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ScienceDirect
Journal of Hazardous Materials 148 (2007) 346–352
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Distribution of chloride ion in MSWI bottom ash and de-chlorination performance

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Received 18 November 2006; received in revised form 15 February 2007; accepted 17 February 2007
Available online 23 February 2007

Abstract

When recycling bottom ash from municipal solid waste incinerators (MSWIs), salts and heavy metals contents must be considered; in particular, chloride ions must be addressed because they cause serious corrosion in metals. Therefore, only limited amounts of bottom ash can be utilized as a substitution for material or the bottom ash must be treated at high temperatures prior to use. These factors markedly decrease the applications of bottom ash. In addition to the distribution characteristics of chloride ions, this study also investigates the characteristics change before and after de-chlorination using a counter-flow pipe column and three different flow fluxes for different refuse incinerators as the experiment variables. Thus, this study attempts to determine the appropriate conditions for de-chlorination and an appropriate policy for use of bottom ash as concrete aggregate. The experimental results show that a negative correlation exists between the natural logarithm of the chloride ion concentration and particle size in bottom ash. Characteristics of de-chlorinated bottom ash, such as pH value, mud content, loss on ignition, chloride ion concentration, turbidity, and species intensity, all decrease, meaning that de-chlorination decreased chloride ion content and generates a cleaning effect. The per-unit-time efficiency of de-chlorination is highest in the high flux flow. When flow flux is 80 mL/min, the de-chlorination efficiency is >0.3%/h. However, the shortest time required for bottom ash de-chlorination does not reduce in proportion to the legally prescribed concentration of chloride ion.

Keywords: Bottom ash; Corrosion; Chloride ion; De-chlorination; Concrete aggregates

1. Introduction

According to Taiwan Environmental Protection Administration (EPA) statistics for 2005, incineration is the primary method for treating municipal waste, the success of waste treatment is as high as 99%. The products of incineration are disposed in landfills. Currently, 20 large operating municipal solid waste incinerators (MSWIs) produced 936,480 metric tonnes of incinerated products each year, including 790,836 metric tonnes of bottom ash. The Taiwanese government considers bottom ash a general industrial waste. However, the application is limited by its content of heavy metals and chloride ions. The particle size of bottom ashes is predominantly >1 mm. The main components of bottom ash are glass, magnetic metals, minerals, synthetic ceramics, paramagnetic metals and unburned organic matter [1]. Of these, chloride ions destroy the passivation of metals [2] and results in considerable material and equipment corrosion that limits the range of application. Currently, the recycling products of bottom ash are sub-grade materials, ceramics, mineral admixtures and concrete aggregates [3–5]. However, only 10–20% of aggregates are substituted by bottom ash in Taiwan due to the allowable limits for chloride ion.

Chloride ions exist in concrete in three different types: free chloride ions, chemically bonded ions and physically absorbed ions [6]. Of these, free chloride ions are the most appropriate indicator [7], meaning that free chloride ions have the highest ability to corrode metals. In contrast to free chloride ions, physically absorbed and chemically bonded chloride ions have higher stability and relatively lower ability to corrode metals. According to Taiwan's regulations, only free chloride ion content is considered when using bottom ash as concrete aggregates.

Alkaline washing (sodium hydroxide solution) clearly resulted in better contaminant removal than did distilled-water washing. The chemical properties of alkaline-leached bottom ash were not significantly different from those of water-leached ash [8]. Extraction of chloride ions from MSWI bottom ash

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doi:10.1016/j.jhazmat.2007.02.046

increased as the temperature of the extraction medium increased [9]. Chloride is readily leached easily from MSWI bottom ash in landfills; roughly 80% of chloride ions in bottom ash are discharged annually. Compared with other salts, chloride has a low retention rate [10].

This study only investigates free chloride ions in bottom ash. Bottom ash contains a high concentration of chloride ions and, therefore, has limited applications. Additionally, to eliminate the pipe blocking problem caused by traditional consequent flow equipment and the issue of declining de-chlorination efficiency due to short-circuited flow, the counter-flow process is adopted to investigate the influences of flow flux and duration on de-chlorination effects. In considering the economics and limitations of chloride ion content in fine aggregates, which is regulated by Chinese national standards (CNS, Taiwan), this study proposes an optimum de-chlorination condition and recycling policy.

2. Methodologies

Bottom ash used in this study were obtained from four municipal waste incineration plants in northern Taiwan: the Nan-Liao plant in Hsinchu City, the southern region plant in Taoyuan County, the Bali plant in Taipei County, and the Muzha plant in Taipei City. Bottom ash was sampled four times while on a conveyor belt. The amount sampled each time was 15 kg; a total of 60 kg of bottom ash was obtained. Because the municipal solid waste in Taiwan is not classified completely, and bottom ash is from mixed combustion of a fixed-bed incinerator, the efficiency in burning waste of the incinerator is low. Therefore, in this study, bottom ash larger than 3/8 in. was sieved out, most of these residues are glass, ceramics and metals, thus non-representative residues were eliminated. After eliminating metals and glasses, bottom ash was ground and passed through a 3/8 in. mesh. Bottom ash was classified into the following seven particle sizes: 3/8 in.; #4, <4760 μm; #8, <2380 μm; #16, <1180 μm; #30, <600 μm; #50, <150 μm; #100, <75 μm. Bottom ash was non-hazardous waste.

The sources of bottom ash, particle size and flow flux of the pipe column were variables in this study. The pipe column flow was distilled water at room temperature. First, the relationship between particle size of bottom ash and chloride ion concentration was analyzed. A counter flow pipe column (diameter, 100 mm; length, 500 mm) was designed. Approximately 3.0 kg of representative bottom ash was extracted from each batch and analyzed. The bottom ash was placed in to the pipe column to a height of 300 mm. Then, de-chlorination was conducted for 120 h using the following three flux rates: 20 mL/min, 50 mL/min, and 80 mL/min.

Bottom ash characteristics were determined, including weight, particle size distribution, loss on ignition (600 °C for 3 h), mud content (<75 μm), chemical composition, chloride ion content (chemical titration), and X-ray diffraction (XRD) species. Chemical compositions analysis was performed using inductivity coupled plasma (ICP-AES), Mud content was assessed according to the "Test for Substance in Aggregates Finer than 75 μm Sieve" in the CNS 491 standard (Chinese national standards, CNS, Taiwan) [11]. Chloride ion concentration was analyzed according to the "dissolved chloride ion content test for fine aggregates" (CNS 1240 and CNS 13407) [12,13], and chloride ion concentration in de-chlorinated solution was determined using NIEA W407.51C (National Institute of Environmental Analysis, EPA, Taiwan).

3. Results and discussion

3.1. Distribution of chloride ion in bottom ash

The chloride ion concentration of bottom ashes from four incinerators increases as particles size decreases (Fig. 1). Bottom ash with a particle size <#100 (<150 μm) has the highest chloride ion concentration as bottom ash with fine particles has larger specific surface areas, indicating that chloride ions accumulate easily on fine particles. Table 1 presents that the overall chloride ion concentration is close to that of bottom ash with fine particles. That is, the chloride ion concentration in bottom ash with particles <3/8 in. is close to that for ash <#100 (<150 μm), and the difference is between <3/8 in. and <150 μm is 4–12%. A negative correlation exists between the chloride ion concentration and the natural logarithm of particle size (Fig. 2). The correlation coefficient (R^2) is 0.886.

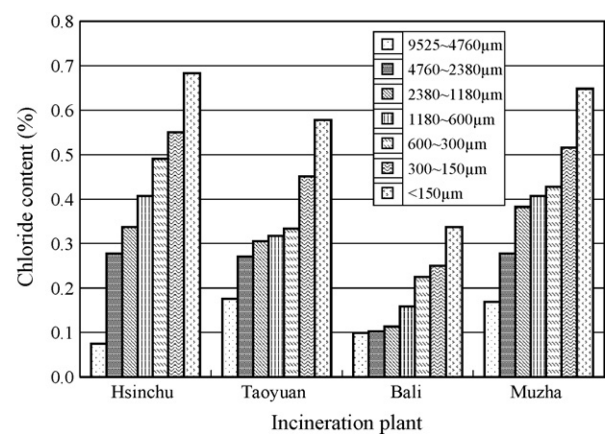

Fig. 1. Chloride concentration of bottom ash.

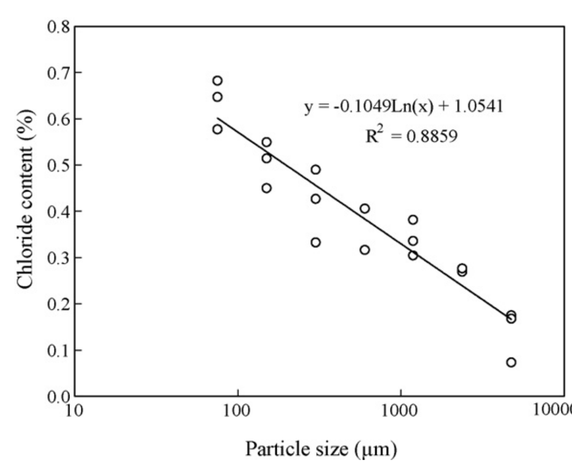

Fig. 2. Regression curve between particle size and chloride concentration.

Table 1
Physical and chemical properties of MSWI bottom ash

	Refuse incinerator							
	Hsinchu		Taoyuan		Bali		Muzha	
	Before[a]	After[a]	Before[a]	After[a]	Before[a]	After[a]	Before[a]	After[a]
Specific gravity	1.7	2.3	1.9	2.4	2.3	2.4	2.1	2.3
Mud content (%)	7.6	6.0	6.7	4.6	8.4	7.3	4.9	3.8
Turbidity (NTU)	14	0.50	26	0.60	29	0.80	11	0.6
Loss on ignition (%)	7.9	4.4	7.6	4.34	5.2	2.9	6.7	3.8
SiO_2	34	48	34	48	31	45	33	48
Fe_2O_3	12	10	15	9.8	16	15	12	11
MgO	0.65	1.2	0.57	0.98	0.43	0.96	0.30	0.94
Al_2O_3	2.5	3.6	6.5	5.4	4.0	5.1	2.7	6.0
K_2O	2.1	2.2	2.5	2.3	1.8	1.8	1.9	2.2
Na_2O	3.5	2.9	3.0	2.5	6.4	5.8	3.0	2.3
CaO	1.7	8.9	7.6	12	5.6	13	3.0	10
ZnO	0.66	0.35	0.38	0.39	1.7	0.80	2.1	0.33
PbO	0.13	0.32	0.21	0.57	1.1	1.2	0.21	0.15
SO_3	1.2	0.65	0.72	0.46	0.69	0.18	1.21	0.45
pH	11	8.2	9.9	8.0	11	8.4	11	8.1
Overall Cl^- content (%)	0.53	ND	0.51	ND	0.34	ND	0.68	ND

ND: not detected. Detection limit is 0.001%.
[a] De-chlorination condition: the flow flux of 50 mL/min and duration for 120 h.

3.2. Characteristic variations of bottom ash before and after de-chlorination

The chemical component changes in bottom ash before and after de-chlorination are analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Table 1 shows analytical results. The predominant chemical components of MSWI bottom ash are SiO_2, Fe_2O_3, Al_2O_3, and CaO. The salts and organic matter not completely combusted in bottom ash were reduced by dissolution after de-chlorination for 120 h (Fig. 2).

Under the flow flux of 50 mL/min and de-chlorination for 120 h, changes in characteristics of bottom ashes before and after de-chlorination are discussed. Table 1 shows that characteristics of bottom ash, such as pH, mud content, loss on ignition, chloride ion content, and turbidity all decreased. After de-chlorination, bottom ash changes from a strong base to a weak base, and the specific gravity increases. This finding results from the de-chlorination process with counter flow removing easily light substances, organics, and fine particles in the bottom ash. The analytical results demonstrate that the de-chlorination process both lowers the chloride ion concentration and has a cleaning effect, which stabilizes the bottom ash and makes it suitable for use as concrete aggregate.

With ash obtained from the Taoyuan plant as an example, the de-chlorination process always reduces the pH and has little effects on that of bottom ash with a low flow flux of 20 mL/min and evident effects when the flux is 50 mL/min and 80 mL/min (Fig. 3). The turbidity of de-chlorination solution of bottom ash has the same trend as pH variation, namely, turbidity is lowered dramatically when the flux is 50 mL/min and 80 mL/min (Fig. 4).

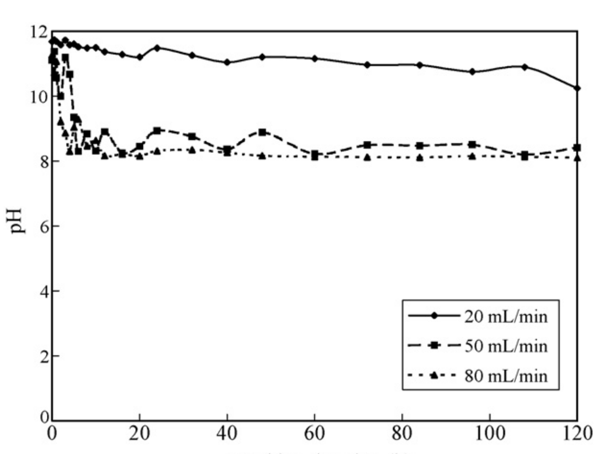

Fig. 3. Relationship between pH and washing duration on bottom ash (Taoyuan incinerator).

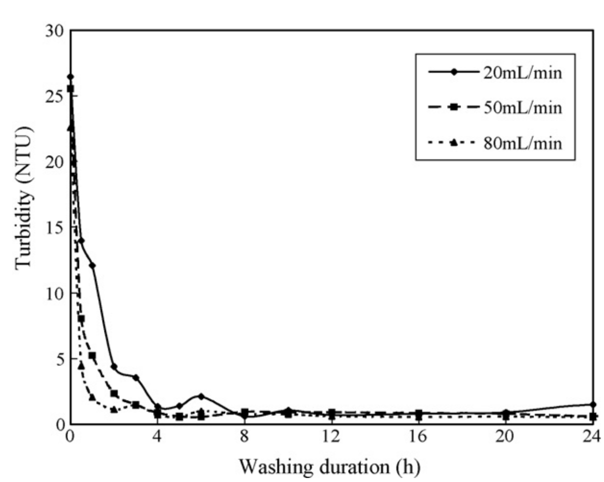

Fig. 4. Relationship between turbidity and washing duration in de-chlorination aqueous solutions (Taoyuan incinerator).

Table 2
De-chlorination performance of MSWI bottom ash by pipe column test

Parameters	Incinerators	Flux (mL/min)		
		20	50	80
Cl^- content of original bottom ash (%)	Hsinchu	0.53	0.53	0.53
	Taoyuan	0.51	0.51	0.51
	Bali	0.34	0.34	0.34
	Muzha	0.68	0.68	0.68
Cl^- content for after washed (10^{-4}%)	Hsinchu	13	15	11
	Taoyuan	17	15	9
	Bali	15	12	12
	Muzha	8	7	9
Minimum de-chlorination duration (h, $Cl^- < 0.012\%$)[a]	Hsinchu	9.9	3.7	2.0
	Taoyuan	10	3.7	1.9
	Bali	12	4.3	3.1
	Muzha	11	5.3	2.6
Minimum de-chlorination duration (h, $Cl^- < 0.024\%$)[a]	Hsinchu	8.0	2.9	1.7
	Taoyuan	9.1	3.8	1.9
	Bali	8.8	2.8	1.8
	Muzha	9.1	3.8	1.9
De-chloride efficiency (Cl^- %/h)[b]	Hsinchu	0.06	0.17	0.30
	Taoyuan	0.08	0.22	0.35
	Bali	0.04	0.12	0.19
	Muzha	0.07	0.18	0.36
Minimum water usage (L/kg)[c]	Hsinchu	3.6	3.2	3.0
	Taoyuan	3.0	2.6	2.7
	Bali	3.9	3.1	3.2
	Muzha	4.0	4.2	3.3

[a] Minimum de-chlorination duration (CNS 1240, $Cl^- < 0.012\%$ for PC, $Cl^- < 0.024\%$ for RC).
[b] Dechloride efficiency = Cl^- content of original bottom ash/Minimum de-chlorination duration.
[c] Minimum water usage (CNS 1240, $Cl^- < 0.024\%$ for RC).

3.3. De-chlorination curve

The dissolved chloride ion concentration of fine aggregates in pre-stressed concretes (PC) and reinforced concretes (RC) must be <0.012% and <0.024%, respectively, according to the “Ready mixed concrete” (CNS 3090) [14] and “Concrete aggregates” specifications (CNS 1240) [12]. Table 2 shows the pipe column experimental data. Table 2, Figs. 5 and 6 present summaries of de-chlorination curve and de-chlorination parameters. All the de-chlorination ratios (i.e., Cl^- content of original bottom ash/Cl^- content after washing for 120 h) are >99% after the de-chlorination process for 120 h (Table 1). The de-chlorination efficiencies (i.e., the de-chlorination concentration per unit time) for flow fluxes of 20 mL/min, 50 mL/min, 80 mL/min are 0.02–0.08%/h, 0.12–0.22%/h, 0.19–0.36%/h, respectively (Fig. 6), meaning that high flow flux increases de-chlorination concentration per unit time. The shortest de-chlorination duration for flow flux of 80 mL/min can be decreased and the de-chlorination efficiency per unit time is higher than those at flow flux rates of 20 mL/min and 50 mL/min (Table 2). In terms of water required for de-chlorination of bottom ash, 80 mL/min uses the least amount of water, followed by 50 mL/min and 20 mL/min (Fig. 7). Furthermore, when the chloride content of fine aggregates in PC and RC meets national standards, the shortest de-chlorination duration required is not decreased in proportion. For instance, the de-chlorination duration for a flow flux of 80 mL/min only increases by 17–39%.

Analysis of the result for de-chlorination concentration per unit time, de-chlorination duration and use of water required for de-chlorination, indicated that de-chlorination efficiency at a flow flux of 80 mL/min was highest, followed by 50 mL/min and 20 mL/min.

Table 3
XRD spectrums of bottom ash before and after de-chlorination

Incinerators	Washed before	Washed after
Hsinchu	KCl, NaCl, $SiCl_4$	$ZnCl_2$, CuCl, $Ca_2SiO_3Cl_2$
Taoyuan	KCl, NaCl, $SiCl_4$, CaClOH	$ZnCl_2$, CuCl, $Ca_2SiO_3Cl_2$, CaClOH
Bali	KCl	$ZnCl_2$, CuCl, $Ca_2SiO_3Cl_2$
Muzha	KCl, NaCl, $SiCl_4$	$ZnCl_2$, CuCl, $Ca_2SiO_3Cl_2$

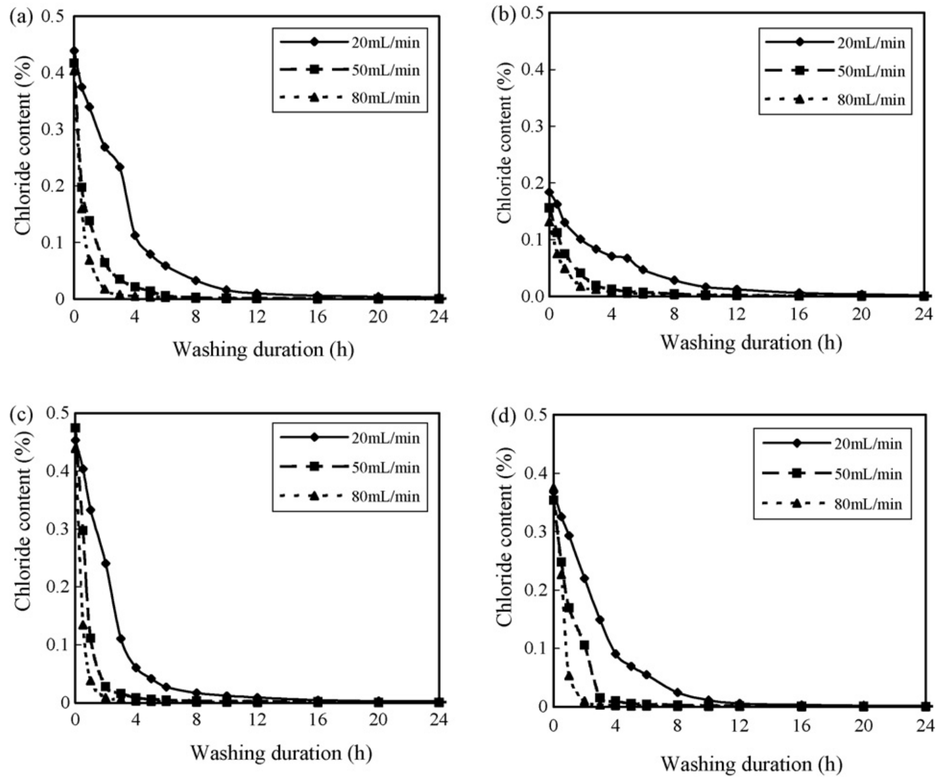

Fig. 5. De-chlorination curve of MSWI bottom ash. (a) Muzha incinerator; (b) Bali incinerator; (c) Taoyuan incinerator; (d) Hsinchu incinerator.

3.4. Species variations of chloride ions in bottom ash

Using the flow flux of 50 mL/min as the basis for comparison, species changes in bottom ash before and after de-chlorination were analyzed by XRD. Table 3 and Fig. 8 present analytical results. Only KCl in the chloride ions in the bottom ash from the Bali incinerator; however, KCl, NaCl and $SiCl_4$ were found in those from the Muzha incinerator (Table 3). Moreover, KCl, NaCl, $SiCl_4$ and CaClOH were found in bottom ash from the Taoyuan and Hsinchu incinerators. However, chloride ion species, such as $ZnCl_4$, CuCl, $Ca_2SiO_3Cl_3$, were found the bottom ash from all four incinerators after de-chlorination for 120 h. Additionally, CaClOH was found in bottom ash from the Taoyuan incinerator. These analytical results show that the species in bottom ash changed during the de-chlorination process, which primarily eliminates KCl, NaCl, and $SiCl_4$, likely because these species are easily dissolved in water. The intensity of these species in bottom ash decreased after the de-chlorination process (Fig. 8). Only KCl was found in the bottom ash from the Bali incinerator (Table 3 and Fig. 8); thus, its chloride ion content is clearly lower than that in the other three incinerators.

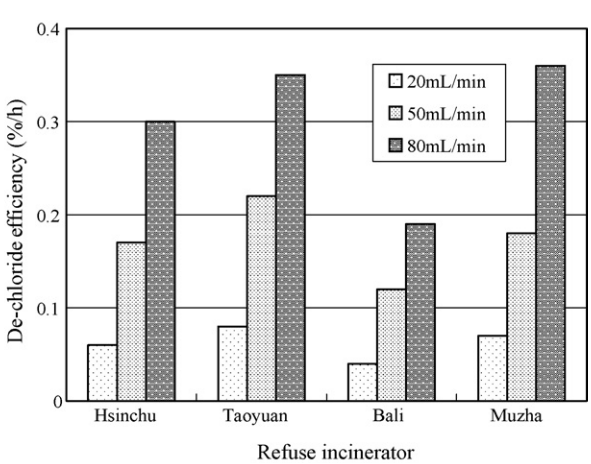

Fig. 6. Relationship between de-chloride efficiency and flux for bottom ash.

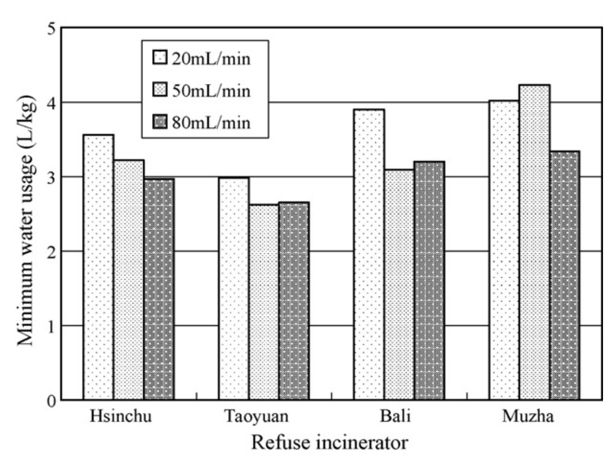

Fig. 7. Relationship between de-chloride water usage and flux for bottom ash.

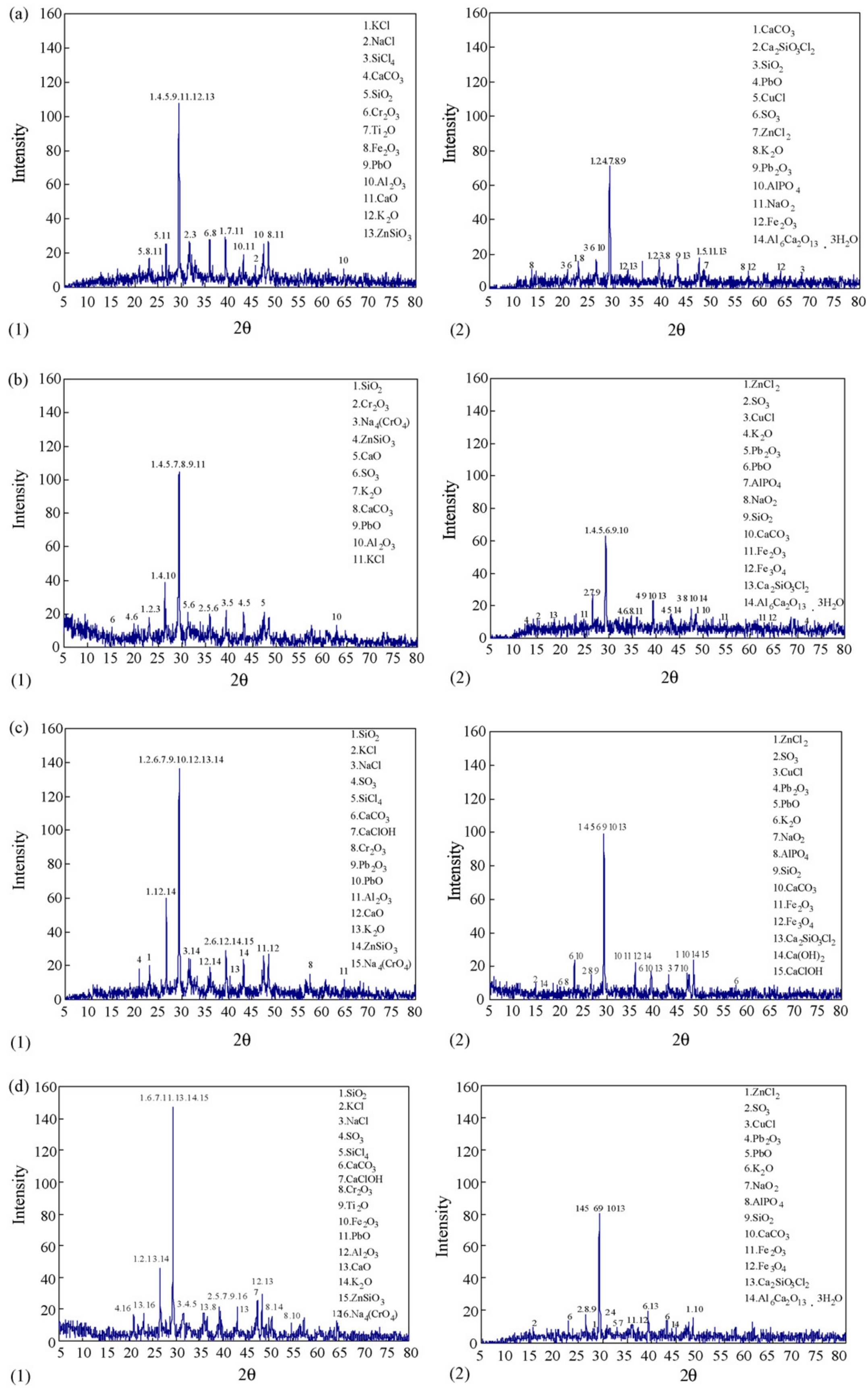

Fig. 8. XRD spectrums of MSWI bottom ash. (a) Muzha incinerator: (1) before washed, (2) after washed; (b) Bali incinerator: (1) before washed, (2) after washed; (c) Taoyuan incinerator: (1) before washed, (2) after washed; (d) Hsinchu incinerator: (1) before washed, (2) after washed.

4. Conclusion

(1) There is a negative correlation between the natural logarithm of chloride ion concentration in bottom ash and particle size, because the fine particles have large specific surface areas.
(2) The chloride ion concentration in bottom ash with particle sizes <3/8 in. is close to that of ash sized <#100 (<150 μm); the difference is 4–12%.
(3) Following de-chlorination, the characteristics of bottom ash, such as specific gravity, pH, mud content, loss on ignition, chloride ion content, and turbidity, all typically decrease, and the bottom ash is transformed from a strong base to weak base. Thus, the de-chlorination process decreases the chloride ion concentration and has a cleaning effect that renders bottom ash relatively more appropriate for used as concrete aggregates.
(4) The de-chlorination concentrations per unit time for flow flux of 20 mL/min, 50 mL/min, 80 mL/min are 0.02–0.08%/h, 0.12–0.22%/h, 0.19–0.36%/h, respectively, suggesting that de-chlorination concentration per unit time is highest under high flow flux. The shortest duration required for de-chlorination and to meet content standards are not reduced in proportion.
(5) The main species of chloride ions are KCl, NaCl, and $SiCl_4$ before de-chlorination; these species change to $ZnCl_2$, CuCl, $Ca_2SiO_3Cl_2$ after de-chlorination. Species intensity of bottom ash decreases after de-chlorination.

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