

Distribution of Chloride in Municipal Solid Waste Incineration Bottom Ash

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ABSTRACT

Chloride content is a critical problem for the reuse of incineration bottom ash as raw material in cement. The effect of dechlorination procedure largely depends on the existence form of the chlorides. However, limited information about the distribution and identity of chlorides in bottom ash can be obtained by bulk analysis methods. In this paper, the investigation towards a more comprehensive understanding about chloride in bottom ash was carried out by means of optical microscopy and scanning electron microscopy. Two types of bottom ashes with different cooling methods were studied. It was revealed that chloride was mainly contained by the glass in the air-cooled bottom ash and, moreover, a strong association between chloride and calcium was disclosed. Water quenching altered the morphology of ash particle and formed fragile phase, which concentrated relatively high content of chloride. The crystalline chloride of Friedel's salt was also identified in the water-quenched bottom ash.

Keywords. bottom ash, chloride, dechlorination, distribution and identity, microscopy

INSTRUCTION

The management of municipal solid waste (MSW) in many countries has become a complicated task owing to the stress of limited landfill site. To reduce the quantity to be landfilled and recover energy from MSW, incineration is widely applied. Through incineration, 85% of the original volume of the MSW can be reduced. But incineration is not the final waste treatment stage; with the process going, incineration residues are produced as bottom ash and fly ash, of which MSWI bottom ash occupies 85-95% of the total weight. Though bottom ash is not as hazardous as fly ash, the disposal of it is still a big concern. Recycling/reusing the MSWI ash as raw material for cement production is considered to be a good strategy from the viewpoint of environmental protection and resource conservation. But the chloride content in MSWI bottom ash poses a problem. Due to the occurrence of chloride-induced corrosion on steel in concrete (Glasser, 1999), the cement-based industries have very strict tolerable concentration of chloride in cement material. Japan has the strictest regulation: the chloride content in portland cement

need to be lower than 0.035 wt%, for instance. Thus, studies and efforts have been conducted to lower the chloride content in MSWI ash to meet the standard.

The chloride in MSWI ash is mainly sourced from plastic materials such as PVC (Themelis, 2005). During incineration most of the chloride will be volatilized as HCl and transfer into fly ash, and the remaining chloride content in bottom ash is 1~3.5 wt% (Chandler, 1997). Water washing as a prevalent dechlorination method is very effective to remove soluble chloride, but the insoluble chloride compounds will remain. To maximize the reuse of bottom ash, the chloride content must therefore be reduced as much as possible. Thus, it is very important to know the existing form of chloride in bottom ash so suitable treatment can be used. Previously, researchers have studied chloride in MSWI ash with the focus on the solubility of chlorides by washing or leaching experiment (Boghetich, 2005). Some studies utilized X-ray diffraction (XRD) and successfully identified chlorides as NaCl, KCl, CaCl₂, Friedel's salt and so on. But XRD can only reveal the presence of crystalline chloride compounds.

The prime objective of this study is to carry out a comprehensive investigation on the existence and distribution of chloride in MSWI bottom ash. We examined two types of bottom ash (i.e. air-cooled bottom ash and water-quenched bottom ash which were both sampled from real incineration facilities). Direct observation and analysis of the ash particle thin section by optical microscope and scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDX) were conducted. Based on analysis results the contents of chloride in different (glassy/crystalline/metallic) phases inside bottom ash could be unveiled. The influence of water quenching process on the morphology of bottom ash particle and the distribution of chloride was also evaluated.

MATERIALS AND METHODS

Both the air-cooled and water-quenched bottom ash samples were collected from real incineration facilities in Japan. During sampling, the large incombustible and unburned items were removed. The left of the ash was then stored in plastic bags for laboratory analysis and usage (drying, particle selecting, and milling). The chemical and mineralogical composition of the ash samples were obtained by carrying out XRF and XRD on the powder sample respectively. Comparably, the analysis of the intact ash particle is the major focus of the study. Polished thin sections of the ash particles were prepared according to the conventional method. The thin sections were primarily subjected to identification of the various phases. This is achieved by using a petrographic polarized microscope (BX51-33MB, OLYMPUS) under different optical modes (PPL, plain polarized light; XPL, cross polarized light; and RL, reflected light). The chemical compositions of each phase, with an emphasis on the chloride, were determined by SEM/EDX.

RESULTS

Characterization of MSWI Bottom Ash. Table 1 showed the chemical and mineralogical compositions of the two bottom ash samples. It revealed that the incineration products were silicate- and calcium-based materials with different weight proportions of other elements. Besides SiO₂ and CaO, Al₂O₃ and Fe₂O₃ were also the dominating components (>10 wt %). Minor constituents (1~10 wt %) consisted of Ti, Mn, P, Na, K, Cl and S. Heavy metals were included in trace constituent group (<1wt%), of which Zn and Cu had the highest

contents. The mineral phases were identified by XRD and attention was paid to chloride compounds. Semi-quantitatively by comparing the height and sharpness of peak, quartz, calcite, gehlenite were found to be the major crystalline phases in the two ash samples. Due to the variation of MSWI ash, there was always the occurrence of XRD peaks' shifting and overlapping, so the identification of low-content mineral was difficult. Halite was identified in both two samples with uncertainty. In water-quenched bottom ash, Friedel's salt was identified as one major mineral phase.

Table 1. Chemical and mineralogical composition of the two bottom ash samples analyzed by XRF and XRD

Chemical composition	Air-cooled	Water-quenched	Mineral phase	Air-cooled	Water-quenched
SiO ₂ (wt %)	30.27	25.56	Quartz	High content	High content
Al ₂ O ₃	10.74	11.37	SiO ₂		
Fe ₂ O ₃	12.38	6.47	Calcite	High content	High content
CaO	33.79	38.76	CaCO ₃		
TiO ₂	1.34	2.59	Gehlenite	Abundant content	Abundant content
P ₂ O ₅	4.12	3.23	Ca ₂ Al ₂ SiO ₇		
MgO	2.52	2.63	Lime	High content	Not detected
Na ₂ O	2.13	1.61	CaO		
K ₂ O	0.52	0.71	Anorthite	Medium content	Medium content
Cl	0.97	2.03	(Ca,Na)(Si,Al) ₄ O ₈		
S	0.21	0.50	Hematite	Medium content	Not detected
LOI	0.215	3.834	Fe ₂ O ₃		
Zn (ppm)	3001	2538	Halit	Small content	Small content
Cu	1616.5	2538	NaCl		
Pb	425	2538	Portlandite	Not detected	Small content
Ni	89	2538	Ca(OH) ₂		
Ba	1039	2538	Friedel's salt	Not detected	High content
Sn	169.25	2538	3CaO · Al ₂ O ₃ · CaCl ₂ · 10H ₂ O		

Optical Microscopic Observation of Ash Particle Thin Section. Due to the low content of chloride in the ash samples, the distribution of it was mainly revealed by optical and scanning electron microscopy. The polished thin sections of the ash particles were used for this analysis. Figure 1 presented the thin section images of air-cooled and water-quenched bottom ash particles under optical microscope. They were found with very different morphological appearance: spatially, the air-cooled ash contained one single phase, namely melt phase in this paper; the water-quenched ash composed of two parts as melt phase and fragile phase with an obvious division (highlighted by red-dash line in Figure 1 (b)) between them.

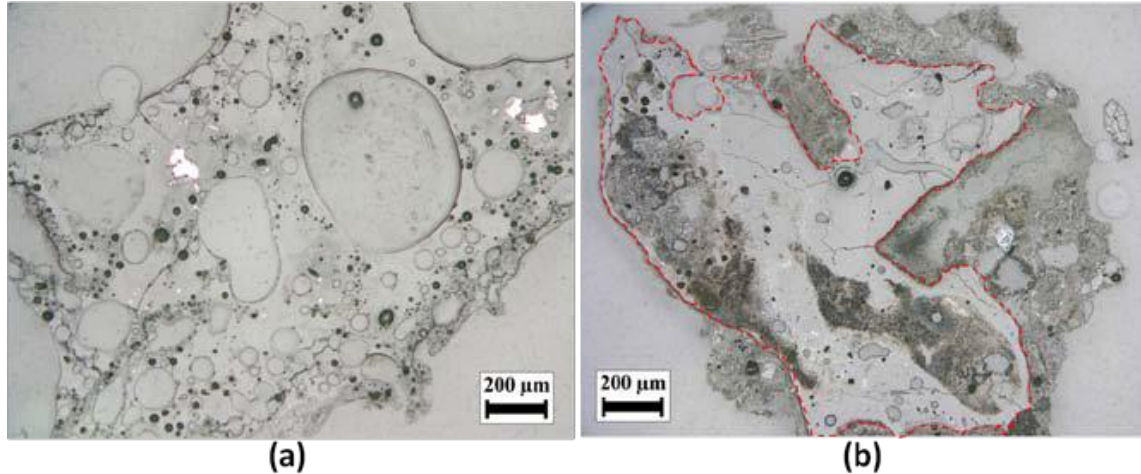


Figure 1. Photomicrographs of air-cooled (a) and water-water quenched (b) bottom ash particles under reflected light (RL) mode of optical microscopy

The melt phases, as the name implies, are the outcomes that produced in the incineration process of MSW, mainly as glass, mineral and other refractory material. They usually exist as the core of the ash particle. The fragile phases are the fine ash particles that adhere to the melt phase during water quenching process. They are aggregates of fine particles with various chemical compositions. Due to the dramatic change that water quenching process had brought to the ash particle, the following results of chloride distribution in air-cooled and water- quenched bottom ash were presented separately.

Chloride distribution in the air-cooled bottom ash. The petrographic and chemical analysis of the ash particle was conducted by combining optical and scanning electron microscopy in this study (seen in Figure 2). The main part of air-cooled ash particle was identified to be melt phase, which could be further differentiated as glass, crystalline (mineral) and metallic phases: the glass phases are generally considered to be the principal incineration products of MSWI bottom ash. By adopting the standard glass addition method (Font, 2010), the glass content in the air-cooled bottom ash was estimated to be around 40 wt%. The optical and electron microscopy analysis revealed the melt glass phases served as a matrix for bottom ash and normally with the coexistence of voids, mineral species and refractory components. For thin section observation, glass phases appeared isotrope, transparent or translucent under PPL, but dark under XPL (Figure (a) and (c)); crystal or crystalline phases are the solid materials whose constituent atoms, molecules, or ions are arranged in an ordered pattern extending in all three spatial dimensions. They have a variety of shapes and sizes. Under XPL, a range of interference colours would appear on the crystalline phase so it can be differentiated from the others (Figure 2 (b)). Under electron microscopy, crystal material is normally found with relatively regular shape and obvious boundary with the background phase (Figure 2 (d)); metallic or metal components like Fe and Al are often presented in relatively high concentrations in bottom ash. These metals usually exist as various chemical combinations or inclusions (Wei, 2011). The metallic phases have higher reflective index compared with glass and crystalline phases, so they are easy to be told under RL mode (Figure 2 (c)).

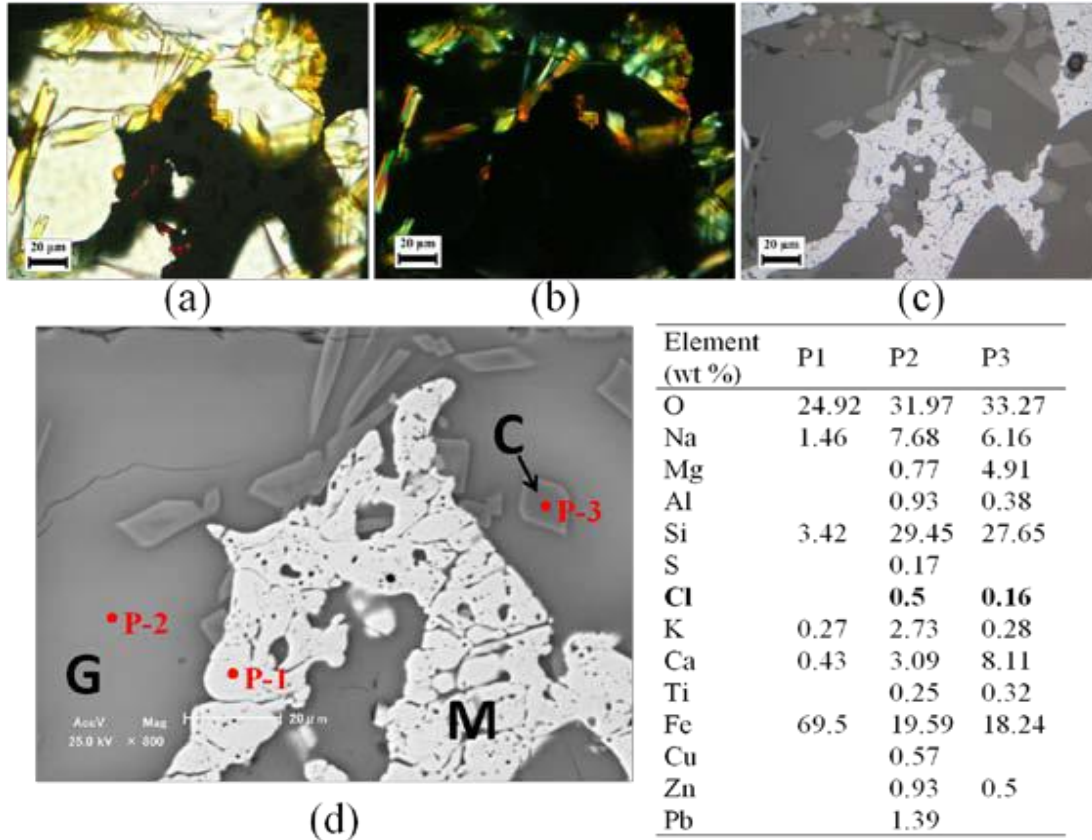


Figure 2. Photomicrograph of the coexistence of glass, metallic and crystalline phases in the air-cooled bottom ash sample. (a) under PPL, (b) under XPL, (c) under RL, (d) under SEM (G: glass; C: crystalline; M: metallic).

After the glass, crystalline and metallic phases of the particle thin section being differentiated, the chemical composition of each phase was determined by SEM/EDX. The analytical points were designated onto the target positions (see in Figure 2 (d)) and corresponding quantitative results were obtained (presented by the table in Figure 2). For the purpose of investigating the distribution of chloride among different phases, line analysis and mapping by EDX were found not effective in this study. That was due to the relatively low content of chloride in these samples. The main analytical strategy adopted by this study was point analysis. For better accuracy and reliability, totally 18 air-cooled bottom ash particle thin sections were prepared. 239 analytical points were designated onto different targets and their chemical compositions were obtained. By averaging and comparing the data, two conclusions related with chloride distribution could be reached:

1) The chloride content in glass is higher than those in crystalline and metallic phases

Figure 2 showed a thin section target with the co-existence of glass, crystalline and metallic phases. The analytical points were designated onto each phase (P-1: metallic phase, P-2: glass phase, P-3: crystalline phase). No chloride content was found in the metallic phase. Glass phase and crystalline phase had chloride concentrations of 0.5 wt% and 0.16 wt% respectively.

Of all the 239 analytical points, 71 points were designated on the glass phases. 41 points were found to contain chloride with an average concentration of 0.69 wt%. For crystalline and metallic phase, the amount of points containing chloride was found very little. Even there was chloride contained, the concentration of it would be very low. So the chloride content in these two phases was considered to be neglectable.

2) The chloride content in Ca-rich glass phase is relatively higher

The glass phases in MSWI bottom ash are the main melting products under the high temperature and complex conditions of the incinerator. During its formation, various components and materials are encapsulated into the glass, and some of them can significantly influence the characteristics of the glass phases both chemically and morphologically. In this research, Ca was found worthy of extra attention. Figure 3 (a) presented a comparison between Ca-rich and Ca-poor glass observed in one thin section target. The lower left part of the particle was with the enrichment of Ca around 10.0 wt%. In the upper right, the Ca content was only 0.5 wt %. Several quartz particles scattered in the middle and lower right. A very clear boundary existed between the Ca-rich and Ca-poor parts.

It can be seen the Ca-poor glass was with highly vesicular texture. The vesicles of the glass phase were due to the entrapment of air and gas bubbles during glass formation. How much the entrapment would occur was decided by the viscosity of the melted material. It was considered that the content of Ca was negatively correlated with the viscosity of glass. So when Ca content was low, the viscosity of became high, and then more air and gas bubble would be captured by glass.

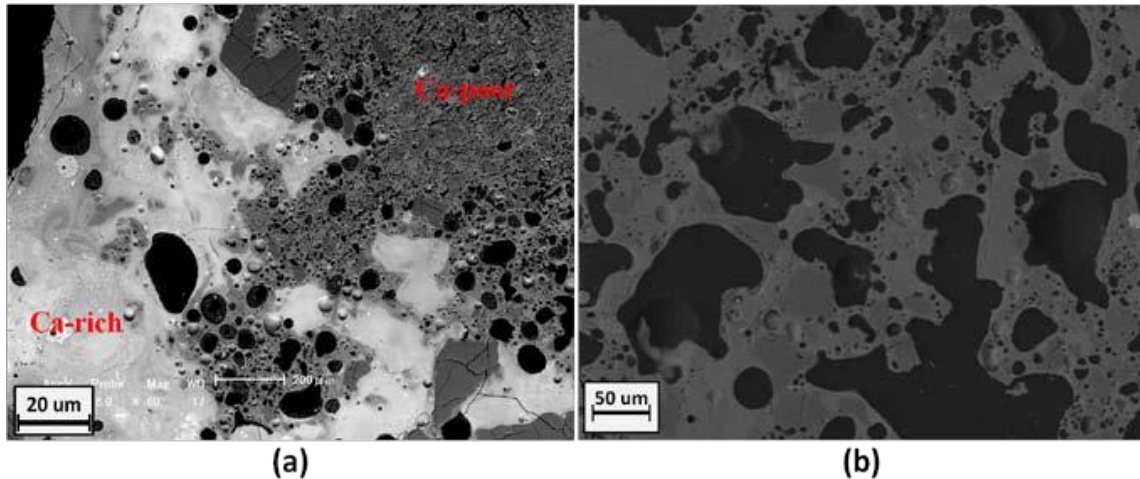


Figure 3. SEM image of Ca-rich and Ca-poor glass phases. Ca content ranged from 0.5~10 wt % (a); Ca content ranged from 0.1~3 wt% (b).

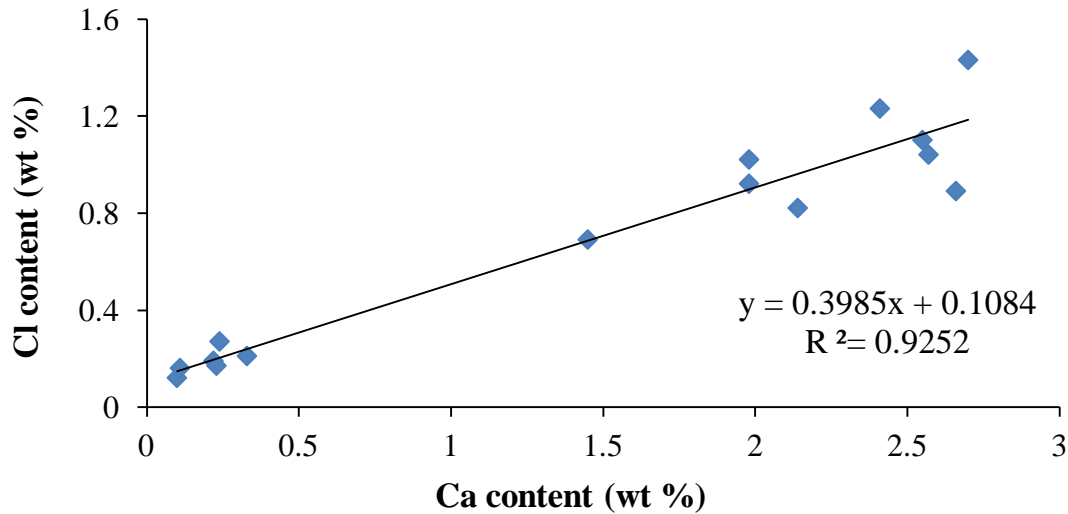


Figure 4. The correlation between Ca and Cl contents in glass phase of the air-cooled MSWI bottom ash

The Ca also affected the chloride content around it. Figure 4 exhibited the correlation between Ca and Cl in the air-cooled bottom ash. The results were obtained from the point analysis of the thin section target presented by Figure 3 (b). In this case, the contrast between Ca-poor and Ca-rich glass phases was not so obvious, which was due to the range of Ca content only from 0.1 to 3 wt %. Totally 14 analytical points were designated onto the glass phases and the results were plotted on Figure 4. Apparently, the Ca and Cl contents were positively related. This correlation is considered to be formed through following process: during the incineration process, chloride is mainly volatilized as HCl, and part of the HCl is bound by CaO. The HCl and CaO will then form CaCl_2 . Since CaCl_2 has a boiling temperature of 1600 °C, it will remain in the incinerator. However, the melting temperature of CaCl_2 is only 772 °C, which is normally lower than the combustion temperature (>850 °C). So after its formation, the CaCl_2 will be immediately melted. The products will re-solidify and yield Ca- and Cl- rich glass when incineration process is over.

Chloride distribution in the water-quenched bottom ash. The freshly produced MSWI bottom ash sample was still a thermodynamically unstable material and should have undergone dramatic evolution during water quenching. The products of this process are the fragile phases. A series of reactions might be related with the formation of fragile phases, such as dissolution, precipitation, carbonation, and even bacterial activities. XRD had revealed high crystallinity of water-quenched bottom ash compared with air-cooled one. Crystalline chloride of Friedel's salt was identified. Thin section observation found that the fragile phases were with fairly loose structure and heterogeneous appearance. They normally showed dark brown under PPL and opaque under XPL. Due to the highly nonuniform morphology of the fragile phases, it was difficult to further differentiate them into amorphous, crystalline or metallic phases. But direct mapping by SEM/EDX exhibited very clear distribution trend regarding to chloride in this case. As it can be seen in Figure 5, chloride in water-quenched ash was mainly contained in the fragile phases. It was estimated that the average chloride content in the fragile phase was around 2 wt% by designating 15 analytical points in this area.

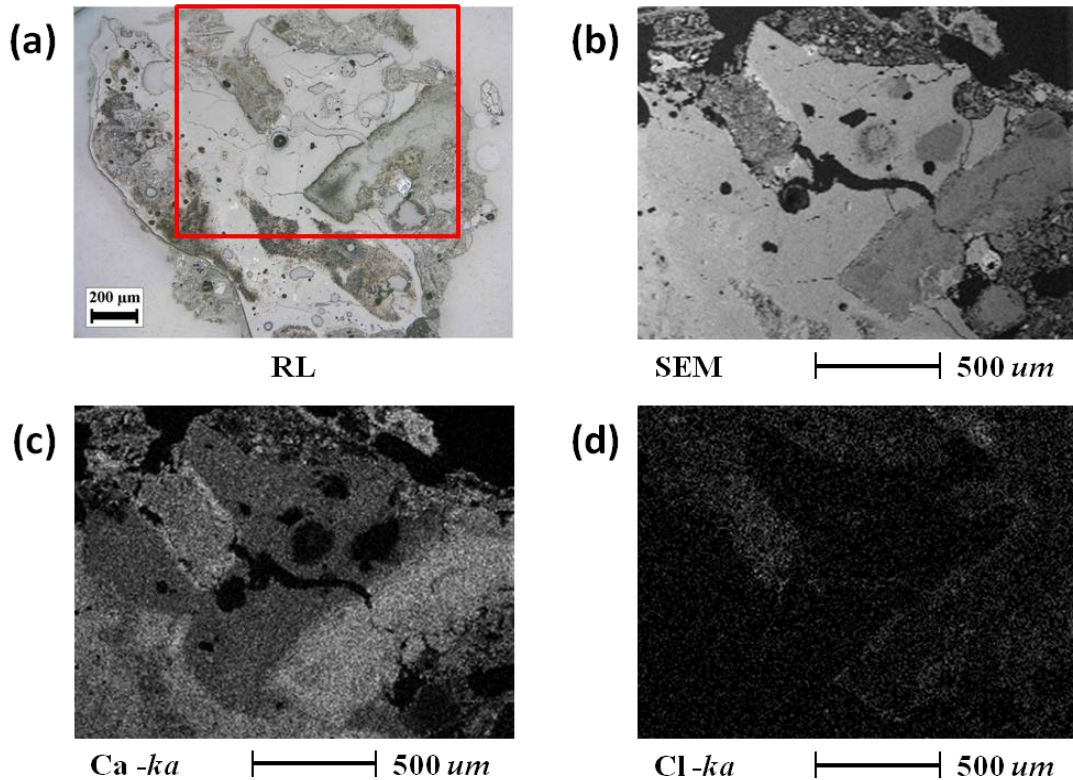


Figure 5. Photomicrograph (a) and SEM image (b) of the water-quenched bottom ash particle, and corresponding mapping results of Ca (c) and Cl (d) by EDX

The study on air-cooled ash had revealed that chloride in melt phases was mainly contained by glass, which could not easily be incorporated into other phases. It is considered the chloride in the fragile phase came from the water quenching stage. During the previous quenching processes, considerable amount of soluble chloride compounds must have been concentrated in the quenching water and part of them will be precipitated by the ash again during quenching process. The microscopy analysis also found certain targets with chloride concentration up to 5~6 wt%. Some of them appeared significant evidence of crystallization. It indicated the existence of crystalline chloride like Friedel's salt in the fragile phases.

DISCUSSION AND CONCLUSIONS

The current research was designed to investigate the distribution of chloride in MSWI bottom ash. Both air-cooled and water-quenched ashes were selected as the research targets. The novelty of this study is the direct microscopic analysis on the ash-particle thin section, through which a relatively comprehensive understanding about the existence of chloride is achieved. Figure 6 summarized the whole transformation process of the chloride from the raw solid wastes to incineration bottom ash based on the present research results: most of the chloride in the

municipal solid is volatilized as HCl during incineration. But due to the content of alkaline materials in the incinerator, especially CaO, part of HCl will be bound and stay with the incineration residues. The chloride binding process will form products such as CaCl_2 , which have melting temperature lower than combustion temperature ($>850^\circ\text{C}$), so they will be melted and further entrapped into glass. Through phase differentiation and sequential quantitative analysis, the presence of Ca- and Cl- rich glass in the bottom ash was observed. Water quenching process alters the morphology of ash particle and forms the fragile phases. It also significantly affects the existence and distribution of chloride. Crystalline chloride as Friedel's salt was identified in the water-quenched bottom ash sample. SEM/EDX mapping also revealed that the chloride content in the fragile phases was considerably higher than that in the melt phases.

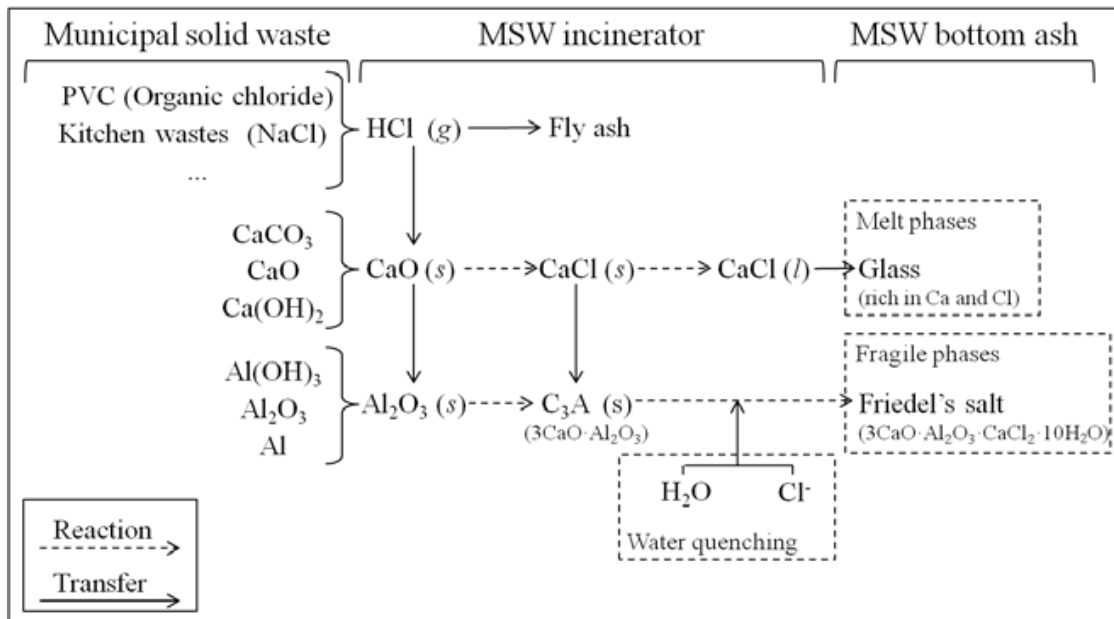


Figure 6. Schematic illustration of the flow and corresponding transformations of chloride from municipal solid waste to incineration bottom ash

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