

EVALUATION OF LONG TERM CHANGES IN ALKALI ELUTION RATE FROM BOTTOM ASH

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ABSTRACT

In order to evaluate the alkali elution rate from MSW incineration bottom ash after a long time has passed, a sequential leaching test of 6 sizes of sieved ashes was conducted with nitric acid as a solvent. In order to reduce pH rapidly, the pH of the solvent was stepwise changed to 1.7, 2.7 and 4. After changing the pH of the solvent to 4, the pH of the leachate remained constant at about 4 where the leaching time was 1 day, and the pH of the leachate remained at about 7 where the leaching time was more than 2 days, with each particle size of bottom ash. The total alkali elution rate (*RA*) was affected by the leaching time. *RA* remained constant at 2×10^{-2} mmol/g/d where the leaching time was 1 day, and at $4 \cdot 6 \times 10^{-3}$ mmol/g/d where the leaching time was more than 2 days with each particle size. The total released alkalis reached the saturation point of 0.03-0.04 mmol/g.

Key Words:

Bottom ash, Alkalinity, Sequential leaching test, Particle size of bottom ash

1. INTRODUCTION

The pH in a landfill layer affects many phenomena in the landfill layer such as dissolution/precipitation of heavy metals, adsorption/desorption of hazardous compounds, activities of microorganisms, CO₂ absorption/emission, etc. On the other hand, some inhabitants around a landfill site that has been constructed or is under consideration are anxious for the environmental safety of the landfill site, and often oppose the construction of the new landfill site¹⁾. Therefore, it is very important to predict the pH of leachates for the risk assessment of landfilled wastes, especially MSW incineration bottom ash, which contains hazardous heavy metals.

There has been much research on the dissolution of heavy metals as a function of pH²⁻⁵⁾, which indicated that the potential for dissolution of heavy metal rises with decrease in

pH. In order to predict the pH of a leachate, the amount and rate of alkali supply is important. Although many researchers measured the acid neutralization capacity (ANC) to find the amount of alkali supply^{2,3,6-8)}, there has been little research on the alkali supply rate. Dijkstra et. al.³⁾ successively predicted the pH of leachate in percolation test using a geochemical and transport model. However, for the duration of their experiments, L/S (liquid to solid ratio) was only 10, and the pH of the leachate was high, 11.2.

This study focuses on the alkali supply (elution) from MSW incineration bottom ash during a long period in which the pH of the leachate is almost neutral. In order to reduce the alkalinity in the bottom ash, a sequential bath leaching experiment was conducted with an L/S ratio of 100, using a nitric solution with a pH less than 4. The main objective was to evaluate the alkali elution rates from the bottom ash under the condition of neutral pH.

2. EXPERIMENTS

2.1 Bottom ash

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Freshly quenched bottom ash was obtained from an incineration plant of MSW (stoker type, capacity 300 ton/day). Prior to the leaching test, the bottom ash was dried at 105 °C for 1 day and sieved into 6 particle sizes: 5-3 mm, 3-2 mm, 2-1 mm, 1-0.5 mm, 0.5-0.125 mm, and less than 0.125 mm.

2.2 Leaching test

A sequential leaching test was conducted using acid solvent. 5 g of sieved ash and 500 mL ($L/S=100$) of solvent were introduced into a plastic bottle and shaken at 200 rpm for a specific time, and separated with a filter having a pore size of 1 mm. The ash on the filter was washed into the bottle with the solvent that was used for the next leaching. The rest of the solvent was added into the bottle until there was a total of 500 mL, and the leaching test was repeated. In this paper, leaching time was defined as the time spent on one leaching. For the first 5 days, leaching time was 1 day, and after the 5th day leaching time was irregular. Distilled water was used as the solvent for the first leaching. After the first leaching, a nitric solution of pH 1.7 was used until the pH of the leachate reached 7, and a nitric solution of pH 2.7 was used until it reached 4 in order to eliminate the easily dissolved alkali and drop the pH of the leachate to neutral. Once it reached 4, a pH 4 nitric solution was used as the solvent except where particle size was less than 0.125 mm. Where particle size was less than 0.125 mm, a rapid increase in pH occurred after the change in the solvent pH to 4; therefore, solvents with pH 2.7 and 4 were used one after the other. After 29 days, only the pH 4 solvent was used.

2.3 Alkalinity

The pH of the leachate and solvent were measured with a pH meter. Alkalinity of the filtrate (AF) was measured by titration with nitric acid to pH 4, expressed in mmol/g-ash. The amount of H^+ in the solvent (AS) which was consumed in one leaching was calculated as follows;

AS expressed in mmol/g = (amount of H^+ in solvent - amount of H^+ in filtrate)/weight of ash (1)

Total alkalinity eluted from the ash for one leaching (AT) was defined as the sum of AF and AS .

The elution rate of total alkalinity, RA , was defined as follows;

$$RA_i \text{ (mmol/g/day)} = AT_i / (T_i - T_{i-1}) \quad \text{at } t = (T_i + T_{i-1}) / 2$$

(2)

where i is i th sampling and T is the sampling time.

3. RESULTS AND DISCUSSION

3.1 pH

The changes in pH of the leachate with time are shown in Figure 1. The pH of the first leachate, which was the natural pH of the ash because distilled water was used as the solvent for the first leaching, was higher in bottom ash with smaller particle sizes. This result was different from that of Bendz et al.⁹⁾ because the bottom ash that they used had been subjected to aging and weathering, whereas the bottom ash used in this study was fresh. Sakanakura¹⁰⁾ reported that there was surface wash-off in the first leaching of a sequential leaching test. In general, the specific surface area is increased with decrease in particle size, so this result indicates that alkali on the particle surface is dissolved in the first leaching.

With a solvent pH of 4 (used after the 28th day for a particle size of less than 0.125 mm) and a leaching time of more than 2 days, the pH of the leachate was kept almost constant at about 7 for any particle size. Especially, for a particle size less than 0.125 mm, the pH of the leachate was about 7 at day 119. On the other hand, where the leaching time of was 1 day, after 20 days the pH of the leachates were about 5. Especially, for a particle size of less than 0.125 mm the pH of the leachate became about 5 at day 120. The pH of about 7 indicated that the bottom ash used in this study was not aged because the pH was less than 8.5, which would be the result of equilibrium with atmospheric CO_2 and calcite ($CaCO_3$)⁹⁾

The amount of acid added as solvent until the pH of the solvent changed to 4 ranged from 3.3 mmol/g for a particle size of 5-3 mm to 8.5 mmol/g for a particle size of less than 0.125 mm. Setting the depth of a landfill layer to be 10 m, we assume that density of landfill layer is 0.5 ton/m³, the annual rain fall is 2 m, which is average in Japan, and the only acid source is acid rain of pH 4, whereby the annual supply of acid is calculated to be 4×10^5 mmol/g/y. Dividing the amount of acid mentioned above by this figure, a period of 83,000 - 210,000 years is obtained. Therefore, the conditions after the pH of the solvent changes to 4 are realized far in the future.

3.2 Alkalinity

The changes in AS are shown in Figure 2. The results of the first leaching were neglected hereafter because this research focused on the long term alkali elution rate. AS depended on the pH of the solvent, and not on the particle size or the leaching time, because the pH of the leachate was higher than that of the solvent, so that the second term in the parentheses in Equation (1) can be neglected. AS was 2, 0.2, and 0.01

mmol/g for a solvent pH of 1.7, 2.7, and 4, respectively.

The changes in AF are shown in Figure 3. With a solvent pH of 4, AF remained almost constant with time, and the values were almost the same with any particle size. Figure 4 shows the comparison of observed AF and AF calculated based on the observed pH in the filtrate and assuming that only strong base remained in the filtrate where pH was more than 7,

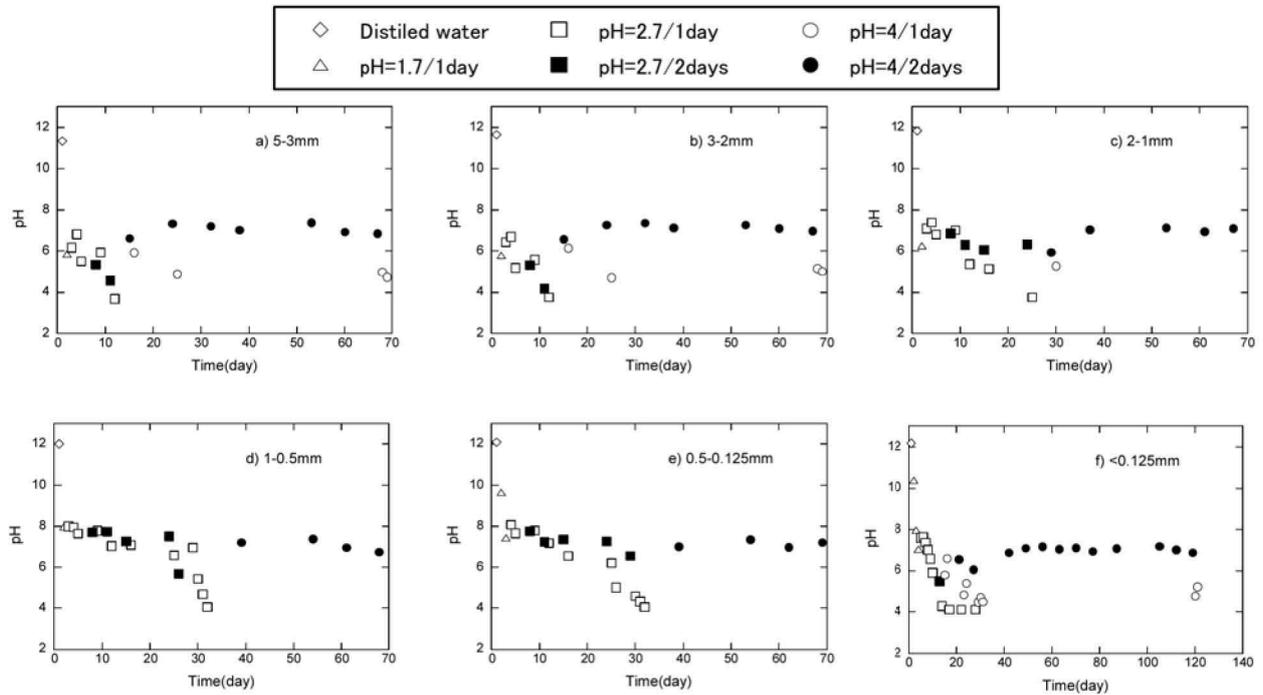


Figure 1. Change in pH of leachate ('1 day', leaching time of 1 day; and '2 days', leaching time of more than 2 days)

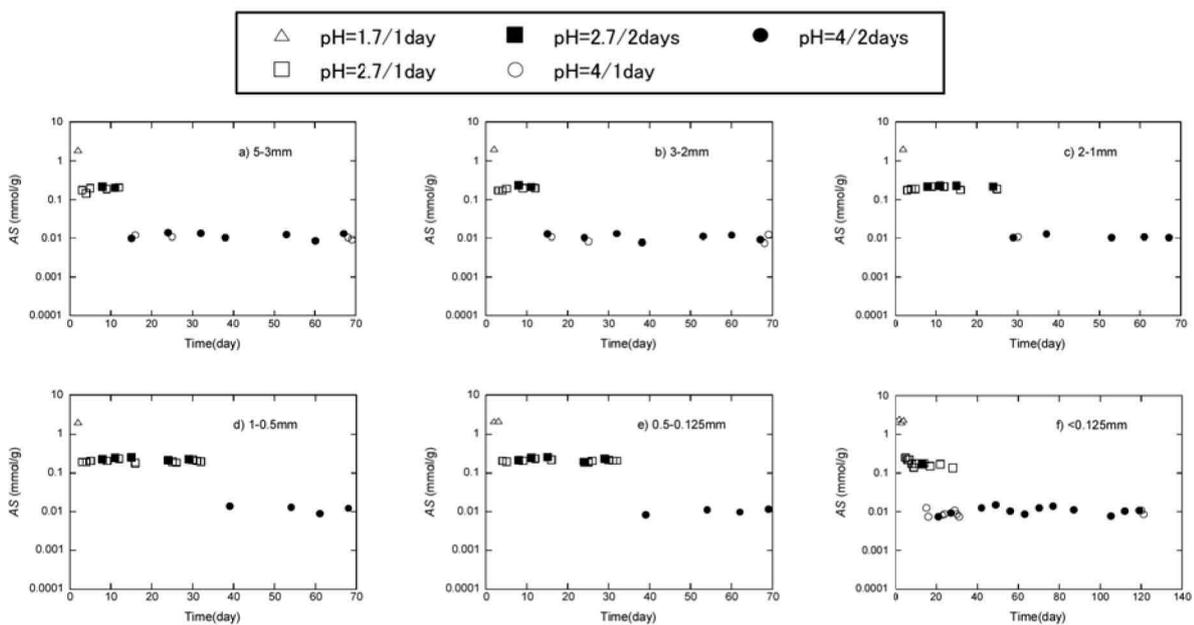


Figure 2. Change in AS of leachate ('1 day', leaching time of 1 day; and '2 days', leaching time of more than 2 days)

or that nitric acid used as a solvent only remained where pH was less than 7. For example, the calculated *AF* was 0.0101 mmol/g for a pH of 8, 0.01 mmol/g for a pH of 7, and 0.0099 mmol/g for a pH of 6. This figure shows that most of the observed *AF* values were larger than the calculated *AF*. This means that some alkali materials other than strong bases were included in the filtrate. Therefore, some weak bases remained in the filtrate.

The changes in *AT* are shown in Figure 5. For solvent pHs

of more than 2.7, the *AT* was similar to the *AS* because the *AS* was more than one order of magnitude greater than *AF*, so that *AF* was negligible. For a solvent pH of 4, the behaviour of *AT* was similar to that of *AF* because *AS* and *AF* were the same order of magnitude, and *AS* was almost constant. As mentioned above, the amount of acid added until the pH of the solvent changed to 4 was equivalent to the acid added over 83,000 - 210,000 years, so that the bottom ash would elute alkali continuously long into the future.

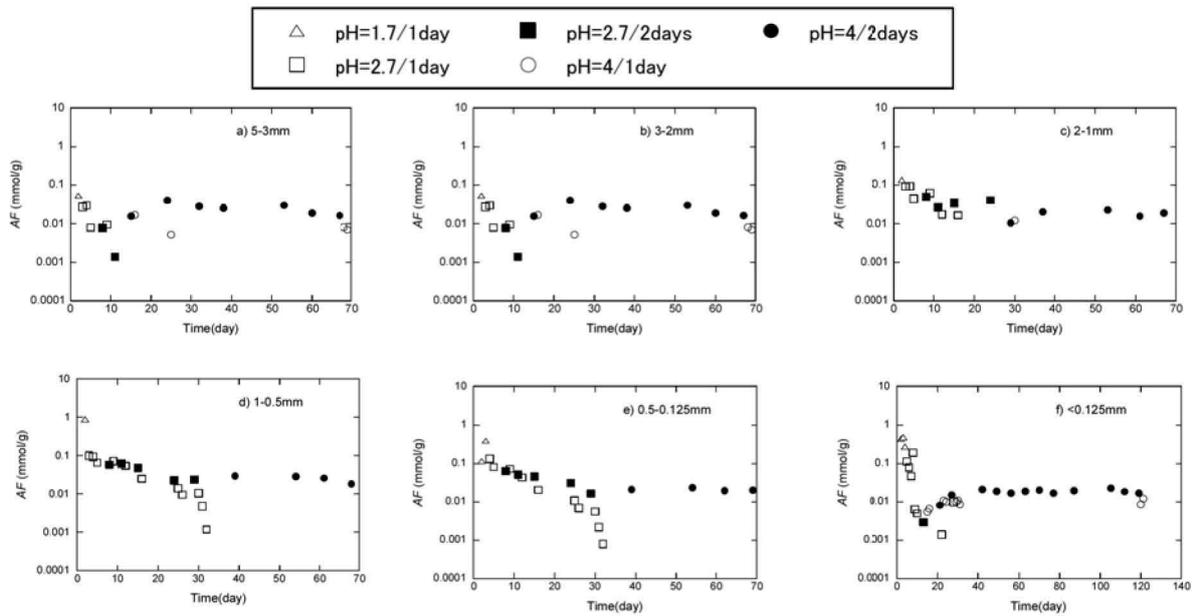


Figure 3. Change in *AF* of leachate ('1 day', leaching time of 1 day; and '2 days', leaching time of more than 2 days)

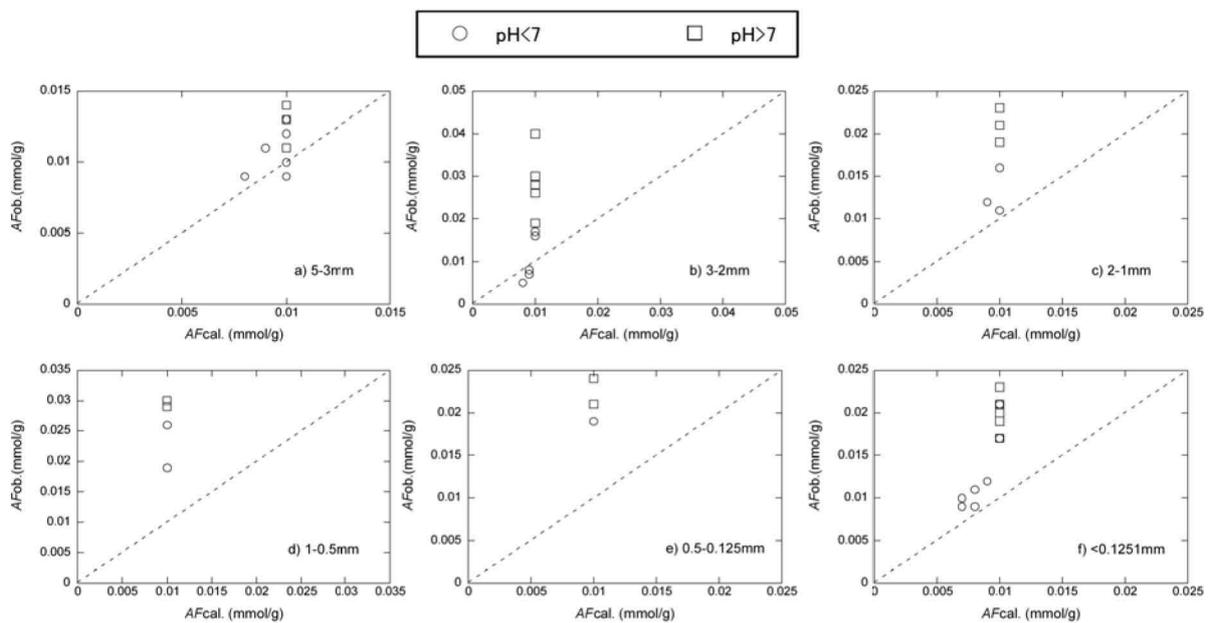


Figure 4. Comparison of *AF* observation with *AF* calculation

3.3 Elution rate of alkalinity

RA is shown in Figure 6. Most of the RA where the leaching time was 1 day was higher than that where the leaching time was more than 2 days. Figure 7 shows the relationship between AT and the leaching time. The lines in Figure 7 were calculated using the following equation:

$$AT = a \{1 - \exp(-bt)\} \quad (3)$$

where t was the leaching time, and a and b were constants.

AT increased with increase in leaching time for about 3 days, after which AT remained almost constant. As Dijkstra (2006) suggested, the increase in AT with time might be caused by the slow dissolution of alkali from the bottom ash matrix.

Where the solvent pH was 4, the average RA where the leaching time was 1 day had a higher value than that where the leaching time was more than 2 days as shown in Table 1, and the average RA hardly varied at all with particle size at 2×10^{-2} mmol/g/d where the leaching time was 1 day, and at $4-6 \times 10^{-3}$ mmol/g/d where the leaching time was more than 2 days. This

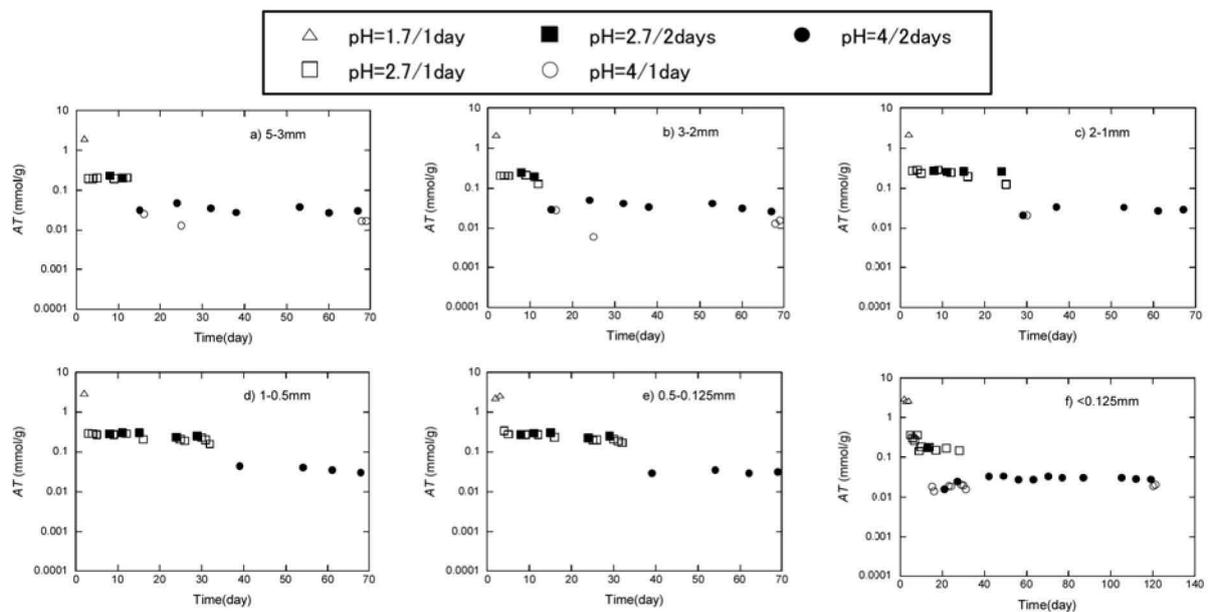


Figure 5. Change in AT of leachate ('1 day', leaching time of 1 day; and '2 days', leaching time of more than 2 days)

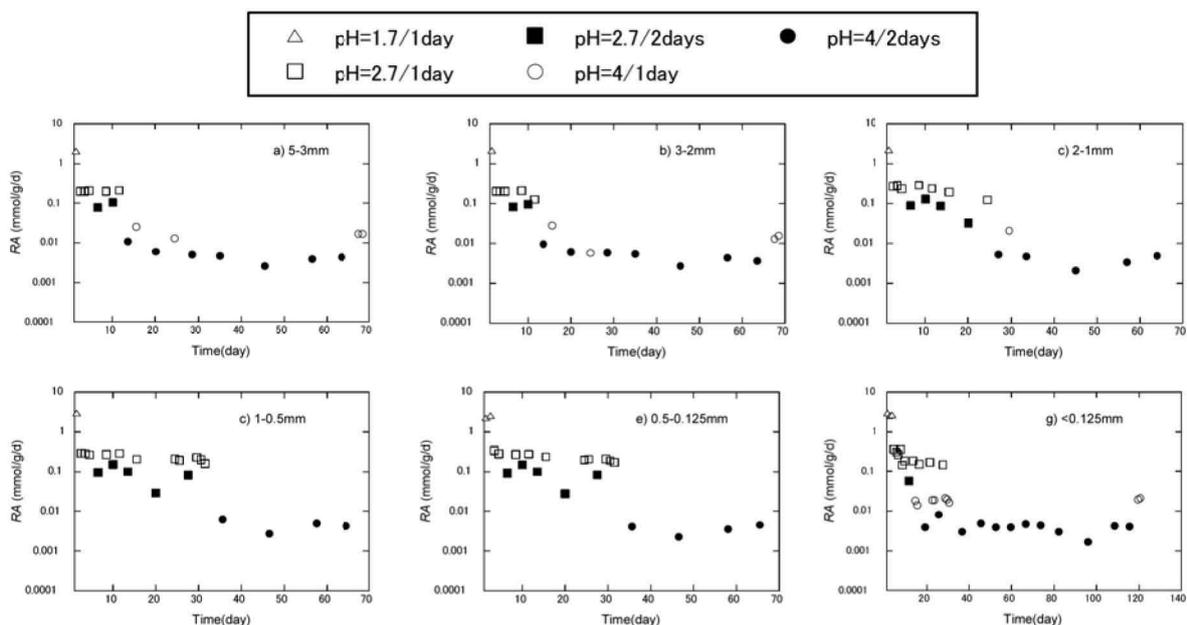


Figure 6. Change in RA of leachate ('1 day', leaching time of 1 day; and '2 days', leaching time of more than 2 days)

Table 1. Average of *RA* for a solvent pH of 4 (mmol/g/d)

Particle size	5-3mm	3-2mm	2-1mm	1-0.5mm	0.5-0.125mm	<0.125mm
Leaching time of 1 day	1.8×10^{-2}	1.9×10^{-2}	2.1×10^{-2}	-	-	1.9×10^{-2}
Leaching time of more than 2 days	5.4×10^{-3}	5.5×10^{-3}	4.1×10^{-3}	4.6×10^{-3}	3.7×10^{-3}	3.8×10^{-3}

result shows that the elution rate was independent of the particle size of the bottom ash. The reason might be the increase in the specific surface area of a large particle by breaking into small ones owing to crashing of particles with each other during extended shaking and/or the decrease in the mass transfer coefficient of small particles because a small particle is easy to move along with the solution and the relative velocity between particle and solution is low. Figure 7 suggests that a saturation point of released *AT* exists, at 0.03-0.04 mmol/g. Unfortunately, in this study the experiments were conducted under the same *L/S*, so that we could not determine whether the concentration or the release amount of total alkali was saturated.

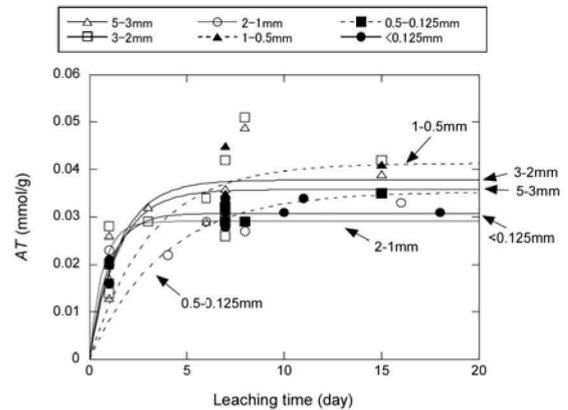
5. CONCLUSIONS

To evaluate alkali elution rate from the MSW incinerator bottom ash over a long time period, a sequential leaching test was conducted with nitric acid as a solvent. The pH of the solvent was stepwise changed to 1.7, 2.7 and 4. The following conclusions were obtained.

- 1) The pH in the leachate from the bottom ash would remain constant, at 5-7, for more than 83,000 years, regardless of the particle size of the bottom ash.
- 2) The elution rate of total alkalinity was affected by the leaching time; it was 2×10^{-2} mmol/g/d where the leaching time was 1 day and $4-6 \times 10^{-3}$ mmol/g/d where the leaching time was more than 2 days.
- 3) The particle size of bottom ash scarcely affected the elution rate of total alkalinity at all.
- 4) The saturation point of the total released alkali, 0.03-0.04 mmol/g, is reached during leaching where the leaching time was 3 days.

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Figure 7. Change in *AT* with leaching time

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