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Removal of Cl from the Incineration Ash of Domestic Municipal Solid Waste

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The removal rate of Cl from municipal solid waste incineration(MSWI) ash(bottom ash and fly ash) by washing was investigated. The Cl contents in the bottom ash and fly ash were 2.6-3.0% and 25-30% respectively, and KCl, NaCl, CaClOH and friedel's salt were main components. From the results on the effects of washing time and temperature, the Cl contents in the bottom ash and fly ash were decreased up to 0.3% and 2.0% respectively by using of water as a solvent within 30 min at 20℃, 300 rpm of agitation speed and 10 of liquid/solid ratio. It is expected that the removal of Cl from the incineration ash by washing could make use of the ash for a cement raw material and so on.
Keyword : municipal solid waste incineration ash, recycling, washing

Introduction

An incineration is one of the main treatment process of municipal solid waste. It is possible to reduce the volume of the municipal solid waste to 90% and the weight of that to 20-30%. Sterilization and disinfection are accompanied effects of the incineration. Also, the combustion heat can be recycled as a energy source. It was estimated that 180 thousand ton of incineration ash was generated in the 14 domestic municipal solid waste incinerators in 1999. Where, 90% of the incineration ash was bottom ash and the fly ash was remainder. In 1995, the wastes generated in Korea were treated as reclamation of 72%, recycling of 24% and incineration of 4%. However, the recycling of the waste rather than simple reclamation has been promoted by the government, also difficult wastes to recycle were incinerated. This policy decreased the simple reclamation to 51.6 and increased the recycling and the incineration to 38.1% and 10.3 % respectively. And the portion of the incineration should be increased continuously.

The incineration is not the final disposal of a waste, hence the generated incineration ash should be recycled or retreated. The final disposal by the reclamation has a difficulty finding a reclaiming ground due to the NIMBY syndrome, then a study on the recycling of incineration ash must be settled without delay. Bottom ash has been used for the light weight aggregate of road building or for the asphalt and concrete in european such as Germany, Denmark and Holland. The recycling portion of bottom ash reached to 60-90%. Also, study on the recycling of fly ash by melting are actively conducting, however simple reclaiming after solidification and stabilization is mainly used due to economical efficiency.

Main components of bottom and fly ash are Ca, Si, Al and Fe which are proper elements for cement raw materials, but soluble salts of 3～10% and 30～50% are contained in the bottom and fly ash respectively. Most of the soluble salts should be in the form of chloride by the chlorine environment in a incinerator, and actually 5～30% of chlorine is contained in the incineration ash. These high concentration of chlorine in the raw material and fuel interrupt the fluid flow in a cyclone because low melting point chloride compounds which evaporate and condense in a kiln and preheating furnace are formed and deposited on the wall of the furnace. Hence, in the case that the raw materials or fuel containing high concentration of chlorine are used for the manufacture of cement, chlorine by-pass facility should be equipped in preheating facility or chlorine concentration in the raw material is restricted to below 100 ppm. Even though the study on the synthesis of chlorine containing ore exhibiting hydaulicity was tried without removing chlorine, the usage was limited to the plain concrete because of the corrosion of iron and chlorine by-pass facility is needed as well. However, it should be possible to expand the usability of recycled cement from the incineration without chlorine by-pass facility ash, provided the chlorine in the incineration ash is completely removed by washing. This is possible because a chlorine compounds is easily soluble in water, and the existing cement manufacturing facility can be used without modification.

Hence, removal characteristics of chlorine contained in the incineration ash by washing were studied. the effects of washing temperature and time were investigated with using of water as a solvent.

Methods and Materials

In this study, two kinds of incineration ashes, one from municipal incinerator of A area in Gyeonggi province (referring incineration ash A) and another one from that of B area in Pusan(referring incineration ash B) were used as raw materials. The municipal solid waste are incinerated by stoker type in the facilities, the capacity is around 200 ～ 300 ton/day. The incinerator type and treatment type of fly ash for each facility are summarized in Table 1. The sampled ashes were transferred to laboratory with bottled in and preserved in a desiccator after drying at 105±5℃ for 2 hrs. Before preserving, water content was measured at 105±5℃ for 2 hrs.

Table 1.Incineration type and treatment process of fly ash for MSWI facilities used in this study

Sample	Incinerator type	Treatment process of fly ash
A	Stoker	WS → SDA → BF → SCR
B	Stoker	SDA → BF → SCR

(WS : Wet Scrubber, SDA : Spray Dry Absorber, BF : Bag Filter, SCR : Selective Catalytic Reduction)

The washing test was performed in a cylinder type reactor surrounded by water jacket with 2L of volume, and the reactor was equipped with condenser and connected to the temperature controllable water bath. Distilled water was introduced to the reactor at a constant temperature and incineration ash with proper solid/liquid ratio was added with agitation. The chlorine content in the solution was measured according to washing time. The some cakes were dried in oven at 105 ±5 ℃ for 30 min and then chemical compositions and mineral phases were analyzed.

The chlorine content in the solution was titrated by silver nitrate, and residual chlorine content in a cake was calculated from the chlorine content in ashes and the solution.

Chemical composition of ashes before and after washing was measured by XRF(XFR-1700, Shimadzu) and ICP(ICP-AES 7500, Shimadzu), and the mineral phase was analyzed by XRD(X'pert, Philips).

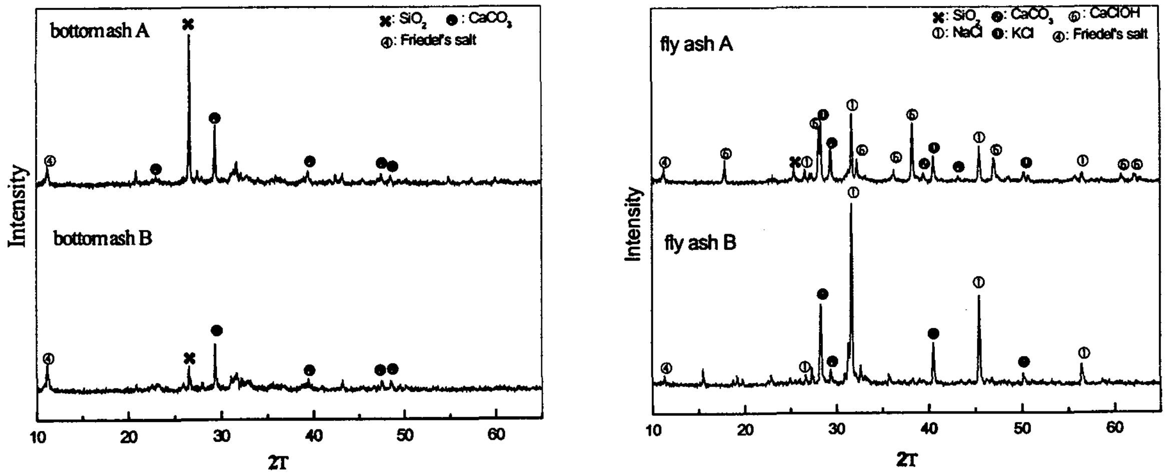
Results and Discussion

Table 2 shows the water content and chemical composition of bottom and fly ashes analyzed by XRF and ICP respectively. As can be seen in Table 2, bottom and fly ashes are composed of Ca, Si, Al and Fe, when each element is converted to CaO, SiO2, Al_2O_3 and Fe_2O_3, 27.15 and 24.13% of CaO, 19.5 and 28.24% of SiO_2, 10.53 and 9.32% of Al_2O_3 and 7.54 and 7.30% of Fe_2O_3 were contained in the bottom ashes A and B respectively. Also, the compositions of the fly ash A and B are 41.86 and 8.85% of CaO, 7.10 and 6.07% of SiO_2, 3.51 and 3.28% of Al_2O_3 and 0.77 and 0.64% of Fe_2O_3 respectively. The main compositions of bottom ashes don't exhibit any significant deviation according to the facilities, while the CaO contents in the fly ashes show large deviation. It was found that Pb and Cu are shown to be relatively high concentration compared to other heavy metals. The chlorine content which may cause a problem for the cement raw material in bottom ashes of A and B are 1.47 and 2.20 % respectively, and 22.9 and 26.0% are contained in the fly ashes. Also, the Na_2O and K_2O content are 5.47, 9.58% and 2.35, 9.58% respectively.

Fig. 1 and 2 show XRD patterns of bottom and fly ashes. In the case of bottom ash, SiO_2, $CaCO_3$ and friedel's salt($3CaO \cdot Al_2O_3 \cdot 10CaCl_2$) are main phases as shown in Fig. 1, while, in the case of fly ash A, $CaCO_3$, SiO_2 as well as chlorine compounds such as

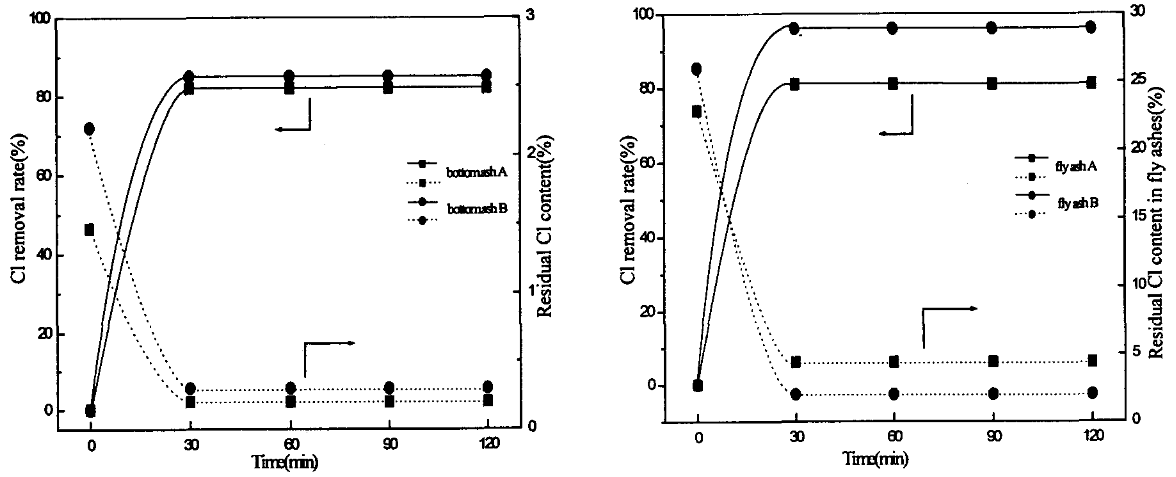
Table 2. Chemical composition of incineration ashes

Element	A		B	
	bottom ash	Fly ash	bottom ash	fly ash
LIO(wt.%)	14.09	15.04	7.66	46.00
SiO_2(wt.%)	19.5	7.10	28.24	6.07
Al_2O_3(wt.%)	10.53	3.51	9.32	3.28
TiO_2(wt.%)	1.34	0.91	1.33	0.92
Fe_2O_3(wt.%)	7.54	0.77	7.30	0.64
CaO(wt.%)	27.15	41.86	24.13	8.85
MgO(wt.%)	1.61	2.21	1.65	1.60
Na_2O(wt.%)	7.83	5.47	9.62	9.58
K_2O(wt.%)	2.35	4.60	3.00	9.58
MnO(wt.%)	0.43	0.05	0.25	0.10
P_2O_5(wt.%)	6.36	2.16	5.65	2.31
Cl(mg/kg)	1.47	22.9	2.20	26.0
Cu(mg/kg)	2,240.0	568.0	1607.9	1365.3
Cd(mg/kg)	10.9	165.9	12.6	506.7
As(mg/kg)	50.1	12.5	80.2	62.1
Cr(mg/kg)	385.0	317.8	301.0	671.2
Pb(mg/kg)	1286.5	2125.3	881.9	5802.2
Water content(wt.%)	22.5	0.8	17.2	0.4



(a) (b)

Fig. 1. XRD pattern of incineration ashes. (a) bottom ashes (B) fly ashes

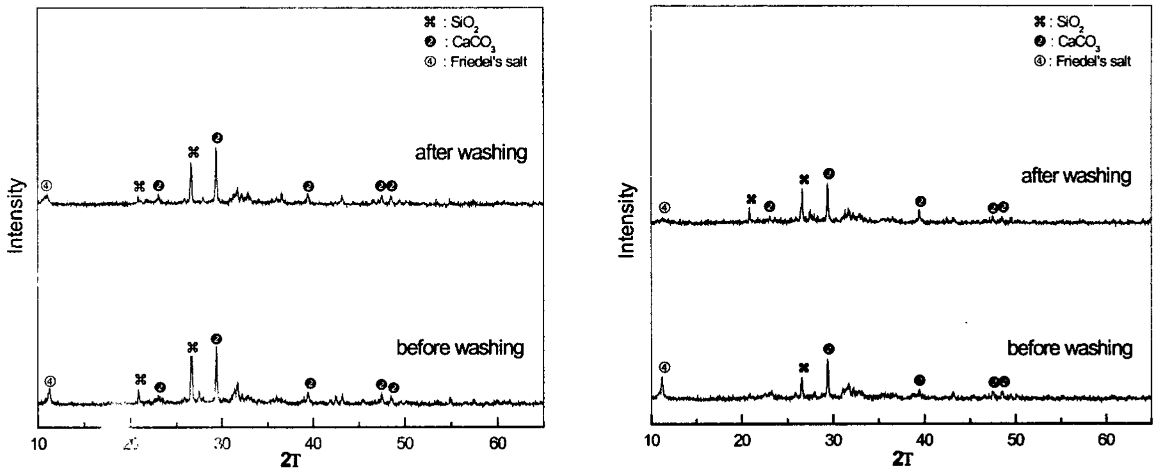


(a) (b)

Fig. 2. Cl removal and residual Cl content in ashes with washing time. (a) bottom ashes (b) fly ashes

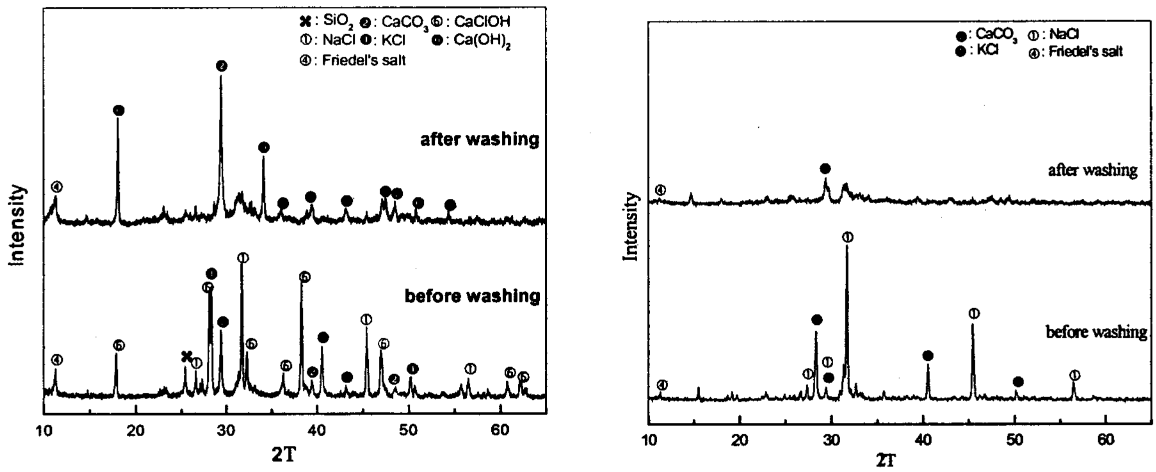
CaClOH, NaCl and KCl are main phases. Fly ash B is mainly composed of NaCl and KCl as shown in Fig. 1. This shows that the fly ash exhibits more significantly different characteristics according to the incinerator then the bottom ash.

Fig. 2 shows the Cl removal rate and residual Cl content in ashes after washing of bottom and fly ashes in agitating distilled water with the liquid/solid ratio of 10 at room temperature according to washing time by measuring of eluted chlorine content. The Cl removal rates of bottom ashes were 80%(residual content in bottom ash : 0.6%) and 85%(residual content in bottom ahs:4.4%) of total chlorine content, while the rates of fly ashes were 81%(residual content in fly ash:4.4%) and 96%(residual content in fly ash:2.0%) at 30 min of washing time. And any significant changes in the Cl removal rate were not observed up to 2 hrs. Fig. 3 and 4 show the XRD patterns of bottom and fly ashes before and after washing respectively. In the case of bottom ash, $CaCO_3$, SiO_2 and friedel's salt were main ore phases before or after washing and there was not any difference in XRD patterns after washing. While, in the case of fly ash of A, NaCl, KCl, CaClOH, $CaCO_3$ and friedels' salt are main phases, but $Ca(OH)_2$, $CaCO_3$, and friedel's are main phases after washing as shown in Fig. 4. Also, KCl, NaCl and friedel's salt are main phases in the fly ash of B before washing, only $CaCO_3$ and friedel's salt are observed after washing. It was found that NaCl, KCl and CaClOH, highly soluble compounds are easily soluble and residual chlorine after washing is remained as mainly friedel's salt. This friedel's salt has been known to be formed from the reaction of cement hydrate with salt in a seawater in the seaside concrete structure.



(a) (b)

Fig. 3 XRD pattern of bottom ashes before and after washing. (a) bottom ash A (b) bottom ash B



(a) (b)

Fig. 3 XRD pattern of fly ashes before and after washing. (a) fly ash A (b) fly ash B

It is believed that the presence of friedel's salt in the incineration ash is attributed to the water, hence the generated incineration ash should be kept in dry place in order to enhance the Cl removal rate.

Table 3 shows the residual Cl content of bottom and fly ashes according to washing temperature respectively. The liquid/solid ratio, washing time and agitation speed were set to 10, 30min and 300 rpm respectively. As can be seen in Table 3, the Cl removal rate of bottom and fly ash increased as the temperature increased.

Table 4 shows main chemical composition of bottom and fly ashes after washing. The liquid/solid ratio,

Table 3. residual Cl content in ashes at various washing temperature

Sample	residual Cl content in ash(%)		
	5°C	20°C	50°C
Bottom ash A	0.91	0.2	0.15
Bottom ash B	0.58	0.3	0.14
Fly ash A	5.0	4.4	1.7
Fly ash B	2.2	2.0	0.8

L/S ratio : 10, washing time : 30 minutes

Table 4. Chemical composition of bottom and fly ashes after washing (unit : wt.%)

sample		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5
bottom ash	A	25.07	9.03	0.95	6.46	2.54	23.08	4.04	1.13	0.48	5.10
	B	36.62	9.00	0.78	7.96	2.54	21.74	4.50	1.12	0.30	5.10
fly ash	A	13.40	5.05	1.25	0.79	3.81	38.44	0.67	0.38	0.13	2.22
	B	20.39	10.08	2.41	2.02	5.55	18.09	1.89	1.09	0.23	4.98

L/S ratio : 10, washing temp. : 20°C, washing time : 30min

washing time, washing temperature and agitation speed were set to 10, 30min, 20°C, 300rpm, respectively. As can be seen in Table 4, the content of K_2O, Na_2O as well as Cl is reduced..

Conclusion

The chlorine content in the bottom and fly ashes were found to be 2.6-3.0% and 25-30% respectively. The chlorine in the incineration ashes were existed in the form of KCl, NaCl, CaClOH and friedel's salt. KCl, NaCl and CaClOH were completely removed by washing within 30 min, and the unremoved chlorine existed in the form of friedel's salt. The dechlorination rate increased as the washing temperature increased. The chlorine content in the bottom and fly ashes were decreased to 0.3% and 2.0% respectively by the washing at the 10 of liquid/solid ratio, 300 rpm of agitation speed and 20 ℃.

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