

Removal of Chloride in Bottom Ash from the Industrial and Municipal Solid Waste Incinerators

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In the present work, recycling of bottom ash from both industrial waste and municipal solid waste incinerators (MSWI) was investigated. In order to recycle bottom ash as raw materials for cement production, it is necessary to remove chloride, which causes metal erosion in reinforced concrete. Therefore, experiments for removing chloride were carried out by washing bottom ash in order to obtain efficient washing conditions. The following conditions were investigated: pH, type of solution, particle size, bubbling and temperature. Although pH is the most effective parameter for reducing Cl content in ash, using acid to lower pH is not an environmental friendly treatment considering wastewater treatment. It was found that CO₂ bubbling in the form of microbubble is a proper treatment to decompose insoluble chloride as an environmental friendly treatment.

Key Words : Bottom ash, Chloride, Recycling, Microbubble

1. Introduction

Bottom ash can be used as raw materials of aggregates and cement products, because these components are very similar to those of them. One pretreatment method for recycling is to put bottom ash into melting process in order to reduce volume and stabilize heavy metals. However, fusion furnaces are not prevalent due to both environmental and economical drawbacks, *i.e.* large CO₂ emission and high-energy cost. In addition, bottom ash contains halogen and heavy metals as impurities that have a negative influence on aggregates and cement. For example, there is a limit on chloride (Cl) content in cement, *i.e.* less than 350 ppm in Japan, and less than 1000 ppm in Europe. As Cl in aggregate and cement causes erosion especially for reinforced concrete, it is necessary to reduce the Cl content before recycling[1].

This paper discusses the removal of chloride from bottom ash not only from municipal solid waste incinerators (MSWI), but also from industrial waste incinerators. Previously there were some researches on removal of chloride from MSWI bottom ash [2,3]. Water extraction, *i.e.* washing method is generally known to be the most economic and simple method. However, it is difficult to lower the Cl content to less than 0.5% because of insoluble chloride, while normally the Cl content of bottom ash is about 0.5-5%. In order to decompose insoluble chloride, influence of the parameter, such as particle size, pH and bubbling method were investigated.

2. Experimental

2.1. Sample

Samples of bottom ash were taken from four incinerators in Japan. Two samples, named as "Ash A" and "Ash B", were from MSWIs, while other samples, named as "Ash C" and "Ash D", were from industrial waste incinerators. Size classification of the samples was performed after drying at 70°C for 2 days because ash includes about 20 wt% moisture. After ash was pulverized to coarse powder and then sieving was performed. There are many parameters that influence the washing efficiency, *e.g.* temperature, agitation method, pulp density (liquid/solid ratio), contact time, the number of washing steps, type of solution, pH (acid concentration), particle size and bubbling method. This study is focused especially on particle size, pH and bubbling method.

2.2. Method of normal washing test

Without bubbling, pulverized bottom ash and the solution were mixed at the pulp density of 10-100 g/L. Washing solutions used in this study were (1) de-ionized water, (2) hydrochloric acid, (3) nitric acid, and (4) sulfuric acid. pH of the solution was controlled by changing the concentration of each acid. Then, the slurry was agitated in a plastic bottle by using a shaker at the rotation speed of 200 stroke/min. for 10 minutes. Then, the slurry was filtrated by using 5C filter paper and de-ionized water was poured in order to wash out the dissolved salts that remained on the surface of ash. After filtration, the residue was analyzed to determine the content of the remaining chloride, using ion-chromatograph (DIONEX DX-100, column: AS10) after alkali

fusion.

2.3. Method of bubbling test

In case of bubbling, the slurry was agitated for 10 minutes by using an impeller, together with bubbling. Air and CO₂ were tested as bubbling gas. Figure 1 shows schematic diagram of bubbling test. In case of normal bubble shown in Figure 1(a), bubbling was performed through glass filter. In case of microbubble shown in Figure 1(b), bubbling was performed by circulating water by a pump at the flow rate of 4 L/min. The water contains gas under pressure. Gas was supplied into the pressurized tank by a pump from outside air and dissolved into water at 0.3 MPa. In case of CO₂ bubbling, plastic bag containing CO₂ was connected to the pump in order to supply CO₂.

When water is discharged from the pressurized tank, microbubbles are generated by rapid pressure reduction. Bubble's diameter is dependent on the flow speed and the speed of pressure reduction. In this experimental device, diameter of microbubble measured by image processing was minimum 4 μm, average 10-40 μm, while that of normal bubble was a few millimeters. The flow speed of gas was kept constant at 0.2 L/min. Thus, total consumption of gas was 2 L. The following procedure after bubbling is the same as method of the normal washing test.

3. Results and Discussion

3.1. Properties of bottom ash

Table 1 shows chemical composition of bottom ash by X-ray fluorescence spectrometer (XRF). Main components were CaO, SiO₂, Al₂O₃ and Fe₂O₃ in all four ashes. Figure 2 shows X-ray diffraction (XRD) patterns of bottom ashes. In Ash A and Ash B from MSWIs, calcite (CaCO₃), gehlenite (2CaO · Al₂O₃ · SiO₂) and Friedel's salt (3CaO · Al₂O₃ · CaCl₂ · 10H₂O) were identified as major crystalline phases. This XRD result corresponds to previously reported data [4]. On the other hand, XRD patterns of Ash C and Ash D from industrial waste incinerators were completely different. Ash C was amorphous with no specific peak. One of the reasons why Ash C was amorphous is that there exist many glassy materials in the surface of Ash C, because ash was partially molten due to high temperature of incineration. In Ash D, NaCl, CaTiO₃ and ZnFe₂O₄ were identified due to high content of Cl, Ti and Zn. Moreover, there was no peak of Friedel's salt (FS) in Ash C and Ash D. In case of Ash D, S content is higher and Al content is lower than those of other ashes, *i.e.* the molar ratio of S to Al (S/Al) is extremely high. By the reaction with sulfate ion, FS is changed into ettringite (3CaO · Al₂O₃ · 3CaSO₄ · 32H₂O)

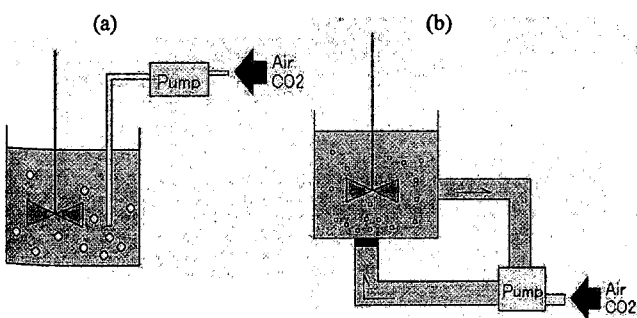


Figure 1 Schematic diagram of bubbling test. (a) Normal bubble, (b) Microbubble

Table 1 Chemical composition of bottom ash by XRF (unit: wt%, ND: non detectable)

	Ash A	Ash B	Ash C	Ash D
Al ₂ O ₃	15.1	9.5	9.8	5.9
SiO ₂	35.5	21.9	39.8	22.4
P ₂ O ₅	ND	0.9	ND	1.6
SO ₃	1.8	5.1	5.4	7.5
Cl	1.2	1.5	1.0	9.7
K ₂ O	1.4	0.6	2.2	1.4
CaO	33.8	51.4	14.2	16.7
TiO ₂	2.0	3.4	4.3	9.0
Cr ₂ O ₃	0.1	0.04	0.1	0.2
Fe ₂ O ₃	7.9	5.0	20.7	13.3
CuO	0.4	0.2	1.2	8.4
ZnO	0.9	0.4	0.8	3.9

or monosulfate (3CaO · Al₂O₃ · CaSO₄ · 12H₂O) [5]. In addition, dissolved chlorine ion once again fails to form FS due to the lack of Al₂O₃. From these reasons, it is inferred that FS was not confirmed in Ash D. It is suggested that FS formation occurs only when S/Al is low and both Ca/Al and Al/Cl are sufficiently high.

Generally, FS is hardly soluble to cold water, while it is soluble to hot water and acid. When FS exists in bottom ashes, it is necessary to decompose FS in order to reduce the Cl content to less than 0.5%.

3.2. Experimental Results

3.2.1. Effect of particle size

Figure 3 shows particle size distribution of four bottom ashes. Mean diameter of ash is 0.4 mm for Ash A and about 1 mm for other three ashes. Figure 4(a) shows the Cl content before

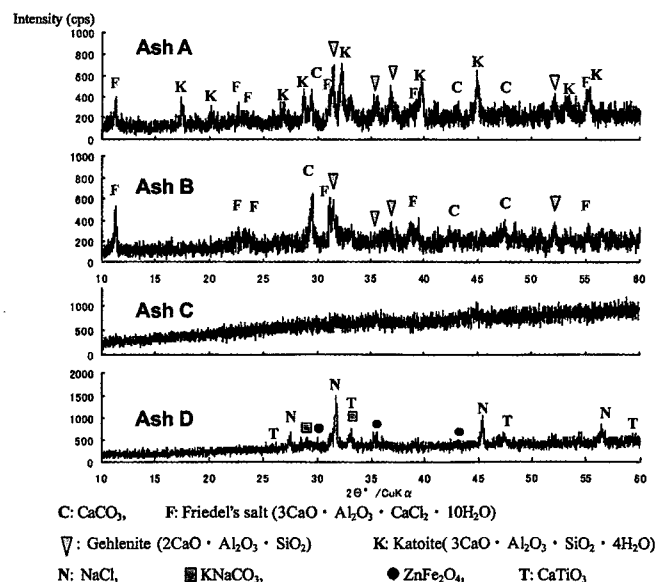


Figure 2 XRD patterns of bottom ashes

washing at various size fractions, which were classified by sieving before grinding. In the same way, Figure 4(b) shows the removal rate of Cl after washing for 10 minutes. The Cl content in ash tends to be higher in smaller particles as shown in Figure 4(a), because smaller particles which have higher specific surface area take in more evaporated chlorine in the incinerated gas and also take in more chlorine ion in the quench water outside the incinerator. Furthermore, as shown in Figure 4(b), when particle size gets smaller, the removal rate of Cl increases. This result suggests that smaller particles contact with water more efficiently due to higher specific surface area. Therefore, grinding before washing is very effective.

3.2.2. Effect of solutions and pH

Table 2 and Figure 5 show the result of washing tests using different solutions. Acid concentrations used in this experiment were 0.1 N and 2 N. In water washing, the removal rate of Cl was very low, only 14%. On the other hand, in acid washing, the removal rate was more than 40%. Although nitric acid was most effective, it is not desirable to use nitric acid because there is an environmental standard for nitrogen content in wastewater. In case of hydrochloric acid (HCl), Cl content after washing by 2N HCl was higher than that after washing by 0.1 N HCl. This means that Cl derived from HCl remained in the residue and HCl is not a proper solution. Considering practical use, sulfuric acid is the most suitable solution.

Figure 6 shows XRD patterns after washing using different solution. In case of washing by water, the peak of FS remained and

Table 2 Table 2. The results of washing tests for different solutions, Sample: Ash A (Cl=7440 ppm), Liquid/Solid ratio: 10

Solution	Concentration of Solution	pH of filtrate	Cl content of residue (ppm)	Residue weight (g/g-ash)	Removal rate of Cl
Water		11.7	6400	0.96	17%
HCl	0.1N	9.5	4400	0.93	45%
HCl	2.0N	0.4	5640	0.50	62%
HNO ₃	0.1N	8.3	4460	0.95	43%
HNO ₃	2.0N	0.6	2540	0.44	85%
H ₂ SO ₄	0.1N	9.8	3670	0.94	53%
H ₂ SO ₄	2.0N	1.0	1880	0.98	75%

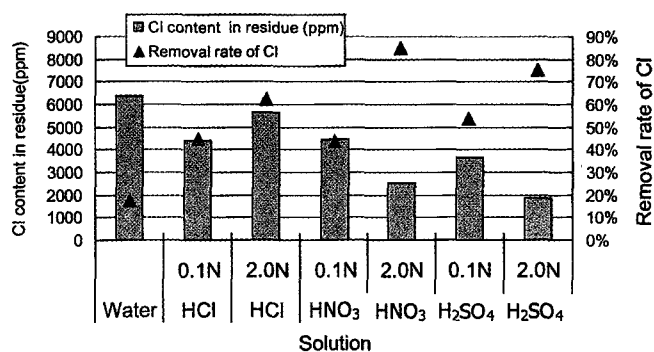


Figure 5 Cl content and removal rate of Cl after washing by different solutions.

Sample: Ash A (Cl=7440 ppm), Liquid/Solid ratio: 10

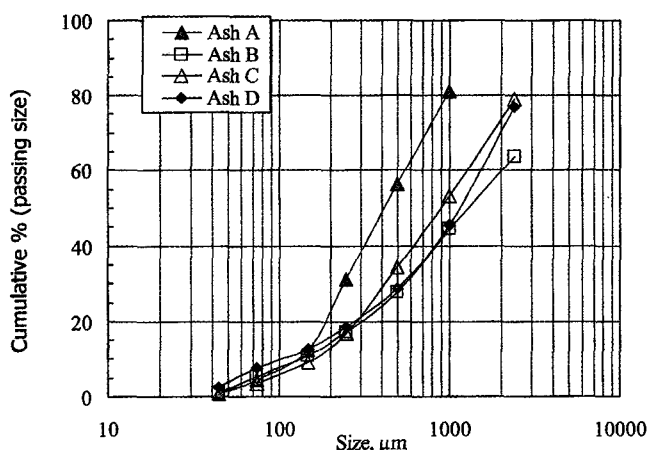


Figure 3 Particle size distribution of bottom ashes

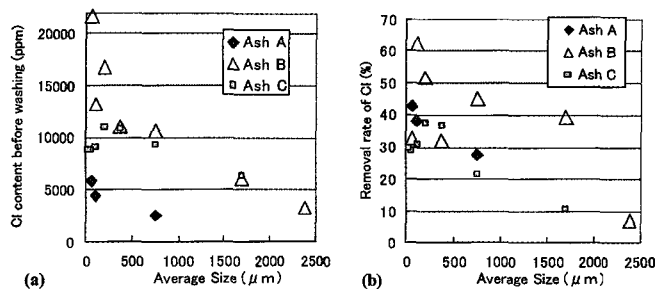


Figure 4 (a) Cl content before washing and (b) removal rate of Cl after washing at various size fractions (Liquid/Solid ratio: 10)

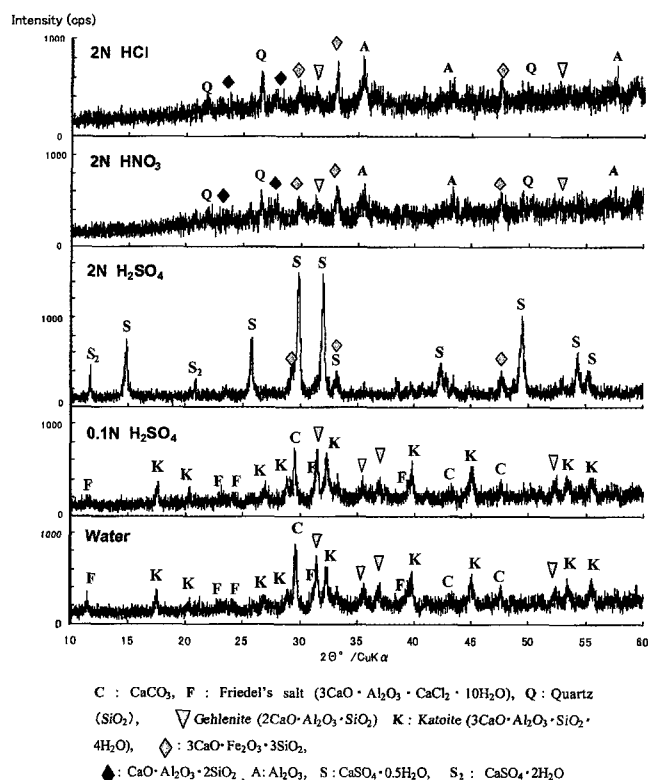


Figure 6 XRD patterns after washing by different solutions (Sample: Ash A)

Table 3 The amount of eluted heavy metals (Cu, Pb and Zn) after washing by H₂SO₄

	pH of filtrate	Residue weight (g/g-ash)	Content in solid (ppm)			Eluted ratio (%)		
			Cu	Pb	Zn	Cu	Pb	Zn
Ash A before washing			1530	368	3920			
After washing by 0.1N H ₂ SO ₄	9.8	0.94	1480	433	3610	9.0	0	13.4
After washing by 2N H ₂ SO ₄	1.0	0.98	731	345	1720	53.2	8.2	57.0

total pattern is the similar to that before washing. On the contrary, in case of washing by 2N acid, the peak of FS salt completely disappeared. In case of both nitric and hydrochloric acid, quartz and alumina were identified instead of calcium carbonate, while calcium sulfate (CaSO₄ · 0.5H₂O and CaSO₄ · 2H₂O) was identified in case of sulfuric acid. As shown in Table 2, residue weight after washing by 2 N sulfuric acid at pH 1 was 0.98 g/g-ash, while those after washing by both 2 N HCl and 2 N HNO₃ were c.a. 0.5 g/g-ash. This result means that the ratio decreased by soluble component at pH 1 is c.a. 50% and the ratio increased by formed calcium sulfate is c.a. 50%. Therefore, the residue weight was kept at almost 1 g/g-ash.

Figure 7 shows the Cl content after washing as a function of pH. pH has a clearly positive correlation with the Cl content and pH is more effective on Cl removal than any other parameters. However, the problem is that low pH causes ash leaching and also leaching heavy metals. Table 3 shows the amount of eluted heavy metals (Cu, Pb and Zn) after washing by H₂SO₄. As pH decreased, elution of heavy metals increased clearly. Therefore, when pH gets lower, the treatment of filtrate gets more difficult and costly.

3.2.3. Effect of bubbling

Table 4 and Figure 8 show the result of bubbling tests under different conditions (gas, ash and bubble size). In case of Ash A, the removal rate increased from 45% to 74% by using CO₂ microbubbles. CO₂ is more effective than air, and as for bubble size, finer bubble is more effective. As for Ash B, the removal rate

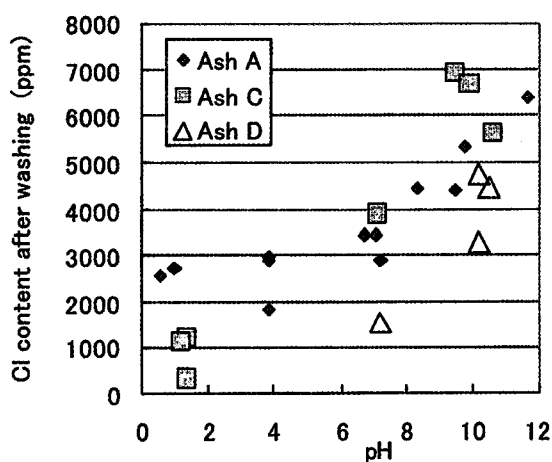


Figure 7 The relationship between Cl content after washing and pH.
Sample: Ash A (Cl=7,440-10,700 ppm), Ash C (Cl=8,830 ppm), Ash D (Cl=70,800 ppm)

Table 4 Cl content and removal rate of Cl after bubbling test for different conditions

Washing method	Ash	Gas	pH of filtrate	Cl content of ash (ppm)	Cl content of residue (ppm)	Residue weight (g/g-ash)
Agitation only	Ash A	-	11.7	10700	6180	0.93
Normal Bubble	Ash A	CO ₂	8.8	10700	4600	0.91
Micro Bubble	Ash A	Air	11.3	9500	3930	*
Micro Bubble	Ash A	CO ₂	7.1	10700	2910	*
Micro Bubble	Ash B	CO ₂	7.2	25500	2120	*

Table 5 Comparing microbubbles and normal bubbles

Parameter	Microbubble	Normal bubble
Diameter (mm)	0.01-0.04	1-10
Specific surface area (mm ² /mm ³)	150-600	0.6-6
Rising speed (mm/s)	0.1-1	100-1000

is 92% after CO₂ microbubbling. When compared with Ash A, Cl removal from Ash B is more efficient. It is likely that Ash B has higher content of soluble chloride than Ash A. Table 5 compares various parameters between microbubbles and normal bubbles. Due to higher specific surface of microbubbles, it is much easier for particles to contact with CO₂. Moreover, in case of microbubbles, rising speed is much slower and dissolution speed of CO₂ gets higher. Thus, microbubbles are more effective in shorter reaction time.

Figure 9 shows XRD patterns of ash after bubbling. As shown in this figure, there is no peak of FS after CO₂ bubbling, while the peak remains after air bubbling. The dissolution reaction of FS by CO₂ is shown in Eq. (1).

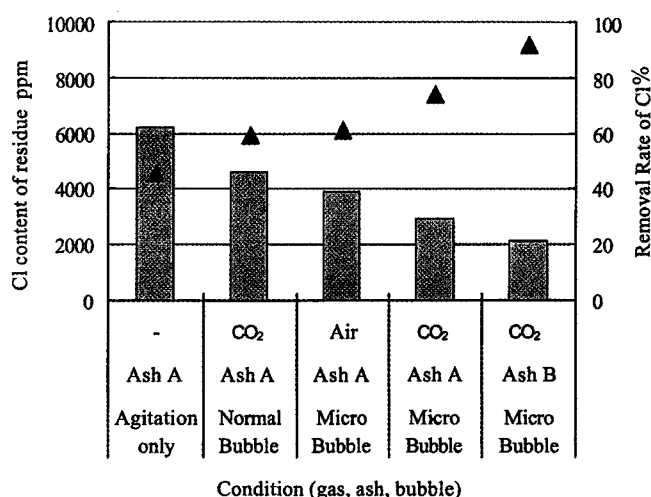
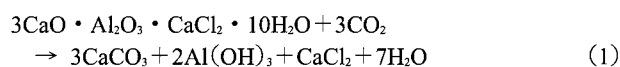


Figure 8 Cl content and removal rate of Cl after bubbling test for different conditions

Table 6 Bubbling test results adding the effect of acid and temperature (CO₂ microbubble: 0.2 L/min.)

Solution	Temperature	pH of filtrate	Cl content after bubbling (ppm)	Removal Rate of Cl (%)
H ₂ O	20°C	7.1	3410	70
0.1 N H ₂ SO ₄	20°C	3.9	2860	75
0.1 N H ₂ SO ₄	90°C	3.9	1830	84

Since CaCO₃ formed by this reaction, the intensity of CaCO₃ peak increased after CO₂ bubbling as shown in Figure 9.

In Eq. (1), the residue after FS dissolution is assumed to be CaCO₃ and Al(OH)₃, because the solubility of these two is very small. Then, the ratio of residue weight is calculated to be c.a. 81% from molecular weight. When the weight percentage of FS in ash is 4% (i.e. Cl as FS=0.5%), the decrease of ash weight by FS dissolution is calculated to be 0.8%. This means that the change in weight by FS dissolution is very small.

Next, the effects of weak acid washing and temperature on Cl removal were investigated, together with CO₂ microbubbles. Table 6 shows the results. By using 0.1 N sulfuric acid, the removal rate of Cl slightly increased from 70% to 75%. Besides, by raising the

temperature up to 90°C, the removal rate increased up to 84%. These results suggest that not only CO₂ in flue gas but also waste heat are available for efficient washing.

4. Concluding Remarks

In order to recycle bottom ashes as raw materials of cement, removal of Cl from ashes was investigated. Friedel's salt was identified as the main chloride by XRD analysis. Both washing by strong acid and CO₂ bubbling were very effective to decompose Friedel's salt. However, CO₂ bubbling is better because strong acid washing is not environmental friendly due to dissolution of heavy metals from ash.

The grinding process is very important to achieve a high efficient removal of Cl, because high specific surface is needed. When bubbling by CO₂ is performed, fine microbubbles are more effective than normal bubbles as they attach more easily to particles. In addition, removal rate of Cl increases by using diluted sulfuric acid at a high temperature in addition to CO₂ microbubbling,

Acknowledgments

The present work was supported in part through the 21st Century COE Program, "Mechanical Systems Innovation," by the Ministry of Education, Culture, Sports, Science and Technology, Japan. Moreover, the work was also supported by cooperation research with the Industrial Waste Recycling R&D Center, Korea Institute of Geoscience and Mineral Resources.

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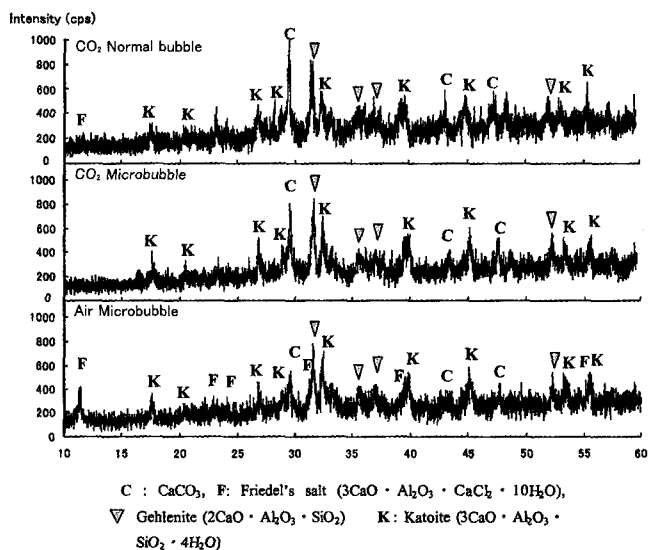


Figure 9 XRD patterns of ash after bubbling test