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A Study on Characteristics of Water Quality in Wastewater according to the Washing of Municipal Solid Waste Incinerator (MSWI) Ash

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In order to recycle the incineration ash (bottom ash and fly ash) generated from the incineration of municipal waste for a cement material, salts as well as heavy metal should be removed by the stabilization treatment. Most of these heavy metal and over 80% of salts are removed by a washing as a pre-treatment. However, wastewater which is another pollutant is generated by a washing, then proper treatment should be developed. First, the characteristics of incineration ashes collected from two domestic full-sized incinerators were investigated and removal rate of salts and heavy metals from them also studied. The wastewater quality was compared to the criteria of the regulation by analyzing the characteristics of generated wastewater during the washing of incineration ash as a condition of liquid/solid ratio. Also, we tried to used this experimental results for the basic data to develop proper processing technique of municipal waste.
Keywords : Bottom ash, Fly ash, Wishing , Wastewater

1. Introduction

Generally the generation volume of bottom ash is varied according to the composition of waste to be incinerated, even though the total generation volume is dependent on various processing conditions. Furthermore, the quantity of fly ash is varied according to the physical and chemical properties as well as the kind of processing technology. The incinerator ash is classified into fly ash and bottom ash, and the bottom ash is divided into grate ash to be exhausted to the bottom of the incineration chamber and the bottom ash to be fallen through the fine gap of the chamber. Finally, the fly ash is divided into boiler ash, collected ash and acidic gas state remnants.

Most of the ash generated during the incineration of ordinary waste exhibits strong alkaline, and volatile pollutants, heavy metals and compounds containing heavy metals are produced while destroying most organic compounds at 800~1000℃. It is most important problems to use the incineration ash for portland cement is a chloride contained in it. When the raw materials or fuels containing high concentration of chlorine are introduced to the incineration process, low melting point chlorides which is evaporated and concentrated at low temperature are formed in the kiln and preheating furnace. It has been reported that the chlorides are deposited and grown on the wall of the preheating furnace, then it cause the clogging of cyclone and unstable operation. Also, the chlorine content in the clinker become higher then the use for the concrete using iron reinforcing rod may be limited. Hence chlorine should be removed by washing prior to use the incineration ash for cement raw material. However, wastewater is generated during the washing process as a stabilization step. Recently, the nutrient and priority pollutants in the waste water is strictly controlled by the regulation, furthermore, organic materials, heavy metal and even dissolved inorganic compound should be removed in order to recycle the waste water. Hence, suspended solids, biodegradable organics, disease-causing germs, nutrient, priority pollutants, refractory organics, heavy metals and dissolved inorganic materials should be precisely controlled in the wastewater treatment. Also, measures for the wastewater treatment should be prepared by understand its characteristics.

In this study, the wastewater quality was compared to the criteria of the regulation by the study of characteristics of generated wastewater during the washing of incineration ash. Also, we tried to used this experimental results for the basic data to develop proper processing technique of municipal waste.

2. Experiment

2.1 Raw materials

In order to understand the characteristics of waste water generated from the washing process of incineration ash, two representative incinerators(incineration ash of I area in Kyonggi and D area in Pusan) in view of the type of incinerator and post-processing method of exhaust gas located in Korea were selected. The scales of the incinerators are 200ton/day and currently being operated. The bottom ash and fly ash were sampled three times with 7 days interval. Table 1 shows the type of the incinerator, capacity and post-processing type of the selected incinerators for this study.

2.2 Experimental procedures

The bottom ash and fly ash sampled from the incinerators were transferred in the sealed containers maintained at 0~4℃, in order to prevent the changes of the compositions. The samples were dried in a drying oven at 80 ± 5℃ for over 1 day and crushed. The mean particles size was ranged from 0.5 ~ 5mm through meshing.

Table 1 MSWI Facilities used in the study

MSWI	Combustion mode	Treatment amounts (tons/day)	Process	Samples
I	Stocker	300	CC(SNCR) o WHBo SDA (Lime) o BF o Stack	ξ Bottom ash ξ Fly ash
D	Stocker	200	CC o WHB o EP o WS (2step, NaOH) o Stack	

※ Abbreviations : CC(Combustion Chamber), WHB(Waste Heat Boiler), EP(Electrostatic Precipitator), WS(Wet Scrubber), BF(Bag Filter), SDA(Spray Dry Absorber), SCR(Selective Catalytic Reduction), SNCR(Selective Non Catalytic Reduction).

Experimental condition of washing with water is presented in Table 2, and the chemical composition, heavy metal content and elution content were analyzed.

Table 2 Experimental Condition of washing

Items	Condition
L/S(v/w) ratio	10
Water Temperature (℃)	About 20 ± 2
Stirring speed (rpm)	About 200 ~ 300
Mixing Time (hour)	About 2

Each incineration ash was washed with the prescribed conditions and held for several hours in order to sediment the solid state residue. The decanted water was sampled and preserved according to the Section 3, Chapter 2 of water pollution test manual(Korea Standard Methods, KSM). The samples needed for the analysis were manufactured to represent the whole specimens. The samples were classified into domestic permitted production limit, organic matters, inorganic matters and heavy metals then analyzed by water pollution test manual and standard methods(US EPA). Through the analysis, the characteristics of the waste water were understood and the main pollutants and matter to be removed were investigated.

3. Results and discussion

3.1 Characteristics of incineration ash

3.1.1 Chemical composition

Table 3 show the chemical composition of incineration ash analyzed by XRF(X-ray fluorescence), the major composition of bottom ash and fly ash are SiO_2, CaO and Al_2O_3.

Table 3 Chemical composition of ashes

Comp. \ Sample	Bottom ash		Fly ash	
	I	D	I	D
SiO_2	19.5	28.24	7.10	6.07
Al_2O_3	10.53	9.32	3.51	3.28
TiO_2	1.34	1.33	0.91	0.92
Fe_2O_3	7.54	7.30	0.74	0.64
MgO	1.61	1.65	2.21	1.60
CaO	27.15	24.13	41.86	8.85
Na_2O	7.83	9.62	5.47	9.58
K_2O	2.35	3.00	4.60	12.37
MnO	0.43	0.25	0.05	0.10
P_2O_5	6.36	5.65	2.16	2.31
LOI	18.09	16.66	15.04	43.27

(Unit : wt.%)

3.1.2 Content of Cl^- and Soluble Salt

Table 4 shows the chlorine and soluble salts in each sample. Chlorine ion concentration in the bottom ash was 1.7%, 1.4% for I, D respectively. In the case of the fly ash, it was measured 21%, 25.1% and for I, D respectively. In the case of bottom ash, 11.3% of I 8.0% of D are contained, while 37.7% of I, 62.7% of D are contained in fly ash.

Table 4 Content of Cl^- and Soluble Salt in Ashes

Sample \ Content (%)		Cl^-	Soluble salt
Bottom ash	I	1.7	11.3
	D	1.4	8.0
Fly ash	I	21.0	37.7
	D	25.1	62.7

From the XRD(X-ray diffraction) result, the soluble salt contained in the incineration ash are KCl, NaCl, $CaCl_2 \cdot 6H_2O$ and $CaCO_3$ as well as small amount of Friedel's salt($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$).

3.1.3 The amounts of Heavy Metals

Table 5 show the content of heavy metal and of each sample. The content of heavy metal, chlorine and soluble salt are much contained in the fly ash than in the bottom ash, and the heavy metals such as Cd, Pb and Zn were from fly ash was slightly higher than the bottom ash. Especially, the Cu content was high in bottom ash, and the Pb and Cd content was over the allowable content.

Table 5 The Total Amount of Heavy Metals in Ashes

Items \ Sample	Bottom ash		Fly ash	
	I	D	I	D
Cr	385.30	301.00	317.76	671.23
Cu	2,244.50	1,607.90	568.04	1,365.30
As	50.10	80.20	12.50	62.10
Cd	10.92	12.63	165.85	506.71
Pb	1,286.50	881.90	2,125.30	5,802.2

(Unit : mg/kg)

3.2 Stabilization characteristics of ash according to washing

3.2.1 Soluble characteristics of chlorine composition

Dissolution quantities of chlorine ion of I and D were measured, in order to understand the dissolution characteristic of chlorine element. Because chlorine may affect environment and cement provide the recycled incineration ash is used for construction raw materials, cement and etc. In the case of bottom ash, I and D, chlorine contents were decreased by 80%(residual chlorine content in bottom ash : 0.6%) and 85%(residual chlorine content in bottom ash : 0.4%) within 30 min. Also, in the case of fly ash, it was diminished by 81%(residual chlorine content in fly ash : 4.4%) and 96%(residual chlorine content in fly ash : 2.0%).

3.2.2 Elution characteristics of heavy metals

The elution content of heavy metals such as Pb, Cd, As and Cr from the bottom ash of D and I were measured below the allowable limit regardless of the number of washing cycles. However, Cu was eluted 5.21 ppm from bottom ash of I by the one washing which is an excess then the allowable limit, and only 2.0ppm was eluted from bottom ash of D. After double washing, elution content of Cu was measured below the limit.

Table 6 show the concentration of heavy metal in leachate of each sample.

Table 6 Leaching Concentration of Heavy Metal

Items \ Sample	Bottom ash		Fly ash	
	I	D	I	D
Cr	0.24	ND	0.17	0.20
Cu	5.21	2.10	ND	ND
As	ND	ND	ND	ND
Cd	ND	ND	ND	36.63
Pb	0.66	0.85	17.86	10.38

(Unit : ㎎/ ℓ , ND : Not Detected)

3.3 Characteristics of the wastewater

In the case that the Liquid/Solid ratio of incineration ash was 10, the analysis of water quality of the waste water thus produced were as followings; The pH of I and D, bottom ash, was around 11, and I , fly ash was over 12 and D was 9 at 20 ± 2℃. It means that most of the incineration ash exhibit alkalies.

3.3.1 Organic matter

COD which is used to analyze the organic matter concentration in wastewater containing toxic material

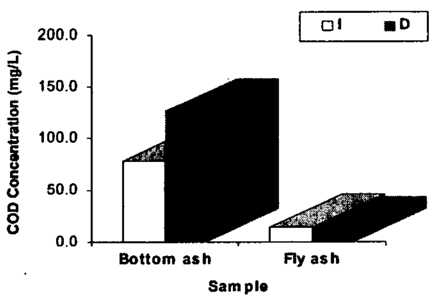

Fig. 1. COD Concentration of the wastewater.

for the growth of microbe as a index of organic pollutant was analyzed because most of microbe was removed during the incineration. The results was shown in Fig. 1.

The concentration increased as the L/S ratio decreased in bottom ash and the COD concentration of bottom ash was higher than that of the fly ash.

3.3.2 Concentration of T-N and T-P

Nitrogen as well as phosphorous which is essential for the growth of a abiogenesis and a plant have been known to be a nutrient or stimulation agent for plant growth. Hence, the nitrogen concentration in wastewater should be completely removed or minimized prior to discharging to an area of the sea, in order to control the growth of algae. In this study, total nitrogen concentrations were 15.8㎎/ ℓ and 2.81㎎/ ℓ for bottom ash and fly ash of D respectively, and 12.1㎎/ ℓ and 3.12㎎/ ℓ for those of I respectively. Total phosphorous concentrations were 3.80㎎/ ℓ and 2.01㎎/ ℓ for bottom ash and fly ash of D respectively, and 7.03㎎/ ℓ and 3.58㎎/ ℓ for those of I respectively. Fig. 2 shows the concentration of T-N(Total nitrogen) and Fig. 3 shows the concentration of T-P(Total phosphorus)

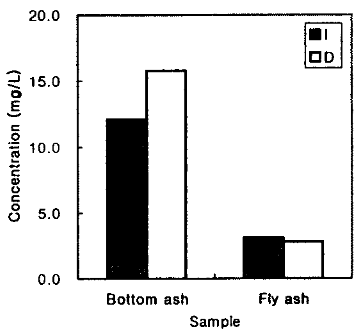

Fig. 2. Concentration of T-N in wastewater

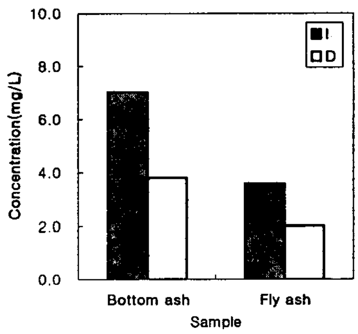

Fig. 3. Concentration of T-P in wastewater.

3.3.3 Contaminants

Pollutant concentrations in the wastewater obtained by the washing of the incineration ash of I and D with the L/S ratio of 10 were measured. Table 7 shows the characteristic of wastewater concentration at the L/S ratio of 10.

Table 7 Characteristics of wastewater

a) Bottom ash

Sample / Items	I	D	Sample / Items	I	D	Sample / Items	I	D
T-N	12.1mg/ℓ	15.8mg/ℓ	Zn	0.03mg/ℓ	0.02mg/ℓ	F	0.30mg/ℓ	0.23mg/ℓ
T-P	7.03mg/ℓ	3.80mg/ℓ	Cu	1.73mg/ℓ	3.17mg/ℓ	Cl	1.7%	1.4%
Phenol	0.00mg/ℓ	0.00mg/ℓ	Hg	0.000mg/ℓ	0.001mg/ℓ	Color	42	103
N-hexane extracts	0.0mg/ℓ	0.0mg/ℓ	Organophos phorus	0.00mg/ℓ	0.00mg/ℓ	ABS	0.56mg/ℓ	0.62mg/ℓ
CN	0.002mg/ℓ	0.004mg/ℓ	As	0.001mg/ℓ	0.020mg/ℓ	E. Coli	< 2	< 2
Cr	0.11mg/ℓ	0.17mg/ℓ	Pb	0.09mg/ℓ	0.09mg/ℓ	PCB	0.00	0.00
Fe	0.05mg/ℓ	0.08mg/ℓ	Cr^{+6}	0.03mg/ℓ	0.10mg/ℓ	TCE	0.000μg/mℓ	0.000μg/mℓ
Cd	0.01mg/ℓ	0.00mg/ℓ	Mn	0.02mg/ℓ	0.01mg/ℓ	PCE	0.000μg/mℓ	0.000μg/mℓ

b) Fly ash

Sample / Items	I	D	Sample / Items	I	D	Sample / Items	I	D
T-N	3.12mg/ℓ	2.81mg/ℓ	Zn	0.27mg/ℓ	0.08mg/ℓ	F	1.47mg/ℓ	3.44mg/ℓ
T-P	3.58mg/ℓ	2.01mg/ℓ	Cu	0.11mg/ℓ	0.10mg/ℓ	Cl	21%	25.1%
Phenol	0.00mg/ℓ	0.00mg/ℓ	Hg	0.005mg/ℓ	0.025mg/ℓ	Color	14	7
N-hexane extracts	0.0mg/ℓ	0.0mg/ℓ	Organophos phorus	0.00mg/ℓ	0.00mg/ℓ	ABS	0.25mg/ℓ	0.56mg/ℓ
CN	0.002mg/ℓ	0.003mg/ℓ	As	0.000mg/ℓ	0.003mg/ℓ	E. Coli	< 2	< 2
Cr	0.21mg/ℓ	0.29mg/ℓ	Pb	2.96mg/ℓ	1.06mg/ℓ	PCB	0.00mg/ℓ	0.00mg/ℓ
Fe	0.40mg/ℓ	0.56mg/ℓ	Cr^{+6}	0.13mg/ℓ	0.19mg/ℓ	TCE	0.000μg/mℓ	0.000μg/mℓ
Cd	0.09mg/ℓ	5.86mg/ℓ	Mn	0.10mg/ℓ	0.09mg/ℓ	PCE	0.000μg/mℓ	0.000μg/mℓ

Cyanogen concentrations were 0.004mg/ℓ and 0.003mg/ℓ for bottom ash and fly ash of D respectively, and 0.002mg/ℓ and 0.002mg/ℓ for those of I respectively.

In the case of fluorine, 0.23mg/ℓ and 3.44mg/ℓ were contained in bottom ash and fly ash of D respectively, and 0.30mg/ℓ and 1.47mg/ℓ were contained in those of I respectively. Chromium concentrations were 0.17mg/ℓ and 0.29mg/ℓ for bottom ash and fly ash of D respectively, and 0.11mg/ℓ and 0.21mg/ℓ for those of I respectively. Hexavalent chromium concentrations were 0.10mg/ℓ and 0.19mg/ℓ for bottom ash and fly ash of D respectively, and 0.03mg/ℓ and 0.19mg/ℓ for those of I respectively. Iron concentrations were 0.08mg/ℓ and 0.56mg/ℓ for bottom ash and fly ash of D respectively, and 0.05mg/ℓ and 0.40mg/ℓ for those of I respectively. Zinc concentrations were 0.02mg/ℓ and 0.08mg/ℓ for bottom ash and fly ash of D respectively, and 0.03mg/ℓ and 0.13mg/ℓ for those of I respectively. Copper concentrations were 3.17mg/ℓ and 0.10mg/ℓ for bottom ash and fly ash of D respectively, and 1.73mg/ℓ and 0.11mg/ℓ for those of I respectively which are higher value than in the fly ash. Cadmium was not detected in the bottom ash of D while 7.03mg/ℓ was contained in the fly ash, and 0.01mg/ℓ and 0.09mg/ℓ were observed in those of I respectively. Mercury concentrations were 0.001mg/ℓ and 0.025mg/ℓ for bottom ash and fly ash of D respectively, while it was not detected in the bottom ash of I but contained 0.005mg/ℓ in the fly ash. Arsenic concentrations were 0.02mg/ℓ and 0.003mg/ℓ for bottom ash and fly ash of D respectively, it was contained 0.001mg/ℓ whereas it was not detected in the fly ash.

Lead concentrations were 0.09mg/ℓ and 1.06mg/ℓ for bottom ash and fly ash of D respectively, and 0.09mg/ℓ and 2.96mg/ℓ for those of I respectively which are higher value than in the bottom ash

Manganese concentrations were 0.01mg/ℓ and 0.09mg/ℓ for bottom ash and fly ash of D respectively, and 0.02mg/ℓ and 0.10mg/ℓ for those of I respectively which are slightly higher value than in the bottom ash. In the case of anionic surfactant, 0.62mg/ℓ and 0.56mg/ℓ were contained in the bottom ash and the fly ash of D respectively, and 0.56mg/ℓ and 0.25mg/ℓ for those of I respectively which were nearly similar value each other. In the case of a colon bacillus, 2 MPN/100mL was detected in whole samples. Color were 103 and 7 for bottom ash and fly ash of D respectively, and 42 and 14 for those of I respectively which means the color of the bottom ash were slightly higher than those of the fly ash.

None of N-hexane extracts, phenolic matters, organophosphorous, PCB, tetrachloroethylene(TCE) and trichloroethylene(PCE) were detected in the samples.

4. Conclusion

1) Chlorine in the incineration ash was removed over 80% by a washing and heavy metals contents were below the standard by double washing. It was found that the elution of heavy metal as copper from bottom ash exceeded the standard and soluble salts which may affect an environment were contained in great quantity.

Hence, the heavy metals and soluble salts contents should be decreased to the allowable limits by a washing in order to recycle the incineration ash.

2) It is possible to obtain the basic data for the stable and proper treatment of the waste water by understand the characteristics of generated waste water as functions of pH, washing time, temperature, liquid/solid ratio, aging period and mixing condition.
3) The wastewater generated from the washing of incineration ash exhibits strong alkali, toxic and oxidative elements such as remanent chlorine as well as high concentration of chlorine ion were contained as trace elements. However it was found that their concentrations didn't exceed the environmental standard.
4) Nutritious salts such as nitrogen and phosphorous which may affect the eutrophication of a lake or a river were detected below the standard of the ministry of environment. Also, the pollutants concentrations like phenolic matters were below the standard.
5) In washing process of the incineration ash, it is necessary to find out the proper wastewater treatment in order to minimize the content of harmful elements which were detected by the water quality analysis.
6) Physical and chemical treatments such as agglutination sedimentation and filtering were found to be more effective in the wastewater treatment than the biological treatment.
7) Judging from economy and effectiveness, the existing incineration facilities should be harmonized with the proposed techniques.

References

[1] Metcalf and Eddy. Wastewater Engineering(Treatment disposal reuse) Third Edition.

[2] Ministry of Environment. 2000. Standard methods from the examination of water and wastewater.

[3] Kanzaburou SUTOU, Hiroshi HARADA, Hiroaki TAKAHASIII, 1999, Recycling of Incineration Residue as Cement Raw Material, *Seramices.*

[4] Masaru KASAHARA, Tomomichi NAKAMURA, etc., 1998, Recycling of Incineration fly ash from Municipal Refuse as Cement Raw Material by Desalination, *cement manufacture technique symposium*, No. 55.

[5] Buchhoiz, B. A., S. Landsberger, 1995, Leaching dynamics studies of municipal solid waste incinerator ash, *Journal of the Air & Waste Management Asso.*.