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ANALYSIS OF THE BREAKTHROUGH PHENOMENA DURING HEAVY METAL ELUTION FROM A COLUMN PACKED WITH MUNICIPAL WASTE INCINERATION ASH

At some point during acid leaching column tests of heavy metals from municipal waste incineration ash, sudden and rapid elution of harmful elements was observed which was called the breakthrough (BT) phenomena. The mechanism was elucidated from the results of measurement of elemental and particle size distribution in the column and batch leaching tests as follows. At the first stage of experimental runs, $CaCO_3$ was dissolved in acidic solution and pH profile along the bed is formed. Some of the minor elements of Zn and Al dissolved by acid at the upper part of the column are precipitated at bottom of the column, leading to the reduction of flow rate of the leachate solution. After leachate pH becomes low by the termination of dissolution of Ca, these deposits are dissolved and thus, the flow rate increases. Most of the trace elements behave as such, which causes the increase of harmful element concentrations in the eluate. Some drastic concentration increase of harmful elements in leachate may occur even after the long period of pseudo stable dissolution behavior in the land-fill site.

1. INTRODUCTION

In Japan, more than 50 million Mg of waste is produced a year and around 87% is incinerated. By introducing the incineration, the waste volume is substantially reduced. As the results vast amount of incineration ash, bottom or fly ash has been produced and used for landfilling. However, new landfilling sites are difficult to be found especially in the city area and recycle use technologies of ash have been developed. In Tokyo area, two new technologies have been adopted. In the 23 wards metropolitan area of Tokyo,

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most of ash is melted at temperature higher than 1300 °C and used for road construction and so on, and in the other areas of Tokyo, ash is converted to eco-cement and used as an alternative of Portland cement. While the landfill problem will be mitigated by adopting these technologies, additional economical costs are often increased [1] and additional energy is sometimes required leading to the increase in environmental impact. The problem of the quality of the eco-cement is also pointed out.

On the other hand, tremendous amount of combustible waste is discarded as it is in various countries and it also causes serious environmental and sanitary problems. From these points of view, it is anticipated that the incineration plants will be introduced without further treatment of ash, which will be used for simple landfilling. When the incineration ash is inadequately treated, heavy metals dissolve into precipitation especially acid rain, and possibly contaminate the surface and ground water [2]. Hence the elution behavior of harmful trace elements, especially into the acidic water, is the next concern.

Though, many researchers have so far reported the elution behavior of heavy metals from incineration bottom ash [3] and fly ash [4], most of them have been limited to only phenomenological description. While some of them reported the results from column experiments, which simulated the behavior in soil layer, the discussion on their mechanism was insufficient.

In the first paper of our present series of studies [5], we examined the leaching characteristics of heavy metals in a column with nitric acidic solution from incineration fly ash obtained at Musashino Clean Center [6] equipped with three stoker furnaces of capacity of 65 t/day for each, located at Tokyo in Japan. As the result, we found that pH of the leachate solution decreased sharply almost to the pH value of original leaching solution, the flow rate of the leachate (i.e., the eluate speed in g/h, almost equivalent to cm^3/h) increased, and the concentrations of the main or minor elements such as Al, Zn and Fe increased sharply and almost simultaneously at a certain stage in some experimental runs. We called these as breakthrough (BT) phenomena. Then we reported that these phenomena are common for various incineration ashes including ashes from Chinese fluidized bed incinerators, and that the final rapid elution is also found for other various harmful minor elements [7].

The BT phenomenon for both of time variation curves of eluate speed and pH is schematically shown in Fig. 1. BT is regarded to start when both of the rapid pH decrease after stable pH and the steep increase in eluate speed after its minimum begin. However, the starting periods of the phenomena were different among experiments depending not only on used ash with different particle diameters but also on packing conditions including pretreatment. Furthermore, in some experiments, these phenomena were not observed even after several days' test. By quantitative analyses, the phenomena were found to be definitely observed by the time of some accumulative amount of acid fed, irrespectively of time or eluate speed, which was affected by the pretreatment condition [5].

These phenomena are thought to possibly be found in other heaped waste layer with various elements: it is possible case that some sudden release of harmful elements may occur at the BT point even after long period of stably suppressed elution of elements. We should recognize that the BT time is also affected by the physical structure of the layer, which could not be predicted directly from the batch leaching test using suspended ash particles.
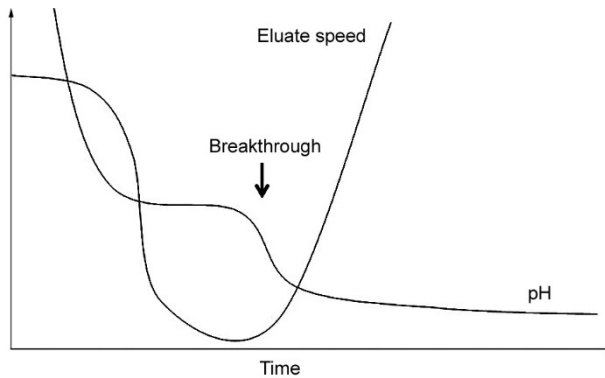

Fig. 1. Model of breakthrough (BT) phenomena;
typical time dependent curves of the eluate speed and pH

This research was conducted for the analysis and elucidation of the mechanism of the BT phenomenon discovered at examining the acid leaching property of a harmful heavy metal in the city waste incineration fly ash during the column test of the sample [5, 7]. Hence, in order to analyze this phenomenon, first of all, batch leaching test was conducted for the Japanese fly ash. Next, column leaching tests were conducted. In the present study, column tests were conducted by using a soft tube in addition to the original glass column and only pH of the leachate was continually measured. In the course of the test, the leaching was stopped and the samples at the bottom and the upper parts of the ash layer in the soft tube were taken. Their elemental contents and ash particle size distribution were measured. The discussion on the results of the column experiments is conducted referring the batch leaching test and finally, the mechanism of the BT phenomenon is elucidated from the above discussion.

2. EXPERIMENTAL

Ash samples. The ash samples used in both of the batch and column experiments originated from Japanese fly ash (J) taken from Musashino Clean Center [6]. The fly ash was collected with bag filters from flue gas after gas cleaning with sodium hydroxide solution.

The yield of fly ash was around 1.5% of the fed municipal waste. The fly ash sample was sieved to get the fraction smaller than 0.5 mm (with the yield more than 99%).

In the column experiments, we also used two other ash samples taken from two waste incineration plants in China, Beijing (B) and Changchun (C), with large scale fluidized bed incinerators with capacity of 200 Mg/day or more, in addition to the J fly ash. The fly ash yield in the Chinese plants is reported to be more than 5% though the other details of their operational conditions are not clarified. The two Chinese ash samples were also sieved to get the fraction smaller than 0.5 mm (yield was more than 98%). The samples used for the analyses and tests were carefully taken from well mixed mother ash samples after drying for one night at 120 °C.

The elemental content of the ash samples was determined by the acid digestion method as follows. After drying the sample in a vacuum desiccator, accurately weighed ash (around 400 mg) was soaked in 10 cm^3 of nitric acid in a 200 cm^3 Teflon beaker for one night. Then 10 cm^3 of hydrofluoric acid was added, kept at 90 °C for 1 h and evaporated to dryness at 180 °C. 5 cm^3 of nitric acid and 10 cm^3 of perchloric acid were again added to the beaker and heated at 90 °C for 40 min followed by heating at 170 °C for 2 h under the cover with a Teflon watch glass. When the digestion is not completed, the present procedure was repeated with smaller quantity of acids at up to 230 °C. In the course of the acid digestion, silica was removed with hydrofluoric acid. After the digestion is completed, the solution was evaporated to start crystallization without the Teflon watch glass cover at 130 °C. After cooling down, the deposit was dissolved with 0.2 mol/dm^3 nitric acid and filled up with distilled water to 100 cm^3.

Table 1

Elemental contents in fly ash samples and solubility of their hydroxides

	Na	Ca	Al	Zn	Fe	Pb	Cd	Cu
Japan (J)	79.4	150.3	31.1	6.25	8.27	1.75	0.103	1.02
Changchun (C)	21.9	139.8	59.5	1.9	28.0	0.87	0.019	0.51
Beijing (B)	69.7	180.0	27.4	2.2	16.1	0.92	0.065	0.32
Hydroxide	NaOH	Ca(OH)$_2$	Al(OH)$_3$	Zn(OH)$_2$	Fe(OH)$_2$	Pb(OH)$_2$	Cd(OH)$_2$	Cu(OH)$_2$
Solubility for hydroxide [8][a]	53.3	0.0203	1.9×10^{-32}	0.012	0.006	1.1×10^{-20}	0.0027	0.0029
	mol/kg			g/dm^3			g/dm^3	
Temperature,°C	25	25	30	25	25	25	18	25
Maximum metal concentration for J, g/dm^3	0.50	0.94	0.194	0.0390	0.0517	0.0109	0.00064	0.0064
Dissolution pH for J	19.1	12.6	4.1	10.0	9.6	6.1	9.8	9.5

Contents in ash in mg/g d.m., solubilities in mol/kg refer to 1 kg of solvent, while those in g/dm^3 to 1 dm^3 of solution. In solubility products of Al(OH)$_3$ and Pb(OH)$_2$, concentrations of ions are expressed in mol/dm^3.

All chemicals used for the analyses were of analytical grade. 1000 mg/dm^3 standard solutions of elements for atomic absorption spectrochemical analysis were used for calibration curve of ICP-AES measurement. The elemental analysis was conducted with ICP-AES by the inductively-coupled plasma atomic emission spectroscopy (Thermo Scientific iCAP6000, Thermo Fisher Scientific Inc., Waltham, USA). The results are shown in Table 1 [7]. In Table 1, the solubility data of the metal hydroxides are also added, by citation from the values given in [8]. The maximum concentrations when the entire element is leached out under the condition of the present batch leaching experiment are also given in Table 1. The maximum pH for complete dissolution of the hydroxides of these elements have been calculated using the solubility constants and the results are shown in Table 1. The definitions of the solubility are easily found from their units though they are different among the elements. The effect of the measurement temperature is not discussed here.

Batch leaching test. In the previous experiments [5, 7], the BT phenomena were definitely found before 10 mmol of nitric acid per g of ash was passed through the column. These phenomena were thought to be affected by concentration profiles of elements through the column layer. Hence, the present experiment was conducted under the uniform condition in a well mixed batch vessel. Under the present condition, the intra-particle mass transfer resistant is also expected to be negligible. Under the room temperature, 5.0 g of dried Japanese fly ash was placed and 800 cm^3 of distilled water was poured. Under magnetic stirring, 2.0 mol/dm^3 nitric acid solution was dropped slowly at the rate around 3 cm^3/h. 2 cm^3 of solution was sampled every 30 min and its pH value and concentrations of various metal ions were measured with the ICP-AES. The present test was finished after 6 h.

Column leaching test. As the acidic leaching solution, 0.1 mol/dm^3 aqueous solution of HNO$_3$ (pH = 1.0) was used. The weighed ash sample was packed in a glass tube of internal diameter 15 mm and 300 mm long with upper pool as shown in Fig. 2a after packing glass wool at the bottom (for test G0). In the other tests (T1–T6), the middle part upper than the bottom glass wool was replaced by plastic (polyvinyl chloride) tube with the inner diameter of 15 mm and fixed to upper and lower glass tube with stainless steel rods as shown in Fig. 2b.

Experimental conditions are given in Table 2. The sample amount was 5 g for Japanese and Changchun fly ashes and 10 g for Beijing ash with high density to get bed height around 4–5 cm. Ash was packed under the wet condition by adding distilled water. After 60 min of wetting (wet-1) or at just after packing (within 15 min, wet-0), the bottom Teflon cock was fully opened. Then the leaching solution was started to be dropped from a burette. The dropping speed was controlled to keep a solution level at 36 cm from the bottom cock within the upper pool. The pH of the leachate was started to be measured.
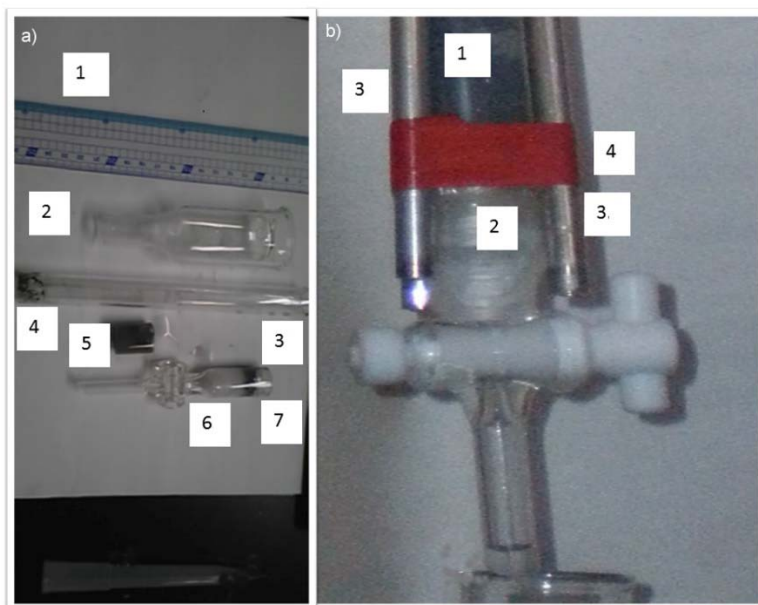
Fig. 2. A general view of apparatus for column experiments;
a) apparatus for G No. 0 (after cutting): 1 – 20 cm scale, 2 – upper pool, 3 – upper part
of glass column (with 4 – glass wool), 5 – glass column with ash sample after test,
6 – lower part of the glass tube (with 7 – glass wool), b) apparatus for tests Nos. 1–6 (only lower part):
1 – flexible plastic tube, 2 – lower part of glass tube, 3 – stainless steel rods, and 4 – adhesive tape

T a b l e 2

Experimental conditions and general results

No.	Experimental conditions				General results				
	Fly ash		Height [cm]	Pre-treatment	Final pH	Duration [h]	Eluate [cm^3]	Dropped (nitric acid) [mmol/g]	BT point from Ca content [mmol/g]
G0	J		5.2	wet-1	7.8	5.0	120	2.4	–
T1			4.5	wet-1	5.9	5.0	282	5.6	–
T2		5 g	4.2	wet-1	7.6	220.0	252	5.0	–
T4			4.8	wet-0	6.0	3.3	114	2.3	
T5			4.9	wet-0	2.2	68.6	280	5.6	7.5
T3	C		4.5	wet-0	1.0	5.7	150	3.0	7.0
T6	B	10 g	5.0	wet-0	1.9	20.0	88	1.9	9.0

G – glass, T – plastic tube, wet-1 started after 60 min wetting, wet-0 started within 15 min, BT – breakthrough.

Differently from the previous papers [5, 7], in the present study, the leaching solution dropping was stopped at a certain stage of the leaching, the leaching solution above the ash layer was removed and the entire column was freezed in a freezer for a night. Then the tube was cut with a ceramic knife in order to prevent the metal contamination by the knife (glass cutter was used in the case of G0). In the case of tests Nos. 0–2, the sample thickness of the top and bottom layers was around 5 mm each and the dried sample weight was around 0.4 g. In the case of tests Nos. 3–6, thickness was around 2 mm each and dried sample weight was around 0.2 g. The contents of various elements in the top and bottom layers inside the column were measured by the acid digestion method followed by the ICP-AES. The particle size distribution of the ash sample was measured using a laser diffraction particle size distribution analyzer, SALD-2100 (Shimadzu Corp., Kyoto).

3. RESULTS AND DISCUSSION

3.1. BATCH LEACHING TEST

The dropped amount of nitric acid is taken as the abscissa in the unit of mmol/g ash and the changes of pH and concentration rate of eight elements defined as
- (elemental concentration in solution, mol/dm^3) × (volume of solution, 0.8 dm^3),
- (elemental content in ash, mol/g d.m.) × (ash sample weight, 5.0 g d.m.),

are plotted as the ordinates in Fig. 3. pH for completion of the leaching out of each element is different among the elements, though some data exceeded or did not reach to 100% of leaching, which will partly be caused by non-uniform distribution of ash components.

In the present paper, the elution order of non amphoteric metals is given as follows with pH values and total nitric acid dropping for almost complete leaching: Na (alkaline to neutral, 0 mmol/g), Ca (neutral to pH 3, 2 mmol/g), Cd (pH 3, 2.5–3 mmol/g), Cu (pH 3, 3 mmol/g), and for Fe, some increase in leaching was found even at the vicinity of pH 1 with addition of nitric acid in amount of 8 mmol/g.

In the case of amphoteric metals – Zn, Al and Pb, almost entire amount of the element was leached out at the relatively initial stage, and the elution order is given as follows: Zn (pH 3, 3 mmol/g), Pb (pH 2.5–3, 3.5 mmol/g), Al (pH 2, 4 mmol/g) though further leaching was observed after pH reached around 1 by addition of nitric acid around 8 mmol/g.

From the present preliminary study, the elution of large amount of Ca was relatively fast and it is suggested to be the main cause of pH change of the leachate. It is considered that Na may not cause the pH change because Na was eluted even at high pH and most of Na is thought to exist as NaCl in the case of municipal waste ash. Among the major or minor elements, the increase in the leached amount at pH lower than 3 was found for

Cu, Zn, Pb, Al. In the case of Fe, leaching was still observed at pH lower than 2. It was also demonstrated that the value of 8 mmol/g of ash is the nitric acid amount which is necessary for most of the elements except Fe to elute out from the ash.
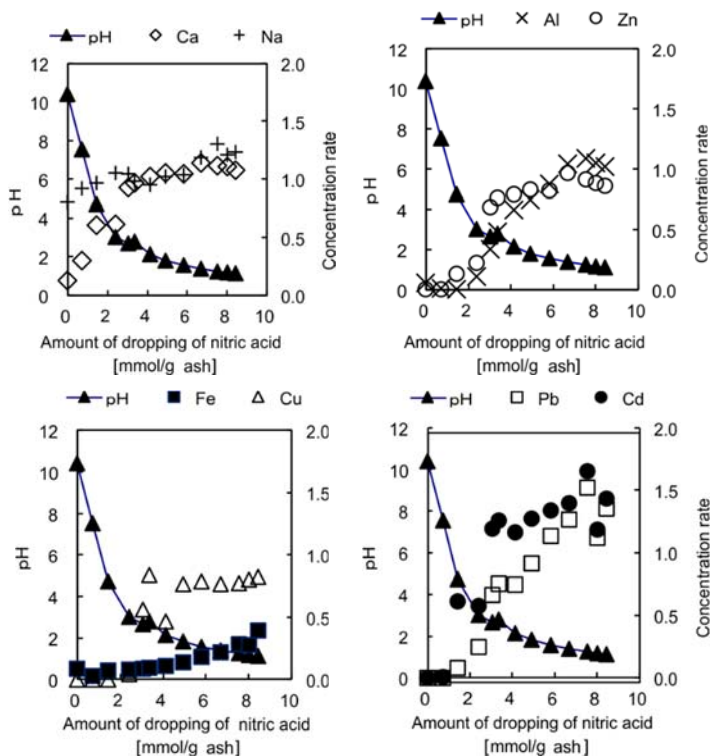

Fig. 3. Results of preliminary experiments: batch elution test (Japanese ash)

Present dissolution behavior suggested that the most of the dissolution of the element became more difficult and the pH for the dissolution is shifted to lower pH than the prediction of Table 1 for hydroxide. The present results might be explained by the existence of other anions such as S^{2-}, SO_4^{2-} or CO_3^{2-} which form salts with less solubility than their hydroxide, in addition to the existence of intra-particle mass transfer resistance. In the case of Fe, most of the ions are suggested to exist not as ferrous but as ferric ion with less solubility.

3.2. GENERAL OBSERVATION OF THE COLUMN TESTS

The variations of the eluate speed and pH are plotted in Fig. 4a–e for Japanese ash and in Fig. 4f, g for Chinese ashes against the "amount of dropping of nitric acid" based on dry ash

sample. The experiments were stopped before breakthrough (BT) in Fig. 4a–d (tests No. 0–3) and stopped around BT in Fig. 4e–g (tests No. 4–6) to get ash layer samples.
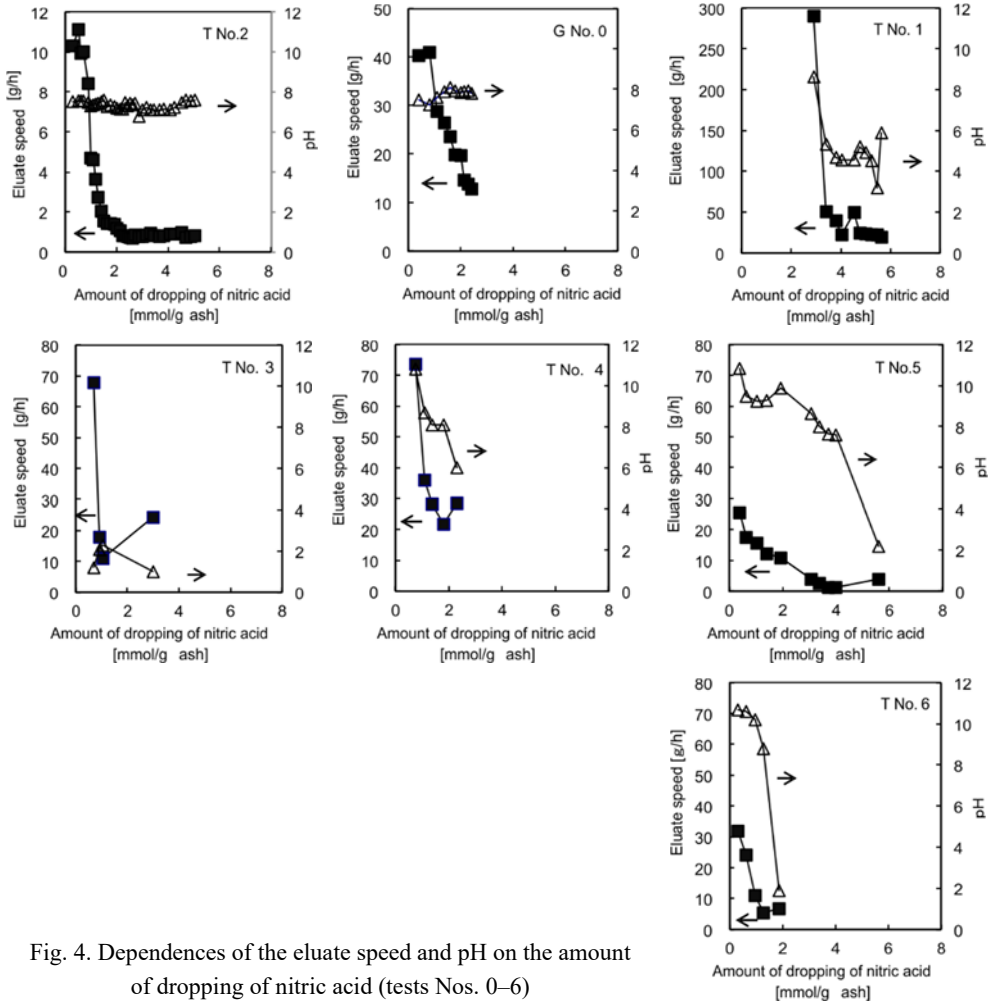

Fig. 4. Dependences of the eluate speed and pH on the amount of dropping of nitric acid (tests Nos. 0–6)

For tests Nos. 0–2 (Fig. 4), the column leaching test was started after 60 min wetting and stopped at pH 6–8, namely under neutral conditions. Though the tendency of the change in the eluate speed was almost the same, namely it decreased with the progress of the test, the absolute value of the speed was from ten to a few hundred times different between tests No. 1 and 2, at the same amount of dropping of nitric acid. The unpredictability of the flow rate change caused by the small difference in the physical structure of the packed bed [5] was also found in the present experiments. In the tests Nos. 0 and 2, the solution was neutral throughout the test and the BT point was not observed under

such neutral conditions. In the case of test No. 1, though some change in pH was found, the drastic increase in the eluate speed was not observed. When a small path is once formed, most of the fresh acidic leaching solution passes through the path, then the path is tend to be expanded and BT time tends to become shorter. On the other hand, when the leaching solution flows uniformly, the BT tends to happen later.

Hence in order to get a higher flow rate, the experiments were conducted without one hour wetting of the samples for tests Nos. 3–6. The variations of the eluate speed and pH for these test runs are shown in Fig. 4. For tests No. 4 and 5, Japanese ash was used. Test No. 4 was stopped at pH corresponding to neutral solution, namely before BT, while test No. 5 was stopped around the BT (namely just after BT started), i.e., pH was drastically decreased and flow rate was increased. For tests Nos. 3 and 6 Chinese ashes (Changchun, and Beijing) were used and the both were stopped after BT started. In the case of test No. 3, the initial eluate speed was high, but after the initial stage the eluate speed soon decreased. The amount of dropping of nitric acid to get BT point in tests No. 3 and 6 for Chinese ashes was smaller than that for the Japanese ash.

3.3. PRELIMINARY DISCUSSION ON THE CAUSE OF THE BREAKTHROUGH

Considering the silica is hardly dissolved in acids, the present BT phenomena are possibly explained by the behavior of the other elements. Na is expected to be eluted first, because the solubility of its hydroxide (Table 1) and salts such as NaCl, which is thought to be main species of Na in ash, are high. While Ca is also one of the major elements, some of Ca salts are not as soluble as Na salts. One possible Ca salt is $CaSO_4$ whose solubility is very low. The salt we noted is $CaCO_3$ which is highly alkaline but not as soluble as Na salts. At the first stage of an experimental run, $CaCO_3$ is dissolved and pH of the leaching solution increases with pH gradient in the column; while the inlet leaching solution is kept acidic at the upper part, its pH is expected to be increased with dissolution of $CaCO_3$ with its moving from the top to the bottom of the column and the pH of the leachate starts from alkaline. However pH of the leachate is gradually reduced with the elution of $CaCO_3$ in ash.

At the first stage, though some of the minor elements other than Si, Na and Ca, namely such as Al, Zn and Fe are dissolved by the acidic leaching solution at the upper part, they deposit at some point of the column by the increase in pH of the leaching solution. This deposition causes the increase in pressure drop of the leaching solution to pass through the bed and eluate speed is decreased. After leachate pH becomes lower by the termination of dissolution of Ca, the pH of the middle/bottom parts of the column is decreased, the deposits are dissolved and thus, the flow rate is increased.

Based on the above discussion, the necessary amount of nitric acid to neutralize $CaCO_3$ in ash was calculated assuming the entire Ca exists as $CaCO_3$ and two moles of HNO_3 are necessary to neutralize one mole of $CaCO_3$ and the results are also shown in Table 2 for three ashes. In the case of Japanese ash, the calculated value of amount of

dropping of nitric acid of 7.5 mmol/g is well coincided with the experimental BT point observed also shown in Table 2. However some discrepancy for two Chinese ashes was found. Furthermore, we are not sure what kind of minor element causes such assumed phenomena. The present BT phenomena should also be affected by the particle diameter of ash sample and its change during the column test. In the present study, we discuss the effect of particle diameter in chapter 3.4 and then the possible element which mainly causes the BT phenomena in chapter 3.5.

3.4. CHANGES IN PARTICLE DIAMETER
AND ITS DISTRIBUTION OF SAMPLES IN THE COLUMN

The measured particle bulk density and median diameter of three ash samples before test are shown in Table 3. The particle size distribution curves measured for tests Nos. 5 (J), 3 (C), and 6 (B) are also shown in Fig. 5 for both of upper and bottom parts of the ash layer around BT, comparing with those for original ash of samples J, C and B before the tests. It is clearly seen that the particle diameters of both of the Chinese ash particles around BT point are drastically reduced (around one fifth to one third) from those of the original ash while the change in the diameter of Japanese ash particles is not so drastic.

T a b l e 3

Selected physical properties of the fly ash
– bulk density and median diameter before and after experiments

Sample	Bulk density ρ [kg/m^3]	Median diameter, d [μm]			
	Before	Test	Before	After (around BT)	
				Upper part	Bottom part
Japan (J)	380	T No. 5	17.0	19.1	20.7
Changchun (C)	500	T No. 3	68.6	12.6	15.1
Beijing (B)	850	T No. 6	115	28.0	20.4

The reduction of the diameter may partly be explained by the fact that the elution of the alkaline main elements of Ca and Na is almost completed around BT point. In our elemental analyses, silica or silicon content could not be measured because HF was used for acid digestion. As shown in Table 1, the main elements are found to be Ca and Na. If they exist as $CaCO_3$ and NaCl, their contents are 37.5% and 20.1% for Japanese ash, 34.9% and 5.5% for Changchun ash and 44.9% and 17.6% for Beijing ash, respectively. Namely half of the ash is expected to be eluted at BT point, however it is about equivalent to 20% reduction in diameter. Therefore this can explain the change in diameter of Japanese ash, while cannot for Chinese ash. Hence, in the case of Chinese ashes, it is suggested that the original ash particles exist as agglomerates and they are

disaggregated in the leaching process. Hence the BT phenomena were observed also for two kinds of Chinese ashes originally with larger particle diameter in addition to the Japanese ash because small particles were formed from large particles by disaggregation of large agglomerate particles. However the BT phenomena were still observed earlier for Chinese ashes than Japanese ash both by time and by dropped amount of acid as shown in Table 2, because of their larger initial particle diameter.
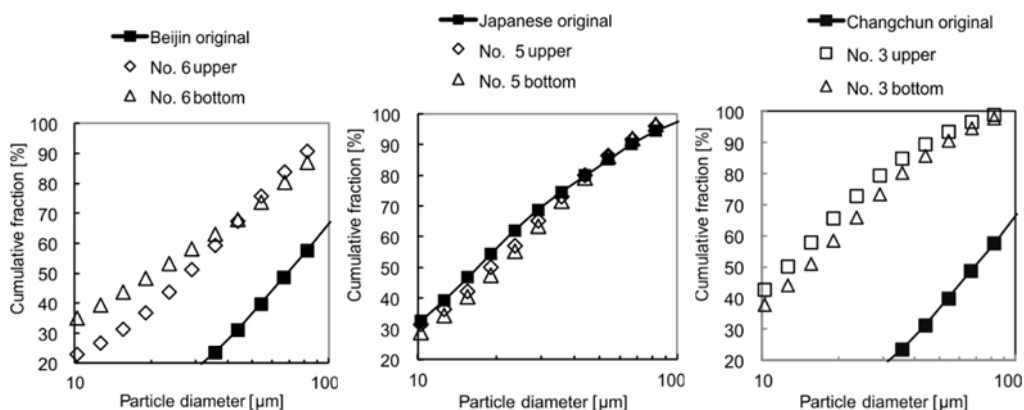

Fig. 5. Particle size distribution of samples and comparison with those around the BT point of ash: Japanese ash, Changchun ash, and Beijing ash

Another possible explanation is the difference in particle diameter between particles at upper and bottom parts of the ash bed. Around BT point, the particle diameter at the bottom part was larger than that at the upper part for tests No. 3 (C) and No. 5 (J), which may be caused by the re-deposition of dissolved major or minor elements, though this tendency was found only for larger particles in the case of test No. 6 (B). In the case of test No. 6 (B), it was suggested that some of the primary particles with smaller diameters were selectively moved to the bottom part with the flow of leachate.

The eluate speed can be roughly estimated by the Kozeny–Carman equation [9]. By assuming the porosity of the bed as 0.4 and pressure drop as water column of 0.3 m, the eluate speed was calculated as 10.9 cm^3/h, which is almost the same as the lowest value at the initial stage of experiment as shown in Fig. 4 for test No. 2 started after 1 h wetting. Higher eluate speed at the initial stage for the other runs is thought to be caused by the heterogeneous packing in the ash layer. Actually in some tests, some large holes were found at the cut cross-section surfaces. On the other hand, in the case of Chinese ashes, larger initial eluate speed was observed, however the speed was rapidly reduced, which may be caused by the above phenomena of movement of primary particles. The rapid decrease in the eluate speed is also explained based on the Kozeny Carman equation, which involves highly sensitive dependence of the flow rate (eluate speed) on porosity and particle diameter. When porosity is changed from 0.4 to 0.2, the flow rate is

reduced to only 7%, and when the particle diameter is reduced to one quarter, the flow rate is reduced to only 6%.

Finally, the discrepancy between experimental and calculated amounts of dropping of nitric acid at the BT point, pointed out at the last part in chapter 3.3 for Chinese ashes, is discussed. One possible reason is the existence of larger particles. Ca in larger particles may not be fully leached out even at the BT point. Another possible explanation is existence of $CaSO_4$ in addition to $CaCO_3$, because it is often the case that furnace desulfurization is conducted in the fluidized bed incinerators, however data on incinerators in China are not available.

3.5. ELEMENT ANALYSES OF SAMPLES IN THE COLUMN

In the present series of the tests, the elemental analysis of the samples of the upper and bottom parts of the ash layer was conducted, only once for one run. In Figure 6, the results for four minor elements of Al, Zn, Fe and Cu are divided by the initial values in the original ash and the normalized contents, C/C_0 are plotted against the final pH shown in Table 2 for all the tests (Nos. 0–6), including tests using Chinese ashes. Hence the results are plotted from left (lower leachate pH) to right, in the order of tests No. 3 (C), 6 (B), 5 (J) and then other test stopped at neutral conditions using Japanese ash.

Among the elements we examined, the contents of Cd and Pb are the smallest as shown in Table 1, and deposition of these small amounts of elements is not thought to cause the BT phenomena. Hence the results only for the other four elements are shown in Fig. 6.

The normalized contents of all of the elements exceed unity, namely the contents of elements exceed those of the original ash before test, when the final pH of the leachate was 7.6 and 7.8. The present results are explained by the fact that most of Ca and Na are expected to be leached out from ash at pH 7.6 or 7.8, as shown in Fig. 3. As discussed in chapter 3.4, the weight fraction of salts of these elements is more than half in case of Japanese ash. Hence the contents of the other elements were increased.

The normalized contents of Fe and Cu tend to decrease upon decreasing the final leachate pH and the difference in content between the samples of the upper and bottom parts is small as shown in Fig. 6. The present observation suggests that Fe and Cu do not make deposits in the column before BT and are not the cause of BT phenomena. The behavior of copper is also suggested from batch test results of Fig. 3 that most of copper is eluate around 3 mmol/g ash of dropping of nitric acid, corresponding to pH equal 2 or higher, so the entire Cu is expected to be leached out before BT point.

Though the behavior of Fe is close to that of Cu in the column test in Fig. 6, the results for Cu and Fe in the batch test were different. The present discrepancy may be explained by the oxidation of ferrous ferric ions in the batch test conducted under the open air condition.
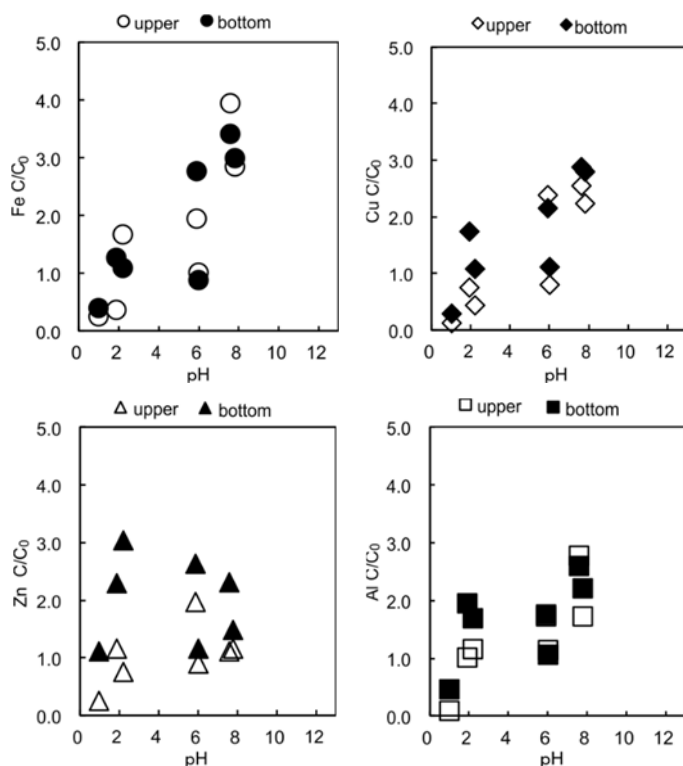
Fig. 6. Normalized contents of selected heavy metals in the samples of the upper and bottom parts
of the ash layer against the final pH of leachate (Nos. 0–6)

The effect of final pH on Zn content inside the column is shown in Fig. 6c. The content of Zn at the bottom part looks higher than that at the upper part of the bed. Furthermore the content at the bottom reaches the maximum between pH 2 and 6 or so, while that the upper part seems to be kept steady or gradually decrease. At the top of the bed, Ca is dissolved and pH is increased so Zn is dissolved but deposited soon below the upper part. Over time, the deposition part is moved downwards. In the batch test (Fig. 3) the elution of Zn starts from around pH 3 and gradually increases almost up to the final acidic condition of the leachate, which also supports the possibility of the deposition of Zn in the bed. Hence it is concluded that the presence of Zn is thought to be the most possible cause of the BT phenomena.

Considering that the elution behavior of Al is very close to that of Zn in the batch test, and that the Al content in the original ash is as high as that of Na, the deposition of Al hydroxide or salts is also thought to be one of the most possible causes of the BT phenomena. A small difference is found between the content of Al at the bottom and upper parts (Fig. 6), and the content at the bottom seems to have maximum around pH 2.

Therefore Al is also thought to be one of the elements which cause the BT phenomena though it is not as clear as in the case of Zn.

3.6. SUMMARY OF DISCUSSION ON THE MECHANISM OF BT

In the column tests of various ashes, rapid and then small decreases in the eluate speed and in the pH of the leachate are observed. At the breakthrough stage, the leachate pH sharply decreases, the eluate speed sharply increases and at the same time, elution of various minor and trace elements including some harmful elements is accelerated.

At the first stage of the experimental run, Ca, one of the major elements, is dissolved from alkaline salt $CaCO_3$ and pH of the leaching solution gradually increases, which forms the pH gradient in the column. Some of minor elements such as Zn and possibly Al dissolve at the upper part of the column after leaching out of Na and Ca and again precipitate at lower part of the column, which leads to the reduction of the flow rate of the leaching solution. After pH of leaching solution becomes lower by the termination of dissolution of Ca, these deposits are dissolved and thus, the flow rate increases, namely BT occurs. The other trace elements are also rapidly leached out by the decrease in pH in the column with increase in flow rate. In the case of Chinese ashes, though the initial diameter of ash particles are much larger than that of Japanese ash, the particles are disaggregated in the leaching process and the BT phenomena are also observed, though the observed period is shorter than that for Japanese ash both by time and by smaller amount of dropped acid.

It should also be noted that the present phenomena are highly sensitive to the physical structure such as initial wetting of fly ash, existence of the cracks, packing density and packing height, etc. and changes in the particle diameter and porosity in the bed, which makes the prediction of the occurrence time of BT difficult.

4. CONCLUSIONS

Incineration is the most popular method to treat the municipal waste. It disintegrates easily harmful organics to harmless gases. However, the elution of harmful trace elements from the incineration ash is one of the most concerned matters for environment. During acid leaching of heavy metals from municipal waste incineration ash, gradual decrease in the eluate speed (flow rate of the leachate) was observed with the gradual decrease in the pH of the leachate. Then pH of the leachate decreased sharply and eluate speed sharply increased, which was called the breakthrough phenomenon. In the present study, the mechanism of the breakthrough was elucidated from the results of measurement of elemental and particle size distribution in the column and batch leaching tests. As the results, the following mechanism was proposed.

At the first stage of experimental runs, $CaCO_3$ is dissolved and pH profile in the bed is formed. Some of the minor elements such as Zn and Al dissolved in acid at the upper

column are precipitated at the bottom of the column, leading to the reduction of flow rate of the leaching solution. After leachate pH becomes lower by the termination of dissolution of Ca, these deposits are dissolved and thus, the flow rate increases. Most of the trace elements behave as such which causes the increase in elution of harmful elements.

Though the occurrence of BT can be predicted by the amount of acid passed through the ash layer, the prediction of flow rate through the layer and time of BT is difficult because various packing conditions and change in the particle diameter strongly affect the flow rate. Hence some drastic increase in the leaching of harmful trace elements may occur even after the long period of pseudo stable dissolution behavior in the landfill site.

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