Effect of Accelerated Carbonation on the Mineral Phase of Alkaline Inorganic Waste

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Abstract

To effectively pre-treat the alkaline inorganic waste by carbonation reaction with CO\(_2\), it is necessary to understand a mineralogical change. This is because mineralogical changes serve as an important key to leaching behavior or stabilization of heavy metals, such as Pb, Cu, Cr, and Ni, contained in the inorganic waste, at the point of environmental influence. Therefore, in this study we investigated the chemical composition and mineralogical characteristics of municipal solid waste incineration bottom ash, which is a type of alkaline inorganic waste, and the material changed by the carbonation reaction in bottom ash. In addition, minerals affected by carbonation reactions were identified based on the ternary diagram of Ca-Al-Si in bottom ash. The relationship between mineralogical changes caused by carbonation reactions and stabilization of heavy metals was also examined.

Key words: Alkaline inorganic waste, MSWI bottom ash, Carbonation reaction, Ternary diagram of Ca-Al-Si

1. Introduction

In South Korea, the industries of many fields have generated massive amounts of inorganic waste such as municipal waste incinerator bottom ash, municipal waste incinerator fly ash, steel slag, power plant bottom ash, waste concrete, and waste lime\(^1\). Most inorganic waste is buried in designated burial sites, resulting in a low recycling rate. While efforts are being made to utilize old burial sites as sports complexes or golf clubs, this is not a fundamental solution to the problem because it is difficult to acquire more sites from the limited land in Korea\(^2\). Thus, there is a need to facilitate waste management by increasing the recycling ratio instead of burying waste.

Carbonation processing technology with CO\(_2\) for effective pre-treatment of the inorganic waste has come under the spotlight as a means of waste-resource recovery and is being developed for the stabilization of hazardous substances. In addition, the sequestration of CO\(_2\) into inorganic waste, along with geologic storage, offers storage of high amounts of CO\(_2\), and the research on CO\(_2\)-based waste processing can be a solution to the challenge of reducing greenhouse gases amid the accelerated pace of global warming\(^3,4\).

In general, for applying carbonation technology to inorganic waste, the below conditions were used to separate the respective alkaline inorganic waste\(^5\):

- Waste exists in solid form
- Waste is fully inorganic
- Waste is in an alkaline state (pH > 8)
- Waste contains non-carbonated Ca and Al compounds

Alkaline inorganic waste satisfying the above conditions easily engages in reactions with CO\(_2\). Using carbonation reactions to pre-treat inorganic waste has the effect of neutralizing the alkaline state, decomposition of insoluble chlorides, and stabilizing heavy metals. In order to understand...
these effects, it is essential to study mineralogical changes of alkaline inorganic waste. Some important factors may be chemical composition and mineralogical characteristics of alkaline inorganic waste, material changes by carbonation reaction, and consequences on the environment. Therefore, in this study, the mineralogical characteristics and mineralogical changes caused by carbonation reaction with a focus on municipal waste incinerator bottom ash that is a type of alkaline inorganic waste. In addition, the material affected by carbonation reaction was identified based on the ternary diagram of Ca-Al-Si in bottom ash and the effect of heavy metals stabilization was also studied.

2. Material and Methods

2.1 Material

Samples of municipal waste incinerator bottom ash were obtained from an incinerator plant in Gwangmyeong-city in Gyeonggi province, Korea. In this incinerator plant, municipal waste was incinerated at a temperature of 1000°C, and the moisture content of bottom ash was 30 w/w.% as it is cooled by water-cooling after incineration. For particle separation, the moisture content of the bottom ash was kept below 1% by drying for 24 hours in an oven of 105°C. For removal of large iron fraction, a magnetic separator with a magnetic strength of 0.38 T was used. After magnetic separation, the bottom ash was passed through a standard sieve to obtain particles larger than 4.75 mm, 4.75–2.36 mm, 2.36–1.18 mm, 1.18–0.6 mm, 0.6–0.3 mm, 0.3–0.15 mm, 0.15–0.075 mm and smaller than 0.075 mm. An X-ray fluorescence spectrometer (Rigak TXRF 3726AI, Rigaku) was used to derive chemical compositions of bottom ash in each particle size. Fig. 1 shows the chemical composition of only Ca, Si, and Al in each particle size because of the most abundant in bottom ash. The concentration of Si increased with an increase in the particle size owing to the increased amounts of glass and synthetic ceramics, whereas Ca and Al increased with a decrease in the particle size.

2.2 Leaching test

A leaching test (standard method of the Korean Standard Leaching Procedure) was performed to measure the leached amount of Cr and Cl and the pH before and after carbonation. The bottom ash and diluted water were in the ratio of 1:10 (Solid/Liquid, w/w.%), and HCl was added to adjust the pH to 5.8–6.3. After stirring for 6 hours at 200 rpm, solid and liquid were separated by a filter paper with a pore size of 0.5 um. The concentration of Cr and Cl and pH in the leachate were measured using an inductively coupled plasma atomic emission spectrometry (OPTIMA 5300DV, Perkin Elmer) and a pH electrode (SN5135011).

2.3 Carbonation reaction

To confirm the mineralogical change of the bottom ash before and after carbonation in terms of the three phases of Ca-Si-Al, samples were prepared for carbonation reactions by selecting particles with a relatively small grain size of 0.6–0.3 mm and because of well distribution of the three phases, as shown in Fig. 1. Cylindrical-type samples were created by mixing polymers and bottom ash, and then cut to reveal cross-sections. 105 particles on the surface of cross-sectional areas of samples were selected and numbered as shown in Fig. 2. Using the SEM and EDX (JSM-6400) equipment, compositional analysis was conducted to analyze the surface of cross-sectional areas. EDX was used for compositional analysis of the subjects with main elements (Ca, Si, Al), heavy metal elements (Fe, Cu, Cr, Pb), and other elements (Na, K, Cl, etc). Next, the samples were sandpapered to remove the Au coating on the surface of cross-sections. The carbonation experiments were performed in a CO$_2$ incubation chamber to keep the CO$_2$ percentage at 30% and the temperature at 25°C during 4 hrs carbonation time, as shown in Fig. 3. The humidity of the reactor was maintained at 50%. After carbonation reaction, mineralogical changes of 105 particles on the surface of cross-sections area were also observed using SEM.
3. Results and Discussion

3.1 Chemical composition and mineralogical characteristics of alkaline inorganic waste

Many references8–11 with an analysis of mineral phases of municipal solid waste incinerator bottom ash explain that the bottom ash consists mostly of quartz, calcite, magnetite, hematite, gypsum, ettringite, akermanite, gehlenite, and cristobalite. These crystalline compounds are comprised of Ca, Al, and Si, and traces of Fe, Na, Mg, Cl, and so on. The bottom ash is more than 40% glassy with particles of the vesicular, porous, coke, or crack type. The morphological characteristics of particles in bottom ash are closely related to exposure in air, contact with water, and the various type of cooling process after incineration, and these factors will form new substances by reacting with those still remaining after incineration. The new substances are largely divided into silicate-type glassy substances and irregular or aggregate-type Ca-Al compounds. In the point of view of the relationship between new substances and carbonation method with CO₂, it is important to determine the conditions for carbonation reactions by confirming the chemical composition and mineral phase of each particle, and identifying minerals capable of easily reacting with CO₂. Therefore, the cross-sectional areas of particles were observed for mineralogical characteristics, particle types, and whether or not carbonation has occurred. The measurements obtained are organized in Table 1. Fig. 4 is a graphical representation for Ca-Al-Si content ratio of 105 particles with main Ca, Al, and Si compounds.

As shown in Table 1, particle types are described as vesicular, silicate, porous, aggregate, whisker, coke, anisotropic, irregular, and crack. Silica-type minerals including silicate existed as aggregate and irregular types, and various forms of minerals of Ca and Al, such as vesicular, porous, coke, and crack, were observed on the surface. To confirm the overall mineralogical characteristics of bottom ash, 105 particles were represented based on the ternary diagram of Ca-Al-Si, as shown in Fig. 4. As seen in ternary diagram, there were hardly any minerals with a high proportion of Al due to the low Al content. Metal substances (Fe, Cu, Al, and Cr) and other elements (Na, Mg, K, and Cl) were also detected in each particle as the form of metal fragments or metal compounds, while Na and K were soluble chlorides. Cl existed as soluble chlorides together with Na and K, or as insoluble Friedel’s salt with Ca12.

More than 40% of bottom ash was minerals with high amounts of Si. They mostly exist as SiO₂ or as a silicate-type compounds and these particles agglomerate with Ca-Al compound to form large clusters. As for Ca, it can be found as calcium carbonate, or as Friedel’s salt and ettringite with Al. The high pH in bottom ash is caused by these Ca-Al compounds and traces of CaOH. Fig. 5 gives the main minerals with Ca-Al-Si in bottom ash. Fig. 5(a) is the typical SiO₂ (silica) and silicate, Fig. 5(b) shows Ca-Al compounds attached to silicate, and Fig. 5(c) and Fig. 5(d) represent calcium carbonate and CaOH₂ respectively. Fig. 6, the same as Fig. 5(b), is the SEM and EDX analysis for Ca-Al compounds attached around silicate-type particles. These aggregate particles are most commonly seen in Ca-Al-Si minerals with various porous structures of the
Table 1  Content ratio of Ca-Al-Si, particle type, and carbonation reaction on the surface of bottom ash sample (including 105 particles)

| No. | carbonation | Ca (%) | Al (%) | Si (%) | Particle type | Note |
|-----|-------------|--------|--------|--------|---------------|------|
| 1   | Not         | 100    | 0      | 0      | Vesicular     | CaCO$_3$ |
| 2   | Not         | 8      | 25     | 67     | Silicate      |      |
| 3   | Not         | 0      | 0      | 100    | Vesicular     |      |
| 4   | Yes         | 27     | 27     | 46     | Large porous  | Na, Mg contained |
| 5   | Not         | 11     | 27     | 62     | Silicate      |      |
| 6   | Not         | 19     | 6      | 75     | Silicate      |      |
| 7   | Not         | —      | —      | —      | Whisker       | Fe-metal |
| 8   | Not         | 75     | 25     | 0      | Coke          |      |
| 9   | Partial     | 28     | 29     | 43     | Vesicular     |      |
| 10  | Partial     | 8      | 23     | 69     | Silicate      |      |
| 11  | Partial     | 10     | 25     | 65     | Silicate      |      |
| 12  | Yes         | —      | —      | —      | Aggregate     | Na-Zn compound |
| 13  | Not         | 20     | 20     | 60     | Large porous  |      |
| 14  | Not         | 4      | 13     | 83     | Silicate      |      |
| 15  | Not         | 74     | 9      | 17     | Anisotropic   | Ca-Zn compound |
| 16  | Not         | 72     | 11     | 17     | Aggregate and porous | |
| 17  | Not         | 43     | 19     | 38     | Aggregate      |      |
| 18  | Not         | 42     | 33     | 25     | Aggregate and porous | |
| 19  | Not         | 20     | 13     | 67     | Aggregate and porous | |
| 20  | Not         | 8      | 34     | 58     | Elliptic      |      |
| 21  | Not         | 7      | 22     | 71     | Vesicular     |      |
| 22  | Not         | 12     | 19     | 69     | Aggregate and porous | |
| 23  | Yes         | 92     | 6      | 2      | Aggregate     | Na, Cl, Mg contained |
| 24  | Not         | 45     | 55     | 0      | Irregular     |      |
| 25  | Not         | 42     | 33     | 25     | porous        |      |
| 26  | Not         | 7      | 13     | 80     | Silicate      | Na contained |
| 27  | Not         | 6      | 12     | 82     | Silicate      | Na contained |
| 28  | Yes         | 50     | 50     | 0      | Irregular     | Cl contained |
| 29  | Not         | 0      | 0      | 100    | Vesicular     | SiO$_2$ |
| 30  | Partial     | 30     | 20     | 50     | Aggregate and crack | |
| 31  | Partial     | 42     | 25     | 33     | Large porous  | Cl, Cr, Fe contained |
| 32  | Partial     | 24     | 19     | 57     | Aggregate     |      |
| 33  | Partial     | 22     | 17     | 61     | Aggregate     | Na contained |
| 34  | Partial     | 20     | 7      | 73     | Silicate      | Na contained |
| 35  | Not         | 26     | 33     | 40     | Large porous  |      |
| 36  | Not         | 15     | 8      | 77     | Silicate      | Na contained |
| 37  | Not         | 9      | 8      | 83     | Silicate      | Na contained |
| 38  | Not         | 27     | 6      | 67     | Silicate and porous | Na contained |
| 39  | Not         | 21     | 36     | 43     | Crack and porous | |
| 40  | Not         | 16     | 18     | 66     | Silicate and porous | |
| 41  | Yes         | 82     | 6      | 12     | Irregular     |      |
| 42  | Not         | 22     | 8      | 70     | Silicate and large porous | Fe-iron contained |
| 43  | Not         | 54     | 18     | 28     | Aggregate and large porous | Fe-iron contained |
| 44  | Not         | 13     | 47     | 40     | Aggregate and large porous | CaCO$_3$ |
| 45  | Not         | 0      | 47     | 53     | Irregular and porous | |
| 46  | Not         | 55     | 27     | 18     | Aggregate and crack | |
| 47  | Not         | 98     | 1      | 1      | Irregular and porous | CaCO$_3$ |
| 48  | Not         | 33     | 44     | 23     | Irregular and porous | |
| 49  | Not         | 97     | 3      | 0      | Vesicular     | CaCO$_3$ containing Cl |
| 50  | Not         | 27     | 18     | 55     | Large porous  |      |
| 51  | Not         | 9      | 3      | 88     | Silicate      | Na contained |
| 52  | Partial     | 16     | 28     | 56     | Irregular and large porous | Fe, Na contained |
| 53  | Not         | 0      | 35     | 65     | Silicate      | Na contained |
| 54  | Partial     | 45     | 27     | 28     | Aggregate and porous | |
| 55  | Not         | 80     | 16     | 4      | Aggregate and porous | |
| 56  | Not         | 0      | 0      | 100    | Silicate      |      |
| No. | carbonation | Ca (%) | Al (%) | Si (%) | Particle type                          | Note                                      |
|-----|-------------|--------|--------|--------|----------------------------------------|-------------------------------------------|
| 59  | Not         | 17     | 16     | 67     | Aggregate and large porous             | Mg, Na contained                          |
| 60  | Not         | 59     | 12     | 29     | Aggregate and porous                   |                                           |
| 61  | Not         | 24     | 9      | 67     | Aggregate and large porous             | Na contained                              |
| 62  | Not         | 0      | 0      | 100    | Silicate                               |                                           |
| 63  | Not         | 32     | 10     | 58     | Aggregate and large porous             | Na, Mg contained                          |
| 64  | Not         | 10     | 4      | 86     | Silicate and crack                      | Na contained                              |
| 65  | Not         | 28     | 0      | 72     | Aggregate                               |                                           |
| 66  | Not         | 57     | 29     | 14     | Vesicular                              |                                           |
| 67  | Not         | 43     | 21     | 36     | Irregular                              | Fe-oxide contained                        |
| 68  | Not         | —      | —      | —      | Viscular                               | Na and Mg compound containing Fe-oxide    |
| 69  | Partial     | 14     | 7      | 79     | Aggregate and porous                   |                                           |
| 70  | Partial     | 36     | 21     | 43     | Aggregate and large porous             | Fe-oxide contained                        |
| 71  | Not         | 50     | 25     | 25     | Vesicular                              |                                           |
| 72  | Not         | 24     | 6      | 70     | Aggregate                               |                                           |
| 73  | Not         | 95     | 4      | 1      | Irregular and porous                    | CaCO$_3$                                  |
| 74  | Not         | 33     | 25     | 42     | Aggregate                               |                                           |
| 75  | Not         | 39     | 30     | 31     | Aggregate and porous                   |                                           |
| 76  | Not         | 24     | 12     | 64     | Aggregate and porous                   |                                           |
| 77  | Not         | 35     | 18     | 47     | Aggregate and large porous             | Na, Mg contained                          |
| 78  | Not         | 0      | 0      | 100    | Viscular                               | SiO$_2$                                   |
| 79  | Not         | 94     | 3      | 3      | Irregular and porous                    | CaCO$_3$                                  |
| 80  | Not         | 32     | 7      | 61     | Aggregate                               |                                           |
| 81  | Yes         | 73     | 12     | 15     | Irregular and crack                     |                                           |
| 82  | Not         | 19     | 35     | 46     | Viscular                               |                                           |
| 83  | Not         | 39     | 61     | 0      | Anisotropic                            | Zn contained                              |
| 84  | Yes         | 71     | 14     | 15     | Irregular and crack                     | Na contained                              |
| 85  | Not         | 99     | 0      | 1      | anisotropic                            | Na contained                              |
| 86  | Partial     | 32     | 23     | 45     | Aggregate and large porous             |                                           |
| 87  | Yes         | 92     | 5      | 3      | Irregular and porous                    | Na contained                              |
| 88  | Not         | 0      | 0      | 100    | Silicate                               |                                           |
| 89  | Not         | 34     | 7      | 59     | Aggregate and large porous             | Fe, Na, Cl contained                      |
| 90  | Yes         | 95     | 5      | 0      | Irregular and crack                     | Cl contained                              |
| 91  | Not         | 46     | 21     | 33     | Vesicular and large porous             | Na, Mg, Cl, K contained                   |
| 92  | Not         | 10     | 0      | 90     | Aggregate and large porous             | Mg-Si compound                            |
| 93  | Not         | 96     | 4      | 0      | Irregular and porous                    | Ca-P compound                             |
| 94  | Weak        | 69     | 24     | 7      | Irregular and porous                    | Na, Cl contained                          |
| 95  | Not         | 1      | 1      | 98     | Silicate                               | K contained                               |
| 96  | Not         | 97     | 0      | 3      | Silicate                               |                                           |
| 97  | Not         | 0      | 0      | 100    | Silicate                               |                                           |
| 98  | Weak        | 60     | 40     | 0      | Aggregate, porous and crack             | Na-Cu mineral contained                   |
| 99  | Weak        | 77     | 23     | 0      | Irregular                              |                                           |
| 100 | Not         | 100    | 0      | 0      | Irregular and crack                     |                                           |
| 101 | Not         | 22     | 17     | 61     | Aggregate and porous                   | Fe-iron contained                         |
| 102 | Yes         | 100    | 0      | 0      | Irregular and crack                     |                                           |
| 103 | Not         | 0      | 0      | 100    | Irregular and porous                    | Amorphous Al-oxide                        |
| 104 | Yes         | 59     | 35     | 6      | Irregular and crack                     | Na, Mg, Cl, K contained                   |
| 105 | Yes         | 79     | 18     | 3      | Irregular and crack                     | Na, Cl contained                          |
| 106 | Not         | 5      | 22     | 73     | Viscular                               | Mg, Cl, Mg contained                      |
| 107 | Yes         | 70     | 27     | 3      | Irregular and crack                     | Na, Cl, K contained                       |
| 108 | Not         | 40     | 25     | 35     | Aggregate and porous                    | Mg contained                              |
| 109 | Not         | 28     | 11     | 61     | Irregular and large porous              | Na contained                              |
| 110 | Not         | 0      | 0      | 100    | Silicate                               |                                           |
| 111 | Partial     | 30     | 32     | 38     | Aggregate                               | Na, Mg, Cl, K contained                   |
| 112 | Not         | 30     | 13     | 57     | Aggregate and large porous              | Na, Mg contained                          |
| 113 | Not         | 0      | 0      | 100    | Silicate                               |                                           |
| 114 | Not         | 98     | 1      | 1      | Irregular and porous                    | Na, K contained                           |
| 115 | Not         | 13     | 19     | 68     | Viscular and crack                      | Na, K contained                           |
bottom ashes generated from incinerator after incineration process.

Next, the characteristics of metal substances in bottom ash were confirmed. Fe-material, which has the highest distribution among metals, accounted for more than 10% of bottom ash. Most Fe was Fe-metal and Fe-oxide that was formed by oxidation from the corrosion of Fe-iron. The majority of Fe-metal coated with Fe-oxide existed independently, whereas some Fe-oxide was aggregated with other particles and difficult to separate by magnetic separation\textsuperscript{3}. Fig. 7(a) and Fig. 7(b) show that Fe-metal and Fe-oxide intertwined with vitreous materials. As shown in Fig. 7(c), the picture shows Al-metal agglomerating with other compounds. This picture may be evidence about the low separation ratio using an eddy current separator as well as the surface oxidized as Al-oxide\textsuperscript{14}. Thus, more research on Al detection and separation has to be studied, because that cracks are formed if Al-containing bottom ash is reused for buildings or pavements. In Fig. 7(a), we can see Cu-metal existing as a whisker type and being surrounded by vitreous materials. Cr-metal, as presented in Fig. 7(d), was found in the inner porous layer of Ca-Al compounds. The existence of heavy metals in bottom ash particles must be determined in more detail since such metals involve a risk of leaching into solution.
3.2 Effect of accelerated carbonation on the mineral phase

The bottom ash produces unstable Ca-Al compounds during the water-cooling process (cooling down the incinerated high-temperature bottom ash before it goes to the landfill) following incineration. Because these substances contain various metal components, they can play an important role in the leaching of heavy metals, which have an environmental impact. These compounds are generated in alkaline bottom ash, as follows below.

In the case of Ca, it changes to CaO when incinerated at a temperature of 1000°C, and the water cooling process appears to control the formation of portlandite (Ca(OH)_2). In addition, ettringite (Ca_6Al_2(SO_4)_3(OH)_12·26H_2O) and Friedel’s salt (or hydrocalumite; Ca_6Al(OH)_6Cl·2H_2O) are controlled by the water cooling process, as they are in an environmental condition in which they can be formed. Regarding the formation and properties of ettringite, the stability domain for ettringite generally lies between pH 10.5 and pH 13. Its formation is generally favored over mono-sulfate at low temperatures, below 50°C. In the case of Friedel salt, it is synthesized in the Ca-Al-Cl system at 65°C and the pH is kept constant at over 11.5 according to the following equation:

\[
6\text{Ca}^{2+} + 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 38\text{H}_2\text{O} \\
\rightarrow 12\text{H}^+ + \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}·26\text{H}_2\text{O}.
\]

Friedel’s salt:

\[
2\text{Ca}^{2+} + \text{Al}^{3+} + \text{Cl}^- + 8\text{H}_2\text{O} \\
\rightarrow 6\text{H}^+ + \text{Ca}_6\text{Al}(\text{OH})_6\text{Cl}·2\text{H}_2\text{O}.
\]

\[
2[\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}·2\text{H}_2\text{O}] + 3\text{CO}_2 \\
\rightarrow 3\text{CaCO}_3 + \text{Al}_2\text{O}_3·x\text{H}_2\text{O} \\
+ \text{CaCl}_2 + (10 - x)\text{H}_2\text{O}.
\]

As shown in chemical reactions, calcite became the main crystalline phase in the carbonated bottom ash upon the decomposition of portlandite, ettringite, and Friedel’s salt. These reactions may be interpreted as suggesting the possibility of the formation of a new amorphous product, Al-oxide, which forms due to the dissolution of ettringite and Friedel’s salt. As presented in Table 1, each particle in bottom ash was checked for carbonation. Fig. 8 shows the ternary diagram of Ca, Al, and Si content ratio in each particle after carbonation reaction, like Fig. 4. As a result, most minerals that have been subject to carbonation were found to exist as Ca-Al compounds. This result indicates that the aforementioned decomposition reactions of Ca(OH)_2, ettringite, and Friedel’s salt are main carbonation reactions in bottom ash. Fig. 9 shows SEM analysis of the surface of particles affected by carbonation reaction. They can be broadly classified into three types. Carbonation reactions can occur either on the entire surface of Ca-Al compounds or on part of the surface of Ca-Al compounds agglomerating with silicate or other materials, and this is believed to be caused by the carbonation reaction of ettringite and Friedel’s salt with CO_2. In addition, the most active reactions took place in Ca(OH)_2, which is illustrated in Fig. 9(c).

3.3 Carbonation effect on heavy metal stabilization

As mentioned above, the three substances with Ca(OH)_2, ettringite, and Friedel’s salt are decom-
posed after carbonation, producing CaCO$_3$ and Al$_2$O$_3$. In particular, Al$_2$O$_3$ is known as an amorphous material, highly adhesive substance with heavy metal ions. As can be seen from many references about the stabilization of heavy metals according to carbonation reaction, the generation of CaCO$_3$ and amorphous Al$_2$O$_3$ has a significant effect on the control of heavy metal’s leaching. Fig. 10 is the SEM image showing mineral changes caused by carbonation reaction on the surface of particles containing Cr-fractions, and can be used as evidence in explaining the effect of carbonation on the stabilization of heavy metal. As seen in Fig. 10, we could confirm that Cr-fractions exist in the inner porous layer of Ca-Al compounds before carbonation reaction, but new and irregularly-shaped substances with CaCO$_3$ and amorphous Al$_2$O$_3$ are wrapped around Cr-fractions after carbonation reaction. This provides evidence of the morphological changes in the particles in what is termed the encapsulation effect.

4. Conclusions

In this study, the effect of accelerated carbonation on the mineral phase of alkaline inorganic waste was investigated. In order to confirm the carbonation effect, the important factors with the chemical composition and the mineralogical characteristics of alkaline inorganic waste, the accelerated carbonation on the mineral phase were also examined with focus on municipal waste incineration.

| Table 2 | Leaching concentrations of Cr, the removal ratio of Cl, and pH changes caused by carbonation reaction |
|---------|------------------------------------------------------------------------------------------------|
| Leaching concentration of Cr (mg/L) | Removal ratio of Cl (wt/wt.%) | pH |
| Before carbonation | 0.40 | 0 | 12.0 |
| After carbonation | 0.01 | 92.4 | 8.9 |

Regarding the confirmation of Cr leaching behavior, Cl and pH, and Cr behaviors during 4 hrs of carbonation reaction time were investigated. Table 2 shows the leaching concentrations of Cr, the removal ratio of Cl, and pH changes caused by carbonation reaction. We can consider the variation of the pH as a function of carbonation time. Before the carbonation reaction, bottom ash is highly alkaline with a pH of 12 due to the presence of ettringite, hydrocalumite, and portlandite, but pH falls when these substances are decomposed during initial carbonation. Eventually, the pH falls below 9 after carbonation reactions, and the value is determined by the newly formed calcite, amorphous Al$_2$O$_3$, and gypsum. The decomposition of ettringite and hydrocalumite from CO$_2$ reactions also affects the removal ratio of Cl from the bottom ash. As shown in Table 2, the removal ratio of Cl increased during the carbonation reaction. In the case of Cr, it decreased until below 0.1 mg/L. Cr-stabilization is supported by two findings by the carbonation reaction. First, the carbonation reaction is to decrease the pH and to form insoluble Cr-material that contributes to a reduction of the leaching. Secondly, the adsorbent compound, which is amorphous Al-material formed by the carbonation reaction and has high affinity of Cr, in the bottom ash, controls the leaching of Cr. In addition, the encapsulation effect, mentioned in Fig. 10, occurring on the surface of the bottom ash particles results in more effective stabilization of Cr leaching behavior.
ator bottom ash that is a type of alkaline inorganic waste.

In this result, the bottom ash was largely divided into silicate-type glassy material and aggregate-type Ca-Al compounds. After carbonation processing with CO$_2$, the carbonation reaction in bottom ash could occur on the surface of Ca-Al compounds agglomerating with silicate, other materials, and heavy metals, and this is to be caused by the carbonation reaction of ettringite, Friedel’s salt, and Ca(OH)$_2$ with CO$_2$.

In addition, we also confirmed the effect of heavy metals stabilization in bottom ash during carbonation reaction, and this result showed that the leaching of Cr, on behalf of heavy metals, started to decrease after carbonation reaction and fell under the initial value of Cr leaching in the untreated bottom ash. Calcium carbonate and amorphous Al-oxide formed by decomposition of Ca(OH)$_2$, ettringite, and Friedel’s salt has a significant influence on the leaching characteristics of Cr. The encapsulation effect, showing the amorphous Al-materials precipitated on the surface of the carbonated bottom ash particles, allowed for more effective stabilization of the leaching behavior of Cr.

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References

1. J.W. Ahn: Treatment technologies of municipal solid waste incineration (MSWI)-bottom ash: Journal of Korean Inst. of Resources Recycling, 43(3), pp. 258–267 (2006)
2. N.I. Um, G.C. Han, K.S. You, H.S. Kim, J.W. Ahn: Characteristic of treatment process from municipal solid waste incineration (MSWI) bottom ash, The Korean Society for Geosystem Engineering, 46(6), pp. 767–775 (2009)
3. R.M. Santos, J.V. Bouwel, E. Vandevelde, G. Mertens, J. Elsen, T.V. Gerven: Accelerated mineral carbonation of stainless steel slags for CO$_2$ storage and waste valorization: Effect of process parameters on geochemical properties, International Journal of Greenhouse Gas Control, 17, pp. 32–45 (2013)
4. D. Zingaretti, G. Costa, R. Baciocchi: Assessment of the Energy Requirements for CO$_2$ storage by carbonation of industrial residues. Part 1: Definition of the process layout, Energy Procedia, 37, pp. 5850–5857 (2013)
5. S.Y. Pan, E.E. Chang, P.C. Chiang: CO$_2$ capture by accelerated carbonation of alkaline wastes: A review on its principles and applications, Aerosol and Air Quality Research, 12, pp. 770–791 (2012)
6. A. Polettini and R. Pomi: The leaching behavior of incinerator bottom ash as affected by accelerated ageing, Journal of Hazardous Materials, B113, pp. 209–215 (2004)
7. J.W. Ahn, N.I. Um, G.C. Han, K.S. You, H.C. Cho: Effect of carbonation in removal of chloride from municipal solid waste incineration bottom ash, Geosystem Engineering, 9(4), pp. 87–90 (2006)
8. S.V. Vassilew, C.G. Vassileva, A.I. Karayigit, Y. Bulut, A. Alastuey, X. Querol: Phase-mineral and chemical composition of composite samples from feed coals, bottom ashes and fly ashes at the soma power station, Turkey, Coal Geology, 61, pp. 35–63 (2005)
9. Y. Wei, T. Shimaoka, A. Saffarzadeh, F. Takahashi: Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases, Journal of Hazardous Materials, 187, pp. 534–543 (2011)
10. P. Piantone, F. Bodenan, L. Chatelet-Snidaro: Comparative study of ageing, heat treatment and accelerated carbonation for stabilization of municipal solid waste incineration bottom ash in view of reducing regulated heavy metal/metalloid leaching, Journal of Environmental Management, 128, pp. 807–821 (2013)
11. Y.D. Jo, N.I. Um, G.C. Han, J.W. Ahn, K.H. Lee, B.C. Ban: Characteristic of chloride in municipal solid waste incineration (MSWI) bottom ash via washing process, The Korean Society for Geosystem Engineering, 44(2), pp. 127–134 (2007)
12. N.I. Um, G.C. Han, K.S. You, H.C. Cho, J.W. Ahn: Separation of ferrous materials from municipal solid waste incineration bottom ash, Journal of Korean Inst. of Resources Recycling, 16(3), pp. 19–26 (2007)
13. G. Pecqueur, C. Crignon, B. Quenee: Behaviour of cement-treated MSWI bottom ash, Waste Management, 21, pp. 229–233 (2001)
14. M. Chrysochoou and D. Dermatas: Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: Literature review and experimental study, Journal of Hazardous Materials, 136, pp. 20–33 (2006)
15. I. Rousselet, C. Taviot-Gueho, F. Leroux, P. Leone, P. Palvadeau, J.P. Besse: Insights on the structural chemistry of hydrocalumite and hydrotalcite-like materials: investigation of the series CaM$_3$(OH)$_6$Cl·2H$_2$O(M$_{iv}$: Al$^{3+}$, Ga$^{3+}$, Fe$^{3+}$, Mg$^{2+}$, Ca$^{2+}$)
and Sc\(^{3+}\)) by X-ray powder diffraction, Journal of Solid State Chemistry, 167, pp. 137–144 (2002)

17. G.C. Han, N.I. Um, K.S. You, H.C. Cho, J.W. Ahn: Change of mineral phases in carbonation reaction of MSWI bottom ash, Geosystem Engineering, 12(1), pp. 21–25 (2009)

18. G. Gadikota, C. Natali, C. Boschi, A.H. Alissa Park: Morphological changes during enhanced carbonation of asbestos containing material and its comparison to magnesium silicate minerals, Journal of Hazardous Materials, 264, pp. 42–52 (2014)

19. J.A. Meima, R.D. Weijden, T.T. Eighmy, R.N.J. Comans: Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum, Applied Geochemistry, 17, pp. 1503–1513 (2002)

20. J.M. Chimenos, A.I. Fernandez, L. Miralles, M. Segarra, F. Espiell: Short-term natural weathering of MSWI bottom ash as a function of particle size, Waste Management, 23, pp. 887–895 (2003)

21. K.H. Lee, J.W. Ahn, H.C. Cho, K.S. You, G.C. Han, N.I. Um: Encapsulation of municipal solid waste incineration bottom ash to immobilize Cu and Pb via carbonation reaction, Solid State Phenomena, 124–126, pp. 1709–1712 (2007)

22. N.I. Um, S.Y. Nam, J.W. Ahn: Effect of accelerated carbonation on the leaching behavior of Cr in municipal solid waste incinerator bottom ash and the carbonation kinetics, Materials Transactions, 54(8), pp. 1510–1516 (2013)

23. E. Alvarez-Ayuso, A. Garcia-Sanchez, X. Querol: Adsorption of Cr(VI) from synthetic solutions and electroplating wastewaters on amorphous aluminium oxide, Journal of Hazardous Materials, 142, pp. 191–198 (2007)