

(48) CO₂ sequestration capacity based on mineralogical composition of MSWI bottom ash and reactivity of each Ca-containing minerals

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Municipal solid waste incineration (MSWI) bottom ash includes a large proportion of Ca-containing minerals (20%-30% CaO by mass), which is a potential source for sequestration of CO₂. Despite the abundance of calcium in bottom ash, not all of them can be carbonated directly. Therefore it is important to make clear the chemical proportion of various Ca-containing minerals in bottom ash. ANC (acid neutralization capacity) experiment of the bottom ash was an effective approach for stepwise dissolution of Ca-containing minerals with the aid of analyzing ANC residuals and associated Ca²⁺ concentrations in equilibrium solutions. Consequentially, nearly 45% of calcium in bottom ash was proved to be easily soluble, decalcified, and furthermore theoretically carbonated. To identify the real sequestration capacity of CO₂, lab-scale accelerated carbonation was performed using freshly quenched bottom ash (from Seibu Incineration Plant, Fukuoka, Japan). Finally it was proved that 1.85 mol Ca²⁺/kg bottom ash can be carbonated, and accordingly the sequestration capacity of bottom ash was determined to be 1.32 mol CO₂/kg bottom ash by subtracting original carbonate in specimens.

Key Words : carbonation, ANC, CO₂ sequestration

1. INTRODUCTION

Global warming has become a severe problem due to the increasing CO₂ content in the Earth's atmosphere. Many researchers have been searching for effective methods to solve this problem, including in-situ mineral sequestration (long-term geological storage) and ex-situ mineral sequestration (artificially accelerated CO₂ sequestration). Most calcium silicates minerals are known to readily react with CO₂, and silicate minerals is responsible for over half of carbonic acid consumption by continental weathering¹⁾. Besides, ex-situ artificially accelerated CO₂ sequestration methods were also popularly investigated. Montes-Hernandez²⁾ invented a sequestration technology using coal combustion fly ash for sequestration of CO₂.

In Japan, nearly 80% of municipal solid waste was incinerated for the purpose of decreasing volume, reducing weight and safe disposal. As a result, about 5.3-5.7 million tons of municipal solid waste incineration (MSWI) residuals were generated annually from 1997 to 2006 (calculated from

Ministry of Environment of Japan, 2006). Of all the MSWI residuals, more than 80% were disposed in landfill site; only 10% was reused by industries in Japan due to the strict law in consideration of potential pollution to the environment and human health posed by reutilization of MSWI residuals. MSWI residuals can be roughly divided into bottom ash and fly ash. This paper only focused on bottom ash. Based on mineralogical analysis conducted previously, MSWI bottom ash mainly contains series of Ca-containing minerals, e.g. lime (CaO), calcite (CaCO₃), portlandite (Ca(OH)₂), hydrocalumite (Ca₄Al₂O₆Cl₂·10H₂O), hydrophilite (CaCl₂), gehlenite (Ca₂Al₂SiO₇), plagioclase feldspar ((Ca,Na)Al₂Si₂O₈), tricalcium aluminate (3CaO·Al₂O₃), gypsum (CaSO₄·2H₂O); and also calcium-free minerals, like quartz (SiO₂), hematite (Fe₂O₃), halite (NaCl) and so on. However, there are still many complex silicates and oxides remain uncertain³⁻⁴⁾. In addition, composition of these Ca-containing minerals also remains uncertain due to the difficulty of quantitative mineral analysis. Of all the Ca-containing minerals, calcite is the most important long-term buffer in MSWI bottom ash as it

buffers solutions during percolation⁵⁻⁷. The pH value of fresh MSWI bottom ash is usually in the range of 11-12.6⁷⁻¹¹. This highly alkaline bottom ash was rapidly weathered (including function of hydration, dissolution, carbonation, etc.), of which carbonation of Ca-containing minerals by CO₂ sequestration from atmosphere was quite important.

Up to now several researches had performed experiments in conditions of higher CO₂ pressure or higher temperature aiming at clarifying the capacity for CO₂ sequestration¹²⁻¹⁴ by MSWI bottom ash. Based on previous research works, the real carbonate-content in bottom ash usually in the range of 0.22-0.82 mol CO₂/kg bottom ash, which was only a small percentage of Ca content in bottom ash (2.5-4.5 mol Ca/kg bottom ash)⁷. It means that only a few amount of calcium in bottom ash are related with carbonation reaction during weathering of bottom ash. This can be ascribed to different reactivity of Ca-containing minerals. It is well known that different chemical forms of Ca-containing minerals have different weathering rate: some minerals can be easily dissoluble and carbonated, which need a short time for final exhausting, like lime, portlandite, and some calcium silicate hydroxide; while other Ca-containing minerals may take a longer time for decalcification (decalcification was dissolution of Ca-containing minerals), thus needs a longer time for carbonation. Although CO₂ sequestration capacity of MSWI bottom ash should differ from one sample to another, there is no theoretical explanation of CO₂ sequestration capacity due to lacking of scientific knowledge on quantitative composition of Ca-containing minerals in MSWI bottom ash.

The objective of this study is to investigate CO₂ sequestration capacity of MSWI bottom ash based on mineralogical composition of MSWI bottom ash and reactivity of each Ca-containing minerals.

2. MATERIALS AND METHODS

2.1 Materials

Freshly quenched MSWI bottom ash was taken from Seibu Incineration Plant, Fukuoka, Japan, which commenced operation since April 1992, with incineration capacity of 750 t/d (250 t/24 hours×3 units) and site area of 143,500 m². Municipal solid waste, and some shredded combustible bulky waste, mainly collected in the western district of Fukuoka city, are incinerated in this plant. MSWI bottom ash, aggregated from combustion grate, economizer and gas/air heat exchanger, was quenched and then discharged into ash pit for short time storage. The noncombustible and unburned materials in bottom ash, such as fabrics, cans, wood, rubber, ceramics and bricks, metallic items etc., which accounts for a proportion of less than 2%, were removed by sieve with opening diameter of 31.5mm. Mineralogical

analysis was performed via X-ray diffraction (XRD) analysis using Cu K α radiation at 30kV and 40mA, and chemical composition was determined by X-Ray Fluorescence (XRF).

2.2 Methodology for chemical distribution of Ca-containing minerals

(1) List of various forms of Ca-containing minerals

In order to clarify the quantitative distribution of Ca-containing minerals in bottom ash, some simplifications were made (all the minerals are based on XRD analysis):

a) Ca-containing minerals existed mainly in eight forms: portlandite (Ca(OH)₂) (Lime can be easily transformed to portlandite once contact with water, so it can be viewed to be an equivalent of portlandite), calcite (CaCO₃), easily-soluble cementitious analog, hardly-soluble cementitious analog, hydrocalumite (Ca₄Al₂O₆Cl₂·10H₂O), gehlenite (Ca₂Al₂SiO₇), plagioclase feldspar ((Ca,Na)Al₂Si₂O₈), anhydrite (CaSO₄) and/or gypsum (CaSO₄·10H₂O).

b) As mentioned before, some Ca-silicates were uncertain. For simplification, this kinds of minerals was classified into two groups: easily-soluble cementitious analog, which dissolves in solutions when solution pH is above 7.5 (including hydrated calcium silicate and some non-hydrated silicate); and hardly-soluble cementitious analog, which dissolves when solution pH is in the range of 4.5-7.5 (mainly non-hydrated silicate), with representative chemical formula listed in Table 1.

c) Cl⁻ in bottom ash existed only in two forms, easily soluble form (NaCl, KCl, and MgCl₂), which dissolves in water rapidly and completely when contact with pure water; another one is hardly soluble form (hydrocalumite), which hydrolyzes and releases Ca²⁺, Al³⁺ and Cl⁻ into acid solutions.

(d) All SO₄ are equated to anhydrite and/or gypsum.

On basis of above assumptions, the list of Ca-containing minerals was shown in Table 1.

(2) Acid neutralization capacity

Batch titration method was used for determining acid neutralization of bottom ash as proposed by C. Annette Johnson⁷. Freshly quenched bottom ash was firstly freeze dried and milled to powder (<100 μ m); subsequently, bottom ash (2.5g) and different volumes of 1 M HNO₃ (0-10 mmol H⁺/g bottom ash) was added to 35 polyethylene bottles containing 250 ml deionized water for obtaining a series of solutions with different equilibrium pH. The prepared bottles were shaken by reciprocator at 200 rpm for 24 hours, settled down, and filtrated using 0.45 μ m membranes. All the filtrates were subjected for pH measurement, and some typical filtrates were used for analysis of Ca²⁺, Na⁺, K⁺,

Table 1 List of representative Ca-containing minerals in bottom ash

| No. | Components | Representative Chemical formula |
|-----|---|---|
| ① | Portlandite | $\text{Ca}(\text{OH})_2$ |
| ② | Calcite | CaCO_3 |
| ③ | Easily-soluble cementitious analog(ES-CA) | $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ $\text{CaO} \cdot \text{SiO}_2$ |
| ④ | Hardly-soluble cementitious analog(HS-CA) | $\text{CaO} \cdot \text{SiO}_2$ |
| ⑤ | Gehlenite | $\text{Ca}_2\text{Al}_2\text{SiO}_7$ |
| ⑥ | Hydrocalumite | $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ |
| ⑦ | Gypsum/anhydrite | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ |
| ⑧ | Plagioclase | $(\text{Ca}, \text{Na}) \text{Al}_2\text{Si}_2\text{O}_8$ |

Mg^{2+} , Cl^- and SO_4^{2-} ; Solid residues were freezing dried, manually milled then subjected to XRD analysis.

(3) Method for quantitative analysis of CO_2 -content in bottom ash

Freezing dried bottom ash (3g) was fully milled ($<100\mu\text{m}$), then allowed to react with 1 M H_2SO_4 solution. The mixed solutions was heated to 150°C , generated CO_2 was absorbed by 160 ml $\text{Ba}(\text{OH})_2$ solution (0.047 M). Un-reacted $\text{Ba}(\text{OH})_2$ was titrated by 0.02M H_2SO_4 , and the volume consumed was written down. Use Na_2CO_3 as a standard CO_2 -containing chemical to substitute bottom ash samples, a curve depicting the relationship of carbonate content and volume of H_2SO_4 consumed for titration were obtained. Finally, the carbonate content of bottom ash samples could be calculated from this curve.

(4) Integrated flow chart for analysis of chemical distribution of Ca-containing minerals

Based on the results of ANC test and simplifications and assumptions made above, integrated flow chart for analysis of chemical distribution of Ca-containing minerals was shown in Fig.1 with the support of CO_2 -content analysis and XRD analysis. Detailed explanation was made in the following RESULTS and DISCUSSION section.

2.3 Lab-scale accelerated carbonation

(1) First-step carbonation

MSWI bottom ash (10 kg with 24% water content) was uniformly placed in a stainless steel container ($40\text{cm} \times 25\text{cm} \times 10\text{cm}$) then incubated at 65°C . Water was added to bottom ash at an interval of 10 days, and the water content periodically alternated from 24% to 2%. The repeated operation of water addition and evaporation at 65°C created a better circumstance for contact and reaction of bottom ash, water and carbon dioxide, thus enhance the carbonation rate and degree under a CO_2 partial pressure of about 0.035 atm. Sub-samples were periodically taken and subjected to CO_2 -content determination and JLT46 leaching test (Japanese leaching test 46, L/S ratio 10, and reciprocating time 6h). pH of solutions from JLT46 was measured; Ca concentration was determined using ion chromatography (Dianex, DX-120).

(2) Second-step carbonation

Second-step carbonation was conducted using partially carbonated bottom ash obtained in the first step experiment. Experiment device was specially made to ensure air-tightness. CO_2 concentration in the device was kept at 50% by mixing with 50% nitrogen. The partially carbonated bottom ash was crushed to powder ($<100\mu\text{m}$); Water content was adjusted to be 20%; Humidity during carbonation process maintained at 60%. After 144 hours carbonation, CO_2 -content was determined.

3. RESULTS AND DISCUSSION

3.1 Elemental and mineralogical compositions of bottom ash

The chemical compositions of MSWI bottom ash was determined by XRF technology as listed in Table 2. As a typical cement-based solid waste, the potential CO_2 sequestration capacity of bottom ash was calculated to be 5.19 mol CO_2/kg bottom ash, using equation (1) with combination of chemical composition analysis. Assuming that CaO was transformed to CaCO_3 , SO_3 to CaSO_4 , MgO to MgCO_3 , Na_2O to NaHCO_3 , K_2O to KHCO_3 at one atmosphere pressure of CO_2 ¹⁵⁾.

$$\text{CO}_2(\text{mol/kg}) = [(\text{CaO}\% / 56 - \text{SO}_3\% / 80) + \text{MgO}\% / 40 + 2 \times \text{Na}_2\text{O}\% / 62 + 2 \times \text{K}_2\text{O}\% / 94}] \times 1000 \quad (1)$$

Of all the sequestered CO_2 , 75% was contributed by Ca-containing minerals, the other proportion was either due to existence of alkali metals, e.g. Na, Mg, K, or due to presence of some S-containing minerals. The author here only focused on the Ca-containing minerals. On the basis of XRD and XRF analysis, all the Ca-containing minerals was 4.44 mol Ca^{2+}/kg bottom ash, mainly including calcite (CaCO_3), portlandite ($\text{Ca}(\text{OH})_2$), lime (CaO), hydrocalumite ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$), cementitious analog, gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), and plagioclase ($(\text{Ca}, \text{Na})\text{Al}_2\text{Si}_2\text{O}_8$).

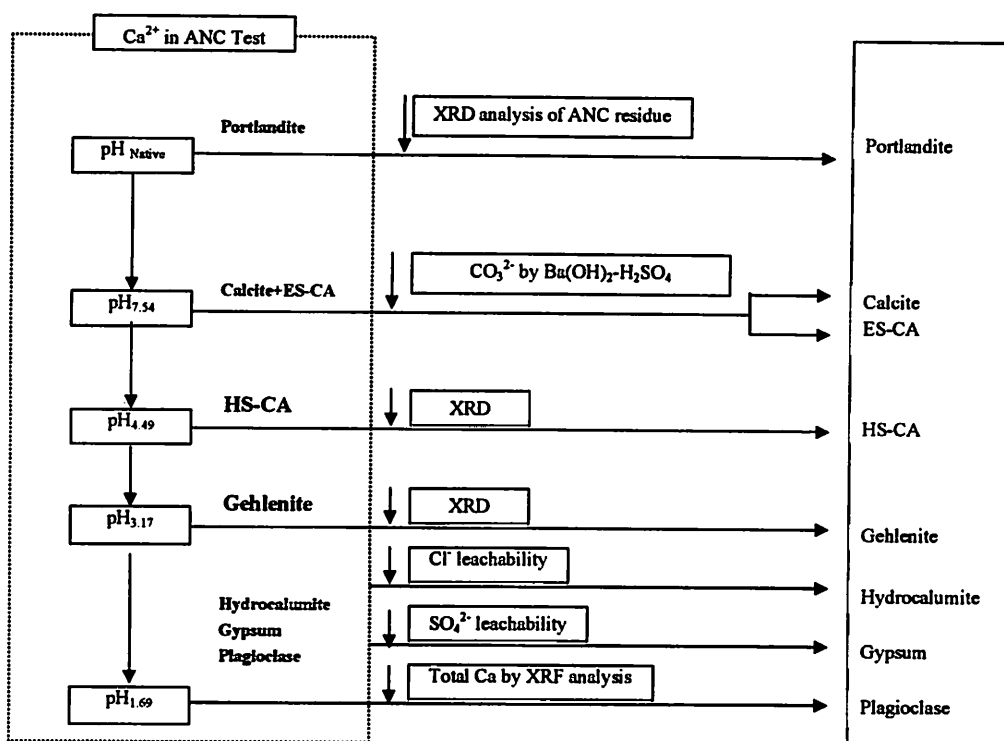


Fig.1 Flow chart of experiment procedure for analysis of chemical distribution of Ca-containing minerals. Ca^{2+} in ANC test: the concentration of Ca^{2+} in filtrates derived from ANC test; $\text{pH}_{\text{Native}}$: the pH value of filtrate with no acid addition to the polyethylene bottle in ANC test; $\text{pH}_{7.54}$, $\text{pH}_{4.49}$, $\text{pH}_{3.17}$ and $\text{pH}_{1.69}$ indicate filtrates with equilibrium pH values of 7.54, 4.49, 3.17, and 1.69 respectively in ANC test; The minerals with bold font in the left column means the minerals dissolved with pH decreasing, e.g. Gehlenite in bottom ash tends to dissolve when pH of filtrate decreased from 4.49 and totally disappear when pH is 3.17 as detected by XRD; The middle column are some assistant method which are explained in details in the following content; and the right column are the final results, e.g. the amount of gehlenite can be calculated from the concentration difference in ANC filtrate between $\text{pH}_{4.49}$ and $\text{pH}_{3.17}$. (More details about this figure please refer to RESULT and DISCUSSION 3.2(2)).

Si_2O_5). etc., as listed in Table 1.

3.2 Results of acid neutralization capacity

(1) Batch titration results

The results of batch titration were shown in Fig.2 as a function of acid added and equilibrium pH. The initial solution pH was 12.05, slightly lower than the pH of saturated $\text{Ca}(\text{OH})_2$. With acid addition, solution pH dramatically decreased to week acidic 5.3, followed by a congruent decreasing from 5.3 to 1.7. $\text{ANC}_{7.5}$ (titration ending point at pH 7.5) was 3.75 mmol H^+ /g bottom ash in this research work, which was much higher than that reported by other researchers, e.g. 0.6-2.3 mmol H^+ /g bottom ash ^{7,9)}. This discrepancy could be ascribed to diversity of original properties (e.g. pH, chemical component etc.) and dissimilitude of titration methods.

(2) Concentrations of Ca^{2+} , Na^+ , K^+ , Mg^{2+} and Cl^-

in equilibrium solutions of bottom ash

Dissolution of Ca^{2+} , Na^+ , K^+ , Mg^{2+} and Cl^- from bottom ash was shown in Fig.3. As proposed by Johnson C.A. ⁷⁾, titration end point $\text{ANC}_{7.5}$ can be defined as the pH at which the hydroxides and soluble basic silicate hydrates and carbonate have been consumed. Here we term all the dissolved Ca-containing minerals before pH 7.5 as “easily soluble minerals”. The easily soluble Ca-containing minerals in MSWI bottom ash was 2.02 mol Ca^{2+} /kg bottom ash (see Fig.3-a), which was nearly half of the total content 4.44 mol Ca^{2+} /kg bottom ash.

With acid addition, Ca^{2+} was gradually released from soluble or leachable Ca-containing minerals according to equations (2)-(7):

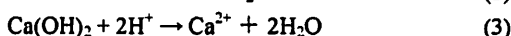
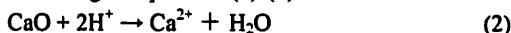
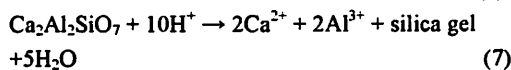
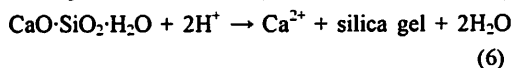
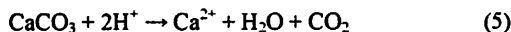


Table 2 Main composition of bottom ash determined by XRF

| Main composition | Average of triplicate (%) | Standard deviation(1σ) |
|--------------------------------|---------------------------|------------------------|
| SiO ₂ | 46.60 | 1.87 |
| TiO ₂ | 1.99 | 0.08 |
| Al ₂ O ₃ | 12.34 | 0.48 |
| FeO | 4.16 | 0.31 |
| MnO | 0.11 | 0.01 |
| MgO | 2.61 | 0.14 |
| CaO | 24.87 | 2.04 |
| Na ₂ O | 2.60 | 0.21 |
| K ₂ O | 2.29 | 0.09 |
| S | 0.27 | 0.03 |



Ca²⁺ concentration in extracted solution with acid addition of 0 mmol/g bottom ash was 5.37 mmol/L, which was quite close to Ca²⁺ concentration calculated from dissolution equilibrium of Ca(OH)₂ at pH of 12.05 (assuming OH⁻ was only from ionization of portlandite). As mentioned before, the extracted solution with pH 12.05 is under-saturated with respect to Ca(OH)₂. On basis of this knowledge we assume Ca(OH)₂ was totally leached out and dissolved when L/S ratio was 100, and quantitative content of Ca(OH)₂ in bottom ash was computed to be 0.54 mol Ca²⁺/kg bottom ash.

Calcite in fresh bottom ash was determined to be 0.53 mol Ca²⁺/kg bottom ash by Ba(OH)₂-H₂SO₄ titration method. And easily-soluble cementitious analog was calculated to be 0.835 mol Ca²⁺/kg bottom ash.

0.312 mol Ca²⁺/kg bottom ash was leached out with acid addition from 3.75 to 5.50 mmol H⁺/g BA (corresponding pH value 7.54 to 4.49), except for the proportion contributed by dissolution of gypsum and hydrocalumite, still 0.194 mol Ca²⁺/kg bottom ash could probably be ascribed to dissolution of hardly-soluble cementitious analog (Fig.3-a).

In combination with XRD analysis of ANC residues, gehlenite (Ca₂Al₂SiO₇) totally disappeared when acid addition increasing from 5.50 mmol H⁺/g bottom ash to 10 mmol H⁺/g bottom ash (pH from

4.49-3.17), as shown in Fig.4. The associated leaching concentration of Ca²⁺ gradually increased by 0.75 mol Ca²⁺/kg bottom ash, which can be roughly attributed to dissolution of gehlenite (Ca₂Al₂SiO₇).

Accessibility of Ca-containing minerals to decalcification was highly related to the stability of its chemical forms. Some minerals in bottom ash are very difficult for decalcification, e.g. at pH 3.17, gehlenite (Ca₂Al₂SiO₇) totally dissolved in water, however, plagioclase ((Ca,Na)Al₂Si₂O₈) had no obvious change within 24-hour extraction, as shown in Fig.4. The residual fraction of Ca²⁺ still remained in bottom ash when equilibrium solution pH was less than 3.17 could be totally viewed as plagioclase feldspar.

(Ca₄Al₂O₆Cl₂·10H₂O) gradually dissolved with more acid addition, as indicated by increasing of Cl⁻ as a function of acid addition (see Fig.3-b). The equivalent hydrocalumite was calculated to be 0.194 mol Ca²⁺/kg bottom ash. Based on the assumptions and calculated results above, gypsum and /or anhydrite was computed to be approximately 0.147 mol Ca²⁺/kg bottom ash.

Hereinbefore, the dissolution behavior of all the Ca-containing minerals was analyzed, and the corresponding quantitative distribution of Ca²⁺ in various chemical forms was illustrated in Fig.5.

Together with Ca²⁺, other cations were also leached out from bottom ash with acid addition, as shown in Fig.3-b. Na⁺ was more soluble than the other two cations in the whole pH range 12.0-1.7. Mg²⁺ concentration is quite stable as controlled by solubility of brucite Mg(OH)₂ or hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·10H₂O) in alkaline solutions, and obviously increased after pH less than 10. While K⁺ leaching concentration was quite stable in alkaline and neutral solutions, and there was only a slight increase with more acid addition. Despite these leaching properties, the total leaching concentration of Na⁺, K⁺, and Mg²⁺ was only 0.32 mol/kg bottom ash at acid addition of 3.75 mmol H⁺/g bottom ash, which was not comparable to Ca²⁺ leaching concentration (2.02 mol/kg bottom ash) at the same acid addition. This could partially prove the dominant status of Ca-containing minerals in both solid and liquid phase of bottom ash.

3.3 Results of lab-scale accelerated carbonation

(1) pH variation of bottom ash

Decalcification of Ca-containing minerals and incursion of carbon dioxide to microscopes in bottom ash were greatly improved by periodical water addition, which finally quickened carbonation process. From the chemical point of view, sequestration of CO₂ by cementitious materials is a neutralization reaction of CO₂ with basic compounds of Ca(OH)₂ or other calcium silicate minerals dissolved in aqueous pore water, resulting in

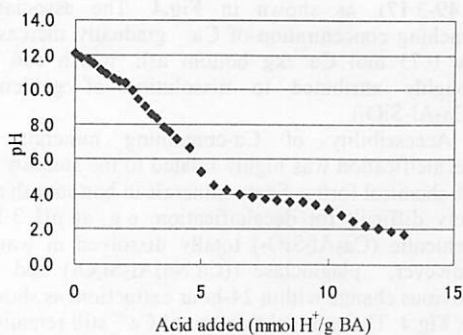


Fig. 2 Batch titration curve of MSWI bottom ash

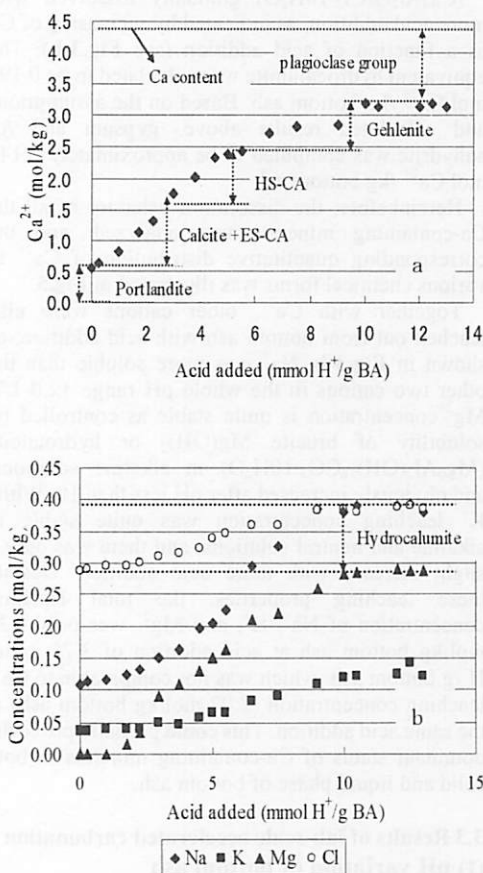


Fig. 3 Dissolution of a) Ca^{2+} ; b) Na^+ , K^+ , Mg^{2+} and Cl^- from bottom ash as a function of acid addition (CSH means calcium silicate hydrate)

decrease of pH. Besides, acid percolation, as well as organic decomposition and intrinsic reactions, also led to pH decreasing. As a simple and effective index for indicating weathering degree of MSWI residuals,

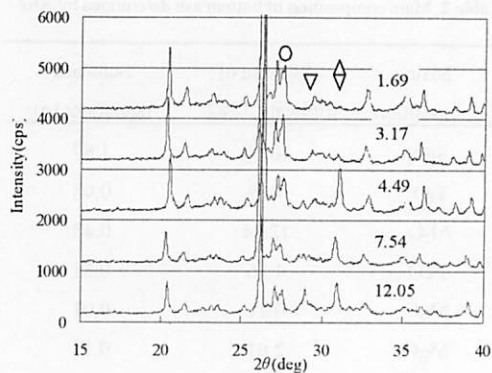


Fig. 4 Mineralogical analysis of bottom ash residuals at titration ending pH of 12.05, 7.54, 4.49, 3.17, and 1.69 with acid addition amount of 0, 3.75, 5.50, 10.00 and 13.00 mmol H^+ /g bottom ash respectively (The circle symbol means Ca-Na group feldspar minerals; symbol triangle indicates position of calcite; while parallelogram represents gehlenite)

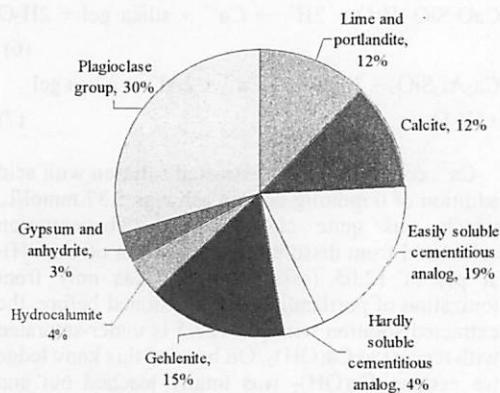


Fig. 5 Chemical distributions of various Ca-containing minerals in bottom ash

pH of bottom ash was periodically measured using solutions of JLT46. The pH of freshly quenched bottom ash has an average value of 12.7 (see Fig.6-b), which is higher than the value calculated from equilibrium of portlandite (12.3); and also, the concentration of Ca^{2+} in filtrate has a value of 36.2 mmol/L (calculated from Fig.6-c), which was nearly two times that of saturated portlandite (20.1 mmol/L).

This phenomenon indicated calcium is over-saturated with respect to portlandite when the L/S ratio is 10, which was consistent with

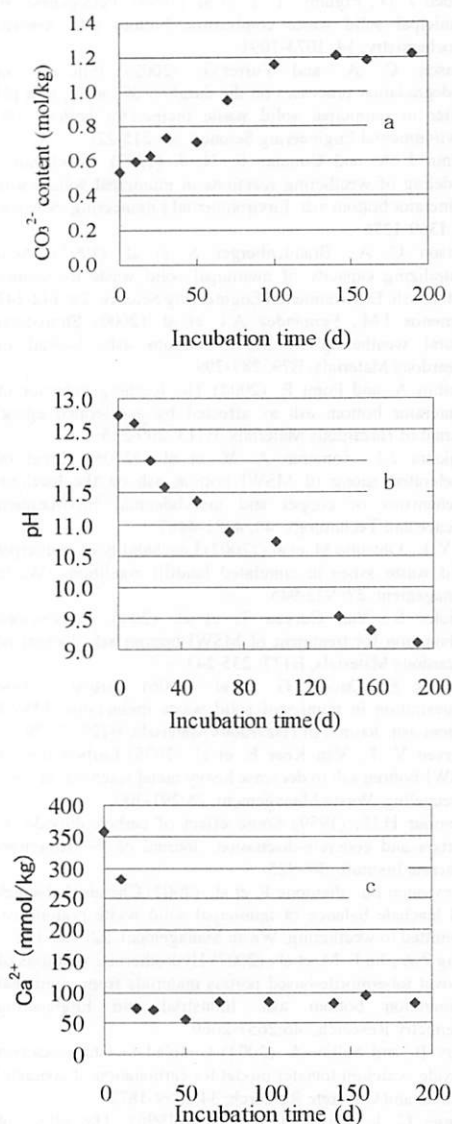


Fig. 6 a) Increase of carbonate content and, b) decrease of pH and c) leachability of Ca²⁺ in solutions of JLT46 as a function of incubation time in the first step experiment

Chimenos's results⁸⁾. With weathering proceeding, lime and portlandite were preferentially consumed, as well as some easily soluble silicate minerals. And pH was simultaneously decreased, finally reached around pH 9.

(2) Evolution of CO₂-content during weathering process

As shown in Fig.6-a, the carbonate content of freshly quenched bottom ash was 0.53 mol CO₂/kg bottom ash, dramatically increased to 1.15 mol

CO₂/kg bottom ash after 100 days, afterwards there was only a slight increase as a function of incubation time, and finally reached 1.21 mol CO₂/kg bottom ash after 200 days. This value was less than the theoretically calculated value via acid neutralization experiment at titration ending pH of 7.5 (2.02 mol Ca²⁺/kg bottom ash). This discrepancy could be attributed to the following reasons:

- 1) existence of large amount of big particle bottom ash inhibiting CO₂ intrusion (either insufficient diffusion time for CO₂, or low partial pressure of CO₂);
- 2) reduction of diffusion coefficient due to precipitation of newly formed calcite (variation of porosity and porous distribution for cementitious materials, proposed by Bary B. et al.¹⁸⁻²⁰). The above two reasons could be intuitionistically proved by Fig.7, the inner part of bottom ash particle turned to pink while the surface remained no change when titrated with phenolphthalein. However, not like cylindrical cement paste or mortar²¹⁻²², the pink area were not centralized but sporadic due to the heterogeneity of MSWI bottom ash particles, as depicted via light microscopy (cross section) photo of thin section²³;
- 3) existence of sulfate compounds in bottom ash.

With incubation proceeding, the leaching concentration of Ca²⁺ in filtrate of JLT 46 sharply decreased to 60-80 mmol/kg, and then kept nearly constant (see Fig.6-c). Decrease of Ca²⁺ leaching concentration from bottom ash also indicates transformation of between different forms of Ca-containing minerals.

For further estimation of maximum sequestration capacity of CO₂ by MSWI bottom ash, second-step carbonation was conducted using fully crushed bottom ash samples. The maximum carbonate content value was determined to be 1.85mol CO₂/kg bottom ash (average value of triplicate) after 144h treatment at conditions of 50% CO₂ and 50% N₂.

4. CONCLUSIONS

MSWI bottom ash, as a highly alkaline solid waste, was a potential source for sequestration of CO₂ due to existence of large amount of

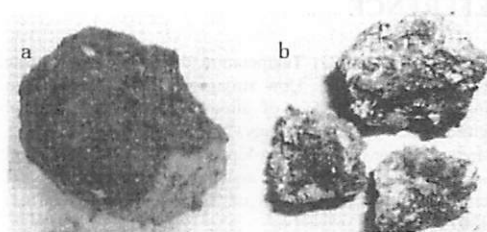


Fig.7 Comparison of bottom ash particle carbonated for 100 days a) before and b) after cracking (Both were titrated by 1% phenolphthalein indicator)

Ca-containing minerals and other alkaline minerals. The maximum sequestration capacity of bottom ash was calculated to be 5.19 mol/kg bottom ash, of which 75% was contributed by Ca-containing minerals. Further more, of all the calcic minerals, 2.02 mol Ca-containing minerals/kg bottom ash could potentially be decalcified and transformed to calcite when pH maintained above 7.5. Minerals like plagioclase and albite, although theoretically can be decalcified, could hardly be carbonated at neutral and alkaline conditions. The real sequestration amount of CO₂ by bottom ash was investigated via lab-scale experiment. After 200 days first-step weathering, the carbonate content increased from 0.53 to 1.21 mol CO₂/kg bottom ash, and finally reached 1.85mol CO₂/kg bottom ash (anticipated value) at the end of second step experiment using milled specimens, which was slightly lower than theoretically calculated value (2.02 mol Ca-containing minerals/kg bottom ash). The corresponding reasons may partially attribute to presence of Ca-sulfate and Ca-chloride minerals. On the basis of above discussions, we can draw conclusions that the potential sequestration capacity of MSWI bottom ash was 1.32 mol CO₂/ kg bottom by subtracting the original carbonate content in bottom ash samples. The total sequestration amount by MSWI bottom ash annually generated in Japan was roughly estimated to be 0.29 million ton-CO₂/year, which could be around 7% for the whole amount of CO₂ in the MSWI process. Besides, carbonation of bottom ash also benefits stabilization of heavy metals existed in bottom ash, thus reduces potential risks to surroundings.

ACKNOWLEDGEMENT: Authors appreciated financial support to this study from Japan Society for the Promotion of Science (JSPS), bilateral cooperative study grant (Nikokukan Koryu, "Adsorption and fixation of atmospheric carbon dioxide in a landfill site of incineration residues in Japan and the United States") and ministry of the environment, Grant-in-Aid for scientific research (KAKENHI, K2138)

REFERENCE

- 1)Velbel M. A. (1993) Temperature dependence of silicate weathering in nature: How strong a negative feedback on long-term accumulation of atmospheric CO₂ and global greenhouse warming, *Geology*, 21: 1059-1062
- 2)Montes-Hernandez G., Perez-lopez R. et al. (2009) Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash, *Journal of Hazardous Materials*, 161: 1347-1354
- 3)Ettoh J., Kawagoe T. et al. (2008) Hydrothermal treatment of MSWI bottom ash forming acid-resistant materials, *Waste Management*, 29: 1048-1057
- 4)Eusden J. D., Eighmy. T. T. et al. (1999). Petrogenesis of Municipal solid waste combustion bottom ash, *Applied Geochemistry*, 14: 1073-1091
- 5)Johnson C. A. and Furrer.G. (2002) Influence of biodegradation processes on the duration of CaCO₃ as a pH buffer in municipal solid waste incinerator bottom ash, *Environmental Engineering Science*, 36: 215-220
- 6)Meima J. A. and Comans R. N. J. (1997) Geochemical modeling of weathering reactions in municipal solid waste incinerator bottom ash, *Environmental Engineering Science*, 31, 1369-1276
- 7)Johnson C. A., Brandenberger S. et al. (1995). Acid neutralizing capacity of municipal solid waste incinerator bottom ash, *Environmental Engineering Science*, 29: 142-147
- 8)Chimenos J.M., Fernández A.I. et al. (2000) Short-term natural weathering of MSWI bottom ash, *Journal of Hazardous Materials*, B79: 287-299
- 9)Poletini A. and Pomi R. (2004) The leaching behavior of incinerator bottom ash as affected by accelerated aging, *Journal of Hazardous Materials*, B113: 209-215
- 10)Dijkstra J.J., Zomer A. V. et al., (2006) Effect of accelerated agong of MSWI bottom ash on the leaching mechanisms of copper and molybdenum, *Environment Science and Technology*, 40: 4481-4487
- 11)Li Y. L., Ohtsubo M. et al., (2007) Leachability of municipal solid waste ashes in simulated landfill conditions, *Waste Management*, 27: 932-945
- 12)Ariekx S., Van Gerven T. et al. (2006) Accelerated carbonation for treatment of MSWI bottom ash, *Journal of Hazardous Materials*, B137: 235-243
- 13)Rendek E., Ducom G. et al. (2006) Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash, *Journal of Hazardous Materials*, B128: 73-79
- 14)Gerven V. T., Van Keer E. et al. (2005) Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling, *Waste Management*, 25:291-300
- 15)Steinour H.H., (1959) Some effect of carbon dioxide on mortars and concrete-discussion, *Journal of the American Concrete Institute*, 30: 925
- 16)Freyssinet Ph., Piantone P. et al., (2002) Chemical changes and leachate balance of municipal solid waste bottom ash submitted to weathering, *Waste Management*, 22: 159-172
- 17)Jing Z.Z., Jin F. M. et al., (2007) Hydrothermal synthesis of a novel tobermorite-based porous materials from municipal incineration bottom ash, *Industrial and Engineering Chemistry Research*, 46:2657-2660
- 18)Bary B. and Sellier A. (2004) Coupled moisture -carbon dioxide -calcium transfer model for carbonation of concrete, *Cement and Concrete Research*, 34:1859-1872
- 19)Lange C. L., Hills D.C. et al., (1996), The effect of accelerated carbonation on the properties of cement-solidified waste forms, *Waste Management*, 16(8): 757-763
- 20)Johannesson B. and Utgenannt P. (2001)Microstructural changes caused by carbonation of cement mortar,Cement and concrete Research, 31:925-931
- 21)Houst F. Y., Wittmann H. F. (2002) Depth profiles of carbonates formed during natural carbonation, *Cement and concrete research*, 32: 1923-1930
- 22)Castellote M., Andrade C. (2008) Modeling the carbonation of cementitious matrixes by means of the unreacted-core model, UR-CORE, *Cement and concrete research*, 38:1374-1384
- 23)Shimaoka T., Zhang R. et al., (2007), Alternations of municipal solid waste incineration residuals in a landfill, *Waste Management*, 27:1444-145