradiation systems have gained popularity recently as a clean and promising technology to remove environmental pollutants. Irradiation effects on leaching behavior and form of heavy metals in MSWI fly ash have not been investigated in any significant detail. An electron beam accelerator was used in this research. Electron beam irradiation on fly ash significantly increased the leaching potential of heavy metals from fly ash. The amount of absorbed dose and the metal species affected leaching behavior. When electron beam irradiation intensity increased gradually up to 210 kGy, concentration of Pb and Zn in the leachate increased linearly as absorbed dose increased, while that of Cu underwent no significant change. Concentration of Pb and Zn in the leachate increased up to 15.5% (10.7 mg/kg), and 35.6% (9.6 mg/kg) respectively. However, only 4.8% (0.3 mg/kg) increase was observed in the case of Cu. The results imply that irradiation has significant effect on the leaching behavior of heavy metals in fly ash, and the effect is quite different among the metal species tested in this study. A commonly used sequential extraction analysis which can classify a metal species into five forms was conducted to examine any change in metal form in the irradiated fly ash. Notable change in metal form in fly ash was observed when fly ash was irradiated. Change in Pb form was much greater than that of Cu form. Change in metal form was related to leaching potential of the metals. Concentration of heavy metal in leachate was positively related to the exchangeable form which is the most mobile. It may be feasible to treat fly ash by electron beam irradiation for selective recovery of valuable metals or for pretreatment prior to conventional processes.

1. Introduction

Electron beam irradiation systems have recently gained popularity as a safer and clean technology to control environmental problems [1,2]. An electron beam can be applied conveniently to gases, liquids or solid materials because such equipments can irradiate electron beam directly in air with high-energy output. The electron beam has a direct collision effect of high-energy electron on surface of substances. It has a destructive effect on contaminants through the production of active species such as H_3O^+, OH^-, ozone, and hydrated electron. Both dry and aqueous electrons are produced in ionizing medium such as air and water [3,4]. The electron beam has very short reaction time of 10^{-18}–10^{-1} s, and at the same time, has very high energy. Thus it has often been applicable to environmental control processes such as industrial flue gases and wastewater treatment to destroy pollutants [4,5]. Electron beam processing technology is also possible without water so that it does not produce additional wastewater. Moreover, it does not produce radioactive materials such as gamma irradiation [1,2].

High-energy electron beam irradiation technologies have been safely used worldwide for more than 40 years [1]. Irradiation chemistry in water and air systems is nowadays fairly well understood, while detailed knowledge of solid state irradiation chemistry is still lacking. However, it is expected that both the destruction of the molecular structure of target compounds and oxidation reaction occurred during this non-thermal destructive irradiation systems [1,2]. The advantages of the systems are (1) no radioactivity is produced, (2) no waste is generated, (3) safe for both operating personnel and the general public, (4) economically competitive, (5) higher efficiencies, and (6) operate at room temperature [2].

Application of irradiation technology to environmental engineering field includes (1) destruction of recalcitrant organic pollutants such as benzene hexachloride (BHC), polychlorinated biphenyls (PCBs), and polypropylene in water and soil systems [3,5–10], (2) removal of heavy metal ions from aqueous solution by hydrated electron (e_{aq}^-) which is a reducing radical produced

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during irradiation [8,11–13], and (3) destruction and conditioning of high organic content waste such as sewage sludge [1]. Heavy metals in wastewater could be removed effectively by electron beam irradiation, as Schmelling et al. [8] showed effective metal removal efficiencies under 100 kGy. Removal rate of heavy metals in wastewater tended to increase linearly up to absorbed dose of 500–1000 kGy [13]. However, there are only a few cases of electron beam application to solid phase wastes [1].

Fly ash contains a large amount of various heavy metals. Throughout the reactions with water, these metals can be leached into the environment. Thus, appropriate management of these kinds of solid wastes is mandatory [14,15]. Management costs of fly ash are very high because they are usually classified as hazardous waste in most countries around the world. When fly ash is treated with the thermal process, leaching potential of heavy metals in the treated fly ash may become low due to the solidification effect [14,16]. However, the thermal process requires considerable expense and energy because of the required high temperature (1100–1300 °C). Although conventional non-thermal treatment processes such as solidification/stabilization process do not consume high energy compared to the thermal treatment technologies, they have several limitations in terms of treatment efficiency, volume increase and long term stability.

When fly ash is irradiated, metal forms in the ash may be changed. As a result leaching potential of the metals may increase due to the destructive mechanism of the high-energy electron beam. No research has been conducted thus far to examine any effect of electron beam irradiation on leaching behavior of heavy metals in fly ash. Also, literature regarding metal form change after irradiation treatment of raw fly ash is not available.

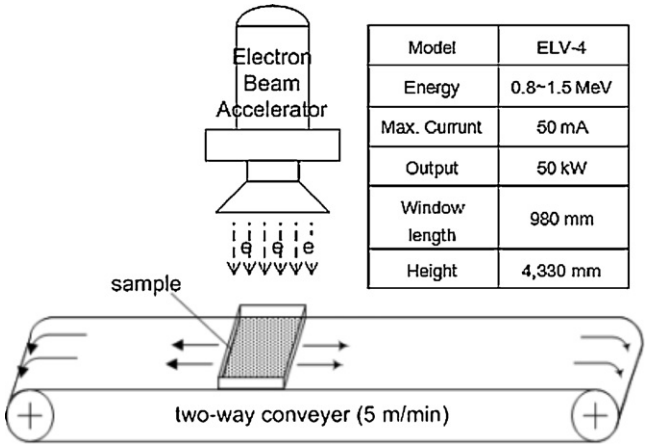
The main objectives of this study were (1) to evaluate the effect of electron beam irradiation on leaching behavior of heavy metals in fly ash from MSWI, (2) to examine the irradiation effect on the heavy metal form change in fly ash, and (3) to examine any relationship between the leaching potential of heavy metal in fly ash and the metal form change due to irradiation. Leaching potential was evaluated by a standard leaching procedure. Sequential extraction analysis of heavy metals in fly ash was performed to examine any change of metal forms in fly ash after irradiation. An attempt was made to correlate the heavy metal concentration in leachate and the exchangeable form of the metal in fly ash.

2. Experimental

2.1. Materials

Fly ash used in this study was obtained from a dust collection system at a MSWI in South Korea. Physicochemical characteristics of fly ash are presented in Table 3. The number of samples analyzed was 5 and the average values are presented. Fly ash collected contained 8.1% volatile matter, and 6.4% sulfur (Table 3). These values indicated that the fly ash contained relatively large amount of unburned carbon. Also sulfur content was fairly high. These values are in good agreement with the data of other studies [15,17,18]. pH of the fly ash, which has effect on leaching behavior of heavy metal, was 11.4. Bulk density (apparent density) which was inversely proportional to penetration of electron beam was 0.4 kg/L.

Fly ash samples occasionally contained relatively large particles. This may happen during improper ash handling. In such cases, fly ash was pulverized (Fritsch GmbH, Pulverisette 6 model) and sieved through a 0.16 mm sieve (100 mesh) to increase the homogeneity of the samples. When storing samples, they were sealed and stored in a drying oven at 90 °C to minimize any possible reactions with water and air. Analytical reagents such as hydrochloric acid for leaching procedure were all high quality reagent-grade



Model	ELV-4
Energy	0.8~1.5 MeV
Max. Currunt	50 mA
Output	50 kW
Window length	980 mm
Height	4,330 mm

Fig. 1. Electron-beam irradiation system used in this study.

designated for heavy metal analysis. Standard solutions for atomic absorption spectrophotometer (AAS) analysis were prepared with distilled deionized water.

2.2. Electron beam irradiation system

An electron beam accelerator used in this study was 1 MeV ELV-4 type with a maximum power of 50 kW. Samples were put on a conveyor system and passed through under the scanning window of the electron accelerator at a speed of 5 m/min as shown in Fig. 1. The basic concept of this approach was obtained from the study by Lawrence et al. [19]. The maximum absorbed dose was selected as 210 kGy based on previous studies [8,13]. Absorbed doses were determined in advance with cellulose triacetate (CTA) film (FTR = 125, Fuji, Japan). Samples with CTA film attached on top and bottom of samples were irradiated, and then the average dose was calculated. Stainless steel reaction vessel (15 cm × 25 cm × 3 cm) was used to contain samples. All samples were sealed with zipper vinyl bag and placed in the reaction vessel to prevent samples from losing fine particles by wind during operation of electron beam accelerator. Considering penetration depth of solids with a 1 MeV electron beam, sample thickness was maintained approximately at 7 mm.

2.3. Determination of total metal content in fly ash

There are several methods that may be used to measure the amount of total metal content in a solid sample. In this study, the method for digestion of samples using HF, $HClO_4$ and HNO_3 was used. The detailed procedures can be seen in the published literature [20,21].

2.4. Leaching procedure

Concentration of heavy metals in leachate was evaluated using a standard leaching procedure. This procedure is a legal test method established by the Ministry of Environment, Republic of Korea (South Korea). Summary of the procedure is given in Table 1. Atomic absorption spectrophotometer (Shimadzu Inc. AA-6501F model) was used to determine the concentration of heavy metals in the leachate. The samples contained high concentrations of metals, so the samples were diluted with distilled deionized water.

2.5. Sequential extraction

Several analytical methods for the determination of metal form in solid state, including soils and ashes, are available. The

Table 1
Summary of leaching test used in this study.

Item	Method	Remarks
Leaching solution	Initial pH adjustment at 5.8–6.3 with HCl	No continual pH adjustment afterwards
Ratio of sample/leaching solution	1:10 (weight:volume)	Total resultant volume should be greater than 1 L
Method of agitation	Horizontal shaking with amplitude of 4–5 cm, 200 strokes/min	Shakers are commercially available in Korea
Time of agitation	6 h	Relatively short agitation time compared with other standard leaching procedure
Separation of particle from liquid	Centrifugation with 3000 rpm	Glass fiber filter may be used instead of centrifugation
Analysis	Atomic absorption spectrophotometer (AAS)	–

Table 2
Summary of sequential extraction procedure used in this study.

Fraction	Metal form	Major extraction reagents	Remarks
F1	Exchangeable	1 M $MgCl_2$ pH adjusted at 7 with HNO_3 or KOH	Leached easily in neutral conditions Affected by sorption–desorption The most mobile in the environment
F2	Carbonate bound	1 M NaOAc pH adjusted at 5 with HOAc	Mainly carbonate forms Mobile at weak acidic condition
F3	Oxides bound	0.04 M $NH_2OH{\cdot}HCl$ in 25% HOAc	Oxides, mainly Fe and Mn Unstable and mobile under anoxic condition
F4	Organic bound	0.02 M HNO_3 and 30% H_2O_2 pH adjusted at 2 with HNO_3, 30% H_2O_2, 3.2 M NH_4OAc in 20% HNO_3	Mainly organic bound and sulfides form Unstable under oxidizing condition
F5	Residual	Digested with HNO_3–HCl	Metal form strongly retained in the crystalline structure Least mobile in the environment

sequential extraction procedure suggested by Tessier et al. [22] is the most commonly used, and was used in this study as well. According to this method, heavy metal forms of solid materials such as soil can be classified as exchangeable fraction, carbonate bound fraction, oxides bound fraction, organic bound and sulfides fraction, and residual fraction. Common abbreviations for each fraction are F1; F2; F3; F4; and F5 respectively. Summary of this procedure is presented in Table 2. Sequential extraction procedure is a very useful method compared to the simple extraction one because behavior of metal in the environment in terms of mobility or leaching potential of heavy metal are able to be evaluated [14,16]. Analytical errors may be expected because of the residual metal in the leachate from the previous extraction step [20,23,24]. The samples at each step of sequential extraction were washed with distilled water and then centrifuged to discard supernatant. This washing and centrifuging step was performed twice. Minimum volume (8–10 mL) of washing water was used to prevent any loss of metal in the samples [20,25].

Table 3
Physicochemical characteristics of the raw fly ash used in this study.

Parameters		Value[a]
Proximate analysis (%)	Moisture[b]	7.5
	Volatile mater[c]	8.1
	Ash[c]	91.9
Ultimate analysis[d] (%)	C	6.37
	H	1.92
	N	0.24
	S	2.14
pH		11.4
Bulk density (kg/L)		0.4

[a] Values are the mean of 5 determinations.
[b] Wet weight basis, loss at 105 °C for 4 h.
[c] Dry weight basis, loss at 550 °C for 3 h.
[d] Dry weight basis, analyzed by an elemental analyzer (Vario EL; Elementar, Japan).

3. Results and discussion

3.1. Amount of heavy metals leached from raw fly ash

Upon analysis of the heavy metal contents in raw fly ash, we found that the ash contained various heavy metals such as Pb, Zn, Cu, Ni, Cd, Cr, and Hg. The major heavy metal species were Pb (611 mg/kg), Zn (2289 mg/kg), and Cu (97 mg/kg). These three heavy metals of relatively high concentration were selected for the study. Amount of heavy metals in MSWI fly ash depends mainly on the components of municipal solid waste (MSW), which are affected by community recycling program [26,27]. Amount of heavy metals leached from raw fly ash may differ depending on the physicochemical characteristics of fly ash tested, amount of heavy metal content in the fly ash, and the leaching method used. Characteristics of MSWI fly ash is greatly affected by the components of MSW incinerated, the flue gas cleaning processes and the furnace temperature [18,28]. A comprehensive investigation was undertaken by Fedje et al. [29] to examine the effect of various leaching solutions on the amount of heavy metals leached from MSWI fly ash. Leaching solutions tested ranged from neutral water to strong acids. Leaching amount as % leached from total amount of heavy metals in the fly ash varied significantly depending on the leaching solution tested. In case of 1 M HCl with liquid/solid ratio (L/S ratio) of 5, leached amount were 23% for Pb, and <1% for both Zn and Cu. In this study, leached amount of Pb, Zn, and Cu were 11.3%, 1.2%, and 6.1% respectively.

Most of the countries in the world have their own standard leaching procedure for regulatory purposes. One major purpose of the standard procedure is to classify whether wastes are hazardous or not. While the basic concept of all these standard procedures is similar to one another, the leaching ability or power of each procedure may differ. Table 4 summarized the amount of heavy metals (Pb, Zn, and Cu) leached from raw fly ash (MSWI fly ash and power plant fly ash) by different leaching procedures adapted by several countries in the world. Broad ranges of reported data are noted depending on the procedure used and the metal species. The Japanese standard leaching method is the same as the Korean method, and the values obtained in this study are within the ranges reported by Shim et al. [27] who used the Japanese standard leaching procedure. Direct comparison among the values summarized in Table 4 is impossible due to the difference in physicochemical characteristics of raw fly ash used for each study. Amounts of heavy metals leached by the American society of testing materials (ASTM) method and toxicity characteristic leaching procedure (TCLP) seem to be relatively greater than those from other leaching procedures (Table 4). It is generally believed that TCLP used in the US is more powerful than other standard leaching procedures

Table 4
Amount of heavy metals leached from raw fly ashes by different standard leaching procedures.

Leaching procedure	Heavy metals	Leached amount[a] (%)	Remarks	Reference
ASTM method[b]	Pb	<2.9	Power plant fly ash	[30]
	Zn	10.9		
	Cu	16.3		
German standard method	Pb	<0.1	Power plant fly ash	[31]
	Zn	0.6–1.1		
	Cu	0.3–0.9		
Japanese standard method	Pb	<0.1–21.8	MSWI fly ash	[27]
	Zn	<0.1–8.8		
Taiwan standard method	Pb	0.2	MSWI fly ash	[32]
	Zn	0.6		
	Cu	ND[c]		
TCLP[d]	Pb	29.4	MSWI fly ash	[14]
	Zn	3.2		
	Cu	32.4		
	Pb	0.2	MSWI fly ash	[33]
	Zn	4.1		
	Cu	2.6		
	Pb	2.6	MSWI fly ash	[34]
	Zn	16.2		
	Cu	28.0		
This study[e]	Pb	11.3	MSWI fly ash	–
	Zn	1.2		
	Cu	6.1		

[a] (mg heavy metal in leaching solution)/(total heavy metal (mg) in raw fly ash) × 100%.
[b] American society of testing materials.
[c] Not detected.
[d] Toxicity characteristic leaching procedure established by Environmental Protection Agency (EPA) in the US.
[e] Korean standard leaching procedure (see Table 2).

because of a higher L/S ratio (L/S ratio = 20), leaching solution with a lower pH (pH = 5.0 with continual pH adjustment), longer leaching time (18 h), and a more vigorous mixing technique (end-over-end rotation) of liquid/solid mixture used for TCLP. Future research for comparison of several standard leaching procedures used in different countries is recommended to evaluate any differences in leaching behavior of heavy metals in solid wastes such as fly ash.

3.2. Effect of absorbed dose of irradiation on the amount of heavy metal leached

Electron beam was irradiated up to 210 kGy to examine any change in leaching potential of heavy metal in the fly ash. When electron beam irradiation intensity increased gradually from 10 kGy to 210 kGy (10 kGy, 30 kGy, 70 kGy, 100 kGy, 140 kGy, 170 kGy, 200 kGy, and 210 kGy), there was a notable change in concentration of heavy metals in the leachate. Pb and Zn concentrations in the leachate increased significantly, while Cu concentration did not show notable change (Fig. 2). Based on linear regression analysis, the leached amount of Pb and Zn increased up to 15.5% (10.7 mg/kg), and 35.6% (9.6 mg/kg) respectively. However, only 4.8% increase (0.3 mg/kg) was observed for Cu. Scattering of Pb data was noted. Correlation coefficient for Pb data was 0.7798, while those of Zn and Cu were 0.9807 and 0.8266 respectively. The exact reason was not clear. Redistribution of Pb during analysis in the method of sequential extraction procedure of Tessier might occur as pointed out by Raksasataya et al. [25,35].

The difference in leaching behavior among the metal species may be due to the difference in mineralogy of fly ash. The mineralogy of fly ash generally represents an assemblage of crystalline and amorphous (or glassy) phases. Minerals in fly ash are formed as a consequence of several mechanisms such as vaporization, melting, crystallization, vitrification, condensation and precipitation occurring during combustion and flue gas cleaning processes [18]. In the short combustion process, thermodynamic equilibrium of minerals in fly ash is not achieved and consequently the first-formed primary minerals undergo chemical reactions such as hydration, carbonation, oxidation and reduction producing secondary minerals. Bayuseno et al. [18] investigated the mineralogical characteristics of MSWI fly ash, where the results from X-ray diffraction (XRD) analysis indicated that the fly ash contains about 40% (by weight) amorphous (glassy) phase and 60% (by weight) crystalline phase. Several crystalline phase Pb and Zn existed in % level. In case of Pb, caracolite [$Na_3Pb_2(SO_4)_3Cl$], massicotate [PbO], and minium [Pb_3O_4] were identified, while potassium tetrachlorozincate [K_2ZnCl_4], and wurzite [ZnS] were identified in case of Zn [18]. Other crystalline forms of Pb and Zn reported in the literature were KPb_2Cl_5, Pb_2FeO_5, and $ZnCl_2$ [34,36,37]. These crystalline forms of Pb and Zn are thermodynamically unstable and subject to the formation of secondary minerals through hydration, carbonation, oxidation and reduction [18].

The melting points of Pb and Zn are 327 °C and 420 °C respectively. They are volatile in the combustion chamber where temperatures are above 900 °C. Pb and Zn were more concentrated in the crystalline phases than the glassy phases (or amorphous phases). Almost 80% of Pb and 50% of Zn were present in the crystalline form [18]. On the other hand, some other heavy metals such as Cr, Cu and Ni seem to be almost completely bound to glassy phases or alloys and thus have little possibility of becoming secondary minerals [18]. Significant increase in concentrations of Pb and Zn in leachate in this study (Fig. 2) might be explained by their unstable crystalline forms which are vulnerable to irradiation.

3.3. Metal form change due to irradiation

There was a remarkable increase in concentration of Pb and Zn in leachate after the electron beam irradiation. However, there was little change in case of Cu. There might be some change in metal form especially for Pb and Zn. Understanding of the distribution of metal form is essential to estimate leaching potential of the heavy metals in fly ash [17,23,26,38].

Metal form in the fly ash samples before and after electron beam irradiation were analyzed by the sequential extraction procedure to examine any metal form change that may have occurred, as shown

Table 5
Results of sequential extraction of Pb from the fly ash used in this study.

Dose (kGy)	F1[a]		F2		F3		F4		F5	
	mg/kg	Δ%[b]	mg/kg	Δ%	mg/kg	Δ%	mg/kg	Δ%	mg/kg[c]	Δ%
0	193.5		23.7		7.3		37.2		349.3	
10	201.0	3.9	23.6	−0.5	9.3	26.1	41.2	10.9	335.9	−3.8
30	201.5	4.1	33.5	41.4	8.6	16.6	38.9	4.5	328.6	−5.9
70	202.3	4.5	27.6	16.6	9.7	32.0	46.1	23.9	325.4	−6.9
100	215.5	11.4	35.4	49.3	14.3	95.2	52.6	41.6	293.2	−16.1
140	199.1	2.9	44.9	89.5	13.0	77.4	43.3	16.5	310.6	−11.1
170	214.8	11.0	37.5	58.4	17.1	133.5	41.8	12.5	299.8	−14.2
200	228.6	18.2	37.6	58.6	14.0	91.3	49.6	33.4	281.1	−19.5
210	227.9	17.8	49.9	110.4	15.3	109.1	61.0	64.1	256.9	−26.5
Average	209.3	9.2	34.9	53.0	12.1	72.7	45.8	25.9	309.0	−13.0
Range	194–229	2.9–18.2	23.7–49.9	−0.5 to 110.4	7.3–17.1	16.6–133.5	37.2–61.0	4.5–64.1	257–349	−26.5 to −3.8

[a] F1: exchangeable fraction; F2: carbonate bound fraction; F3: oxides bound fraction; F4: organic bound and sulfides fraction; F5: residual fraction.
[b] Compared with raw sample (absorbed dose = zero).
[c] Calculated.

in Tables 5 and 6. Fraction 5 (residual form) was not analyzed, and the values of Fraction 5 shown in these tables were calculated values from total. Relative distribution or percent distribution of metal forms in raw MSWI fly ash was examined by several research groups [14,26,36]. Major forms of Pb included F1 (exchangeable form) [26], F3 (oxides bound form) [14], or F5 (residual form) [36]. In the case of Cu, major form was F2 [36], or F3 [14,26]. In this study, the major form of Pb and Cu was both F5 (residual form) as shown in Tables 5 and 6. This kind of discrepancy among the results from similar studies might be due to the difference in fly ash characteristics from different combustion conditions of incinerators.

The results of sequential extraction showed that there were notable changes in metal forms after irradiation implying that irradiation has a significant effect on physicochemical characteristics of fly ash. In terms of Pb (Table 5), all fractions except F5 increased. Increase in oxides bound fraction (F3) of Pb is the most notable. Average increase in F3 of Pb was 72.7% with a range from 16.6% to 133.5%. In case of Cu (Table 6), changes of metal form are much less than those of Pb. Increase in oxides bound form of Cu also was the most notable (average 18.5% increase with a range from 6.1% to 32.3%). Organic bound or sulfides fraction (F4) decreased 12.7% (range from 7.9% to 14.8%). The initial first two fractions of Cu (exchangeable fraction and carbonate bound fraction), which are relatively mobile, changed less than 1%. Overall, average changes in all fractions of Pb were from −13.0% to 72.7%, which were much greater than those of Cu (from −12.7 to 18.5%). Considering the results and discussion in Section 3.2 of this paper, greater changes in metal form of Pb compared to those of Cu are expected.

Irradiation on clay mineral increased specific surface area and solubility of the clay minerals [39]. Pb is a post-transition (or poor) metal, a softer material with a low melting point (327 °C). The major form of Pb in fly ash maybe an unstable crystalline one as we have discussed. Thus, the increase in F3 of Pb in this study (Table 5) may be attributable to the oxidation reaction caused by irradiation. Decrease in residual fraction (F5) which is the final and the most stable form might be associated with the destructive reaction. The increase in carbonate form (F2) and organic bound or sulfides form (F4) of Pb may be explained by the synthesis reaction of metal with organics and sulfur in fly ash. The fly ash used in this study contained significant amount of carbon and sulfur (Table 3).

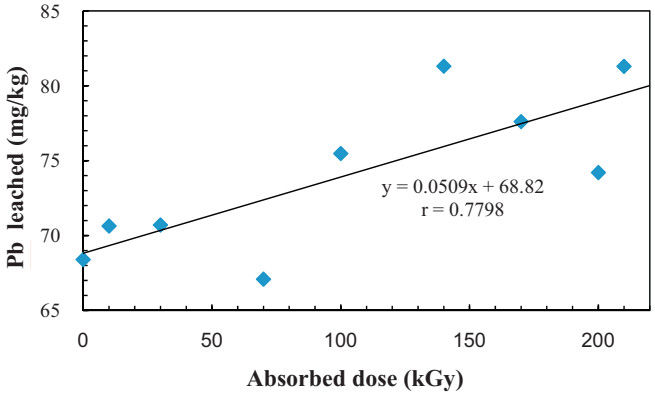
With regards to Cu, a relatively less change in metal forms was observed (Table 6). F1 and F2 changed little, whereas the most notable change was in F3 which increased an average of 18.5%. The increase in F3 and decrease in F4 of Cu might be attributable to oxidation reactions caused by irradiation. Relatively smaller change in Cu forms may be due to the fact that Cu exists mainly as a stable glassy form in the fly ash [18,34]. Cu is one of the transition metals which are characteristically hard and strong metals. The melting point of Cu (1085 °C) is much higher than that of Pb. Heat of fusion of Cu (13.26 kJ/mol) is much higher than that of Pb (4.77 kJ/mol).

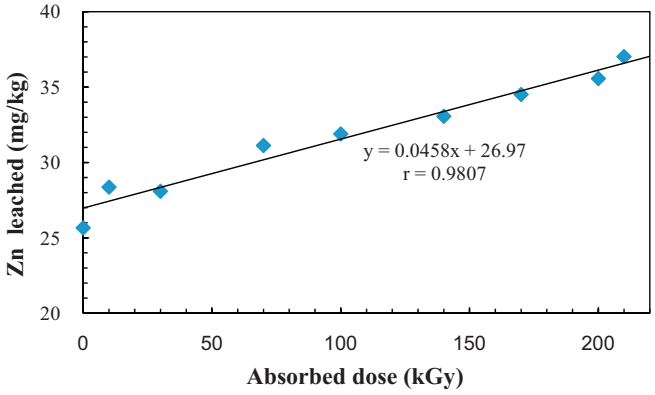
In summary, change in metal forms of Pb was much greater than that of Cu. The change in metal form was related to the leaching potential of the metals. All fractions of Pb and Cu, except F2 and F4 of Pb could be explained by the mechanisms of destruction and oxidation as expected. Increase in F2 and F4 of Pb might be explained by synthesis reactions with organics and sulfur in fly ash. Verification of mechanisms during irradiation is beyond the scope of

Table 6
Results of sequential extraction of Cu from the fly ash used in this study.

Dose (kGy)	F1[a]		F2		F3		F4		F5	
	mg/kg	Δ%[b]	mg/kg	Δ%	mg/kg	Δ%	mg/kg	Δ%	mg/kg[c]	Δ%
0	15.9		21.9		7.2		27.4		24.8	
10	15.2	−4.2	21.6	−1.5	7.8	7.3	25.2	−7.9	27.4	10.5
30	16.3	2.4	21.9	0.1	7.7	6.1	24.5	−10.5	26.8	8.1
70	15.6	−2.1	21.6	−1.5	9.6	32.3	23.6	−13.6	26.8	8.1
100	15.6	−2.0	21.7	−0.9	8.4	15.6	23.6	−13.6	27.9	12.5
140	15.7	−1.4	22.1	0.9	8.5	17.8	23.6	−13.8	27.3	10.1
170	15.7	−1.4	22.0	0.2	8.8	21.4	23.7	−13.5	27.1	9.3
200	15.7	−1.0	22.3	1.9	8.6	18.2	23.3	−14.8	27.3	10.1
210	16.1	1.4	22.6	3.1	9.3	29.1	23.5	−14.1	25.6	3.2
Average	15.7	−1.0	22.0	0.3	8.4	18.5	24.3	−12.7	26.8	9.0
Range	15.2–16.3	−4.2 to 2.4	21.6–22.6	−1.5 to 3.1	7.2–9.6	6.1–32.3	23.3–27.4	−14.8 to −7.9	25.6–27.9	3.2–12.5

[a] F1: exchangeable fraction; F2: carbonate bound fraction; F3: oxides bound fraction; F4: organic bound and sulfides fraction; F5: residual fraction.
[b] Compared with raw sample (absorbed dose = zero).
[c] Calculated.





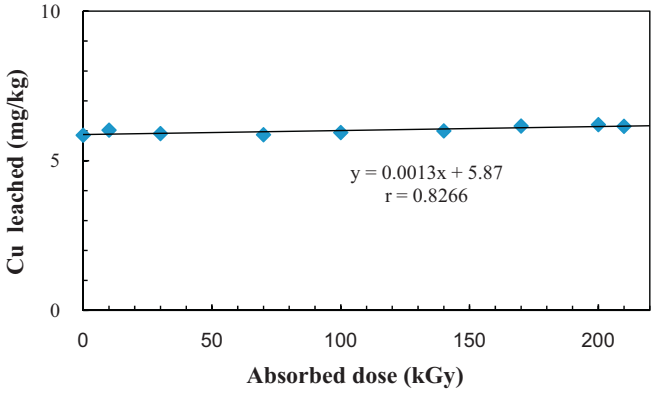


Fig. 2. Irradiation effects on leaching behavior of Pb, Zn and Cu in fly ash.

this research. Further research is recommended for the verification of reaction mechanisms, especially synthesis reactions of Pb with organics and sulfur in fly ash when it is irradiated.

3.4. Relationship between amount of metal leached and exchangeable fraction (F1)

The first fraction (F1, the exchangeable form) may be the major form to increase the leaching potential because F1 is the most leachable form among the five forms of heavy metal. Leaching potential of heavy metal in the environment has been evaluated based on the ratio of F1 to the total metal content [17]. Therefore it is reasonable to try to compare the amount of F1 with the amount of metal leached. The results are shown in Figs. 3 and 4 which include the amount of metal leached (mg/kg), exchangeable fraction (mg/kg), and absorbed dose (kGy). Fig. 3 shows that the exchangeable fraction (F1) of Pb increased by 14.4%, while the amount of Pb leached increased by 15.5% based on linear regression analysis. In the case

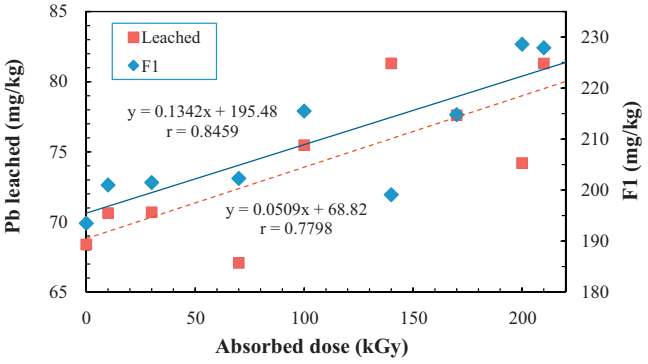


Fig. 3. Increase in exchangeable fraction (F1) and leached amount (mg/kg) of Pb depending on absorbed dose.

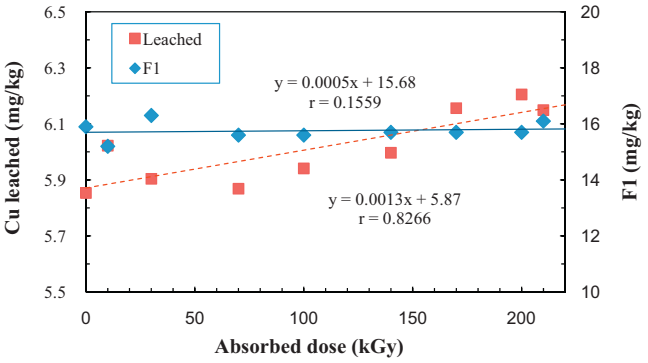


Fig. 4. Increase in exchangeable fraction (F1) and leached amount (mg/kg) of Cu depending on absorbed dose.

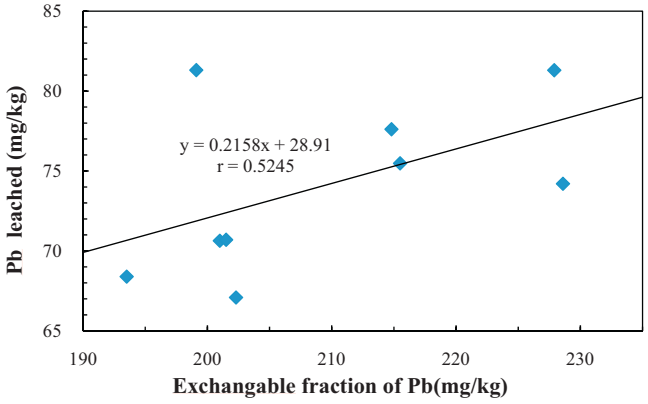


Fig. 5. Relationship between exchangeable fraction (F1) and leached amount (mg/kg) of Pb.

of Cu, change in F1 was insignificant (only 0.8% increased), while Cu leached increased by 4.8%. At an absorbed dose of zero, the ratio of Pb leached (mg/kg)/F1(mg/kg) was 0.352, while the ratio was 0.355 at absorbed dose of 210 kGy, implying that the amount of Pb leached from fly ash was about 35% of F1. For Cu, this ratio was from 0.374 at the absorbed dose of zero to 0.388 at the dose of 210 kGy, implying that the amount of Cu leached was about 38% of F1.

The increase in exchangeable fraction (F1) of Pb was similar to the amount of Pb leached. An attempt was made to correlate these two parameters for the first time. As shown in Fig. 5, there was positive linear relationship between the two parameters, but the correlation coefficient was not high ($r = 0.5245$). This low correlation coefficient may be partially due to the quite narrow ranges of both the dependent and the independent variables.

3.5. Engineering significance of the results

The results of this research are important to environmental engineers for several reasons. Fundamental data on change in leaching potential and form of metals in fly ash when irradiated were evaluated. Irradiation has significant effect on leaching behavior and metal form of heavy metals in fly ash. Electron beam irradiation (up to 210 kGy) on fly ash increased significantly and linearly the leaching potential of Pb and Zn in the ash. Selective recovery of valuable metals from fly ash may be possible. Thus electron beam irradiation may be an advantageous alternative for fly ash treatment. Pretreatment of metal-contaminated soils prior to soil washing for remediation is another alternative.

The current knowledge-base indicates that biologically resistant organic pollutants are successfully decomposed in an economically efficient manner by electron beam irradiation [2,3,5–8,10,40]. The results in this study combined with published data for the treatment of organic-contaminated wastes, indicate that solid wastes such as soils which contain both organic and inorganic contaminants may be treated successfully by electron beam irradiation. A possible example would be the remediation of a contaminated site near leaking underground storage tanks.

Although this promising technology has applicability worldwide, feasibility of this technology applied to solid waste such as fly ash need to be studied in greater detail, since knowledge regarding this technology is limited especially for solid wastes including fly ash. Technical and economical feasibility studies using pilot-scale and small-scale plants for solid waste treatment should be considered [1]. Furthermore, the combination of irradiation process with conventional treatment processes as a treatment train is recommended for further studies.

4. Conclusions

Heavy metal leaching behavior in fly ash after electron beam irradiation was evaluated extensively in this series of experiments. Leaching behavior was tested by a standard leaching procedure, and to gain an insight into metal forms in fly ash which may affect leaching behavior, a sequential extraction analysis was conducted. An attempt was made to correlate the leaching concentration of metal and the exchangeable form of the metal which are known to be mobile. Conclusions are as follows:

1. Electron beam irradiation on fly ash has a significant effect on the leaching behavior of heavy metals in the ash.
2. Absorbed dose and metal species affected leaching behavior. Concentration of Pb and Zn in leachate increased linearly with increase of absorbed dose, while that of Cu had almost no change.
3. When fly ash was irradiated up to 210 kGy, concentration of Pb and Zn in leachate increased up to 15.5% and 35.6% respectively.
4. Notable change in metal form in fly ash was observed when it was irradiated. Change in Pb forms was greater than that of Cu. Change in metal form was related to leaching potential of the metals.
5. Leached amount of metals was positively related with amount of exchangeable form (F1) of the metal.
6. Results of this study imply that solid phase wastes such as fly ash may be treated by electron beam irradiation.

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