Goumans/Senden/van der Sloot, Editors
Waste Materials in Construction: Putting Theory into Practice

THE ACID EXTRACTION PROCESS

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Abstract
Considering from a point of view of the recycling of resources that melting fly ash produced by melting the fly ash and incineration residue discharged from incinerators of municipal refuse is useful resources of concentrated heavy metals, this paper presents acid extraction processes developed for using the useful heavy metals and salts produced from the fly ash and melting fly ash as the resources.
This paper reports the acid extraction processes from the fly ash in terms of the operational results of AES Processes operated at present and the problems to be solved in the future.
This paper also reports the application of the acid extraction processes to the melting fly ash in terms of the description of the separating recovery process of heavy metals operated at present in a bench scale, the experimental results and the problems to be solved in the future.

1. INTRODUCTION

Approximately 50 million tons of the municipal refuse is discharged every year in Japan and 78% of it is incinerated.
The bottom ash and the fly ash are produced as the incineration residue in the incinerators and the fly ash containing low-boiling heavy metals are treated and landfilled by any of four techniques (melting-solidification, cementing-solidification, chemical stabilization and acid extraction) designated for "Specially Controlled Municipal Wastes" by "the Waste Disposal and Public Cleansing Law".
In particular, the melting-solidification technique gains attention as a method for reducing the volume of the bottom ash and the fly ash, making them harmless and using them as resources. Melting fly ash mainly containing low-boiling heavy metals is, however, produced also by the melting-solidification technique.
The fly ash and melting fly ash mainly containing harmful low-boiling heavy metals arouse an environmental problem by the landfill, while viewing from the standpoint of the circulation of resources, they are regarded as useful resources containing concentrated heavy metals.This paper presents two types of the acid extraction processes for alleviating the environmental load and utilizing the heavy metals and salts as the resources.

2. ACID EXTRACTION SULFIDE PROCESS OF FLY ASH (AES PROCESS)

The description of the acid extraction and sulfide stabilization process (AES process) developed for stabilizing the heavy metals contained in the fly ash and for recovering the salts contained in it and the operational results of a commercial plant installed in O Municipal Incineration Plant are described hereafter.

Table 1. Outline of Waste Incineration System at O municipal incineration plant

Item	Description
Type of furnace	Full continuous combustion
Type of incinerator	Stoker
Incinerator capacity	115t/d×2 furnaces
Gas cooling system	Boiler
Precipitation system	Dry type electric precipiter
Exhaust gas treating system	Wet type NaOH- scrubbing

The outline of the facilities installed in O Municipal Incineration Plant is listed in Table 1. The plant has been operated for approximately 12 years since the startup of the operation in 1986 and approximately 3 to 4 tons of electrostatic precipitator (EP) fly ash per day and approximately 20 to 30 tons of the waste water from the gas scrubbing process (scrubbing waste water) per day are produced by incinerating approximately 160 to 180 tons of municipal refuse per day. The EP fly ash and scrubbing waste water are treated together. Approximately 3 to 4 tons of EP fly ash is landfilled as a harmless cake. Approximately 2 to 3 tons of solid salts per day and approximately 18 to 27 m^3 of water per day are recovered by the evaporating crystallization of the scrubbing waste water treated by the waste water treatment method to reuse as the feed salt for the soda-production plant and the cooling water for the whole AES plant without discharging, respectively.

2.1 Outline of AES process

The AES process is based on the following principle,
1)after the acid extraction of the fly ash, the mixture of the fly ash and scrubbing waste water is neutralized with NaHS, 2) the heavy metals contained in the fly ash are converted into stabilized cake consisting of insoluble heavy metal sulfides, and 3) the salts and water are recovered from the filtrate. The flow sheet of AES process in O Municipal Incineration Plant is illustrated in Fig. 1.
O Municipal Incineration Plant mainly comprises the EP ash-stabilizing equipment, waste water-treating equipment, salt-recovering equipment.
The main stages of AES process are as follows.
1)Mixing stage: EP fly ash slurry is prepared by mixing scrubbing waste water with EP fly ash, from which soluble salts including KCl, NaCl and $CaCl_2$ and a part of heavy metals are extracted.
2) Stabilization reaction stage: The pH value of the EP slurry sent from the previous state is adjusted to 6 with HCl to extract the heavy metals. Then the pH value of the extract is adjusted to 8 by adding NaHS to convert into heavy metal sulfides.
3)Dewatering stage: Stabilized slurry from the previous stage is coagulated with polymer flocculant and then is dewatered. Thus the dewatered cake is landfilled.

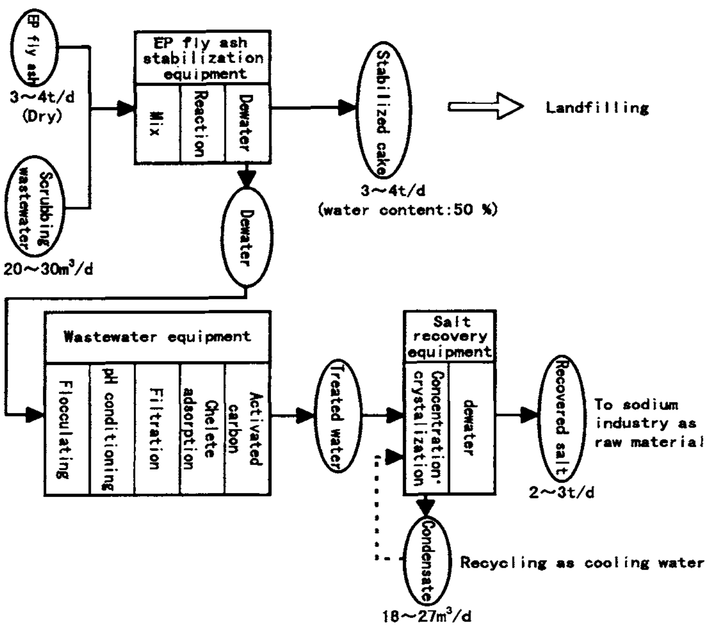

Fig 1. Flow diagram of fly ash and wastewater treatment processes at O Municipal Incineration Plant

Table 2. Results of treating by AES Process

	Chemical analysis					Leaching test		
	disolved salts (%)	T-Hg (mg/L)	Cd (mg/L)	Pb (mg/L)	PCDDs/ PCDFs (ng/L)	T-Hg (mg/L)	Cd (mg/L)	Pb (mg/L)
Scrubbing wastewater	5.25	0.92	0.015	0.45	5.0	–	–	–
Ep fly ash	46.6	1.75	90	1600	0.65 ng/g	0.018	7.5	27.0
Stabilized cake	–	–	–	–	3.6 ng/g	<0.0005	0.014	<0.02
Dewatered filtrate	8.42	0.013	1.0	2.2	2.1	–	–	–
Treated water	5.64	<0.0005	<0.001	<0.02	<0.01	–	–	–
Recovered solid salt	98.9	<0.0005	<0.001	<0.02	<0.01 ng/g	–	–	–

Impurities contained in the filtrate are removed by the waste water treatment method and the solid salts recovered from the water by evaporating crystallization are reused as the raw material for the soda production plant. Meanwhile, the whole evaporated water is condensed and reused as the cooling water for the salt-recovering plant and others.

2.2 Operational results

An example of the operational results obtained from AES process in O Municipal Incineration Plant is listed in Table 2 and the following can be confirmed.

1)T-Hg in the scrubbing waste water is 0.92 mg/l which exceeds the standard of 0.005 mg/l or under. In addition, it contains 5.25% of soluble salts.

2)The EP fly ash contains 46.6% of soluble salts and high-concentration of heavy metals. The leaching concentration of the heavy metals including T-Hg, Cd and Pb are 0.018, 7.5 and 27.0 mg/l, respectively, which exceed the standard of respective heavy metals for landfill.

3)The contents of T-Hg, Cd and Pb in the stabilized cake are below the standard for landfill of each heavy metal. Since those useful heavy metals are concentrated in it, reusing them as the resources are being studied.

4)The solid salt is pure white crystalline and the purity is approximately 99%. It is, therefore, used as the feed salt for the soda-production process because T-Fe as an impurity of heavy metal is contained as little as 3.92 mg/kg.

5)No PCDDs/PCDFs (dioxins) are contained in the solid salt for the soda-production process. The stabilized cake contains, however, as much as 3.6 ng/g, whereupon it must be treated by any method such as high-temperature dechlorination process for reusing as the resources.

3. SEPARATING RECOVERY PROCESS OF HEAVY METALS FROM MELTING FLY ASH

The separating recovery process of heavy metals developed for separating and recovering useful heavy metals from the melting fly ash produced by melting the incineration residue is described hereafter.

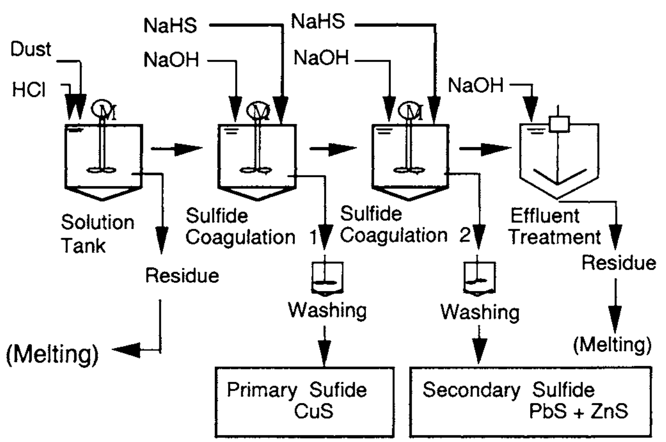

Figure 2 Flow diagram for recovery of heavy metals

3.1 Outline of process

This process proceeds with dissolving the melting fly ash as containing low-boiling heavy metals concentrated by the melting process in hydrochloric acid, adjusting the pH value to that specified to each heavy metal concerned and separating and recovering each heavy metal as the heavy metal sulfide produced by adding NaHS to the solution. Since the theoretical calculation of the solubilitiy product reveals that the solubility products of heavy metal sulfides are much different from each other in a low-pH range, the process utilizes the phenomena.

The outline of this process based on the principle is illustrated in Fig. 2. This process belongs to the wet refining process and comprises the acid dissolving stage, the production and separation stage of sulfide and waste water treatment stage.

These stages are described hereafter.

1)Acid dissolving stage: the melting fly ash is dissolved in hydrochloric acid to extract heavy metals and the concentrations of heavy metals concerned in the solution are analyzed to decide the quantities of chemicals to be used in the following stage. Meanwhile, the dissolution residue is separated from the supernatant liquid, dewatered and melted again.

2)Production and separation stage of sulfide: The pH value of the supernatant liquid sent from the previous stage is adjusted to pH specified to each heavy metal concerned and NaHS of the quantity determined in the previous stage is added to the liquid to produce, precipitate and recover each heavy metal sulfide. The recovered heavy metal sulfide slurry is washed and dewatered to prepare the recovered materials.

3)Waste water treatment stage: The supernatant liquid separated in the previous stage undergoes the pH adjustment and coagulating separation, the separation from the waste water sludge and the discharging. The waste water sludge is dewatered and melted again with the dissolution residue.

3.2 Separating recovery experiment of heavy metals

An experiment for separating and recovering the heavy metals was made using the sample of 60 kg/batch.

Two samples of melting fly ash of A- and B-Ashes listed in Table 3 were used for the experiment. The compositions of both samples are listed in Table 4.

Table. 3 Properties of melting fly ash

Sample	Charactristics of melted materials	Type	Gas treatment
A	Stoker incineration residue (Bottom ash + Fly ash,NaOH blowed)	Surface melting	NaOH blowed
			Electrostatic presipitator
B	Fluidized bed incineration residue (Bottom ash+Fly ash,$Ca(OH)_2$ blowed)	Plazma melting	$Ca(OH)_2$ blowed
			Fabric filter

A- and B-Ash samples contain as high as 21.42% of Na and as high as 29.6% of Ca, respectively , because both ash samples are affected by alkaline components added to the off-gas produced by melting the incineration residue.

The higher contents of heavy metals concerned with recovery were selected as follows: 1.56% of Pb and 2.72% of Zn in A-Ash and 0.75% of Cu, 0.80% of Pb and 0.46% of Zn in B-Ash.

The procedure for precipitating-separating recovery of the heavy metals in the sulfide production process is conducted by selectively separating Pb and Zn from A-Ash and CuS and (PbS & ZnS) from B-Ash, respectively.

1)Properties of recovered materials

The properties of the materials recovered from A- and B-Ash are listed in Table 5.

A sample of A-1 of the Pb-containing material and that of A-2 of the Zn-containing material recovered from A-Ash are judged to be applicable to the raw materials for the refinings of lead and zinc, respectively.

Another sample of B-1 of the Cu-containing material and that of B-2 of the (PbS&ZnS)-containing material recovered from B-Ash are judged to be applicable to the raw materials for the refinings of scrap copper and ISP, respectively.

Table.4 Properties of melting fly ash

Item	Unit	A	B
SiO_2	%	<0.05	0.40
$A\ell_2O_3$	%	0.04	0.38
Fe_2O_3	%	0.12	0.38
Ca	%	0.66	29.60
K	%	20.51	7.83
Na	%	21.42	5.93
PO_4	%	0.23	0.11
Mg	%	0.01	0.12
Ti	%	<0.01	0.02
T-S	%	0.52	2.50
SO_4	%	3.28	7.48
T-Cℓ	%	44.15	22.46
Pb	%	1.56	0.80
Sn	%	0.18	0.01
Cu	%	0.17	0.75
Zn	%	2.72	0.46
Ni	%	<0.01	<0.01
T-Cr	ppm	72.4	80
Mn	ppm	52.6	100
T-Hg	ppm	0.21	0.39
Cd	ppm	21.8	80
As	ppm	27.1	5.65
CN	ppm	<0.5	<0.5

Table.5 Properties of recovered materials

(Unit : %)

Sample	Pb	Zn	Cu	Cℓ
A-1	40.27	15.86	-	1.29
A-2	2.26	61.28	-	0.66
B-1	4.56	0.11	51.56	0.87
B-2	17.57	34.57	0.66	0.60

2)Properties of remelted material

The dissolution residue produced from the acid-dissolving process and the waste water sludge produced from the waste water treatment process are remelted

Fig. 3 illustrates the migration rates of the main elements contained in the melting fly ash of B-Ash to each process. The figure reveals that such elements as Si, Ca, P, Al and Fe with the rate of migration of slag is high migrant to the remelted substance. It is, therefore, confirmed that a problem causing the circulating concentration of the main components is solved by remelting the residue.

It is inferred from the data that the circulating concentration of trace components also does not arouse the problem. The variations of the properties of the ash and the behavior of the trace components will be, however, investigated by a demonstration test.

3)Properties of effluent

The effluent produced by treating B-Ash satisfies the standard of waste water.

An example of the analytical result of it is listed in Table 6.

Fig. 3 reveals that the rates of migration of Na, K and Cl in the treating water of the effluent to the effluent side are high.

Table.6 Properties of effluent

Item	Unit	Effluent	Standard for Effluent
Cd	mg/ ℓ	0.03	0.1
CN	mg/ ℓ	<0.01	1
Org-P	mg/ ℓ	<0.01	1
Pb	mg/ ℓ	<0.01	0.1
Cr6+	mg/ ℓ	<0.02	0.5
As	mg/ ℓ	0.00	0.1
T-Hg	mg/ ℓ	<0.0005	0.005
Se	mg/ ℓ	0.02	0.1
PCB	mg/ ℓ	<0.0005	0.003
BOD	mg/ ℓ	24.40	160
COD	mg/ ℓ	84.80	160
SS	mg/ ℓ	17.00	200
pH		5.90	5.8～8.6

Accordingly, it is able to recover those salts as solid salts by evaporating crystallization and reuse them as the feed salt for the soda-production plant, and condense the evaporated water and reuse it for the whole process.

4)PCDDs/PCDFs (dioxins)

The analytical results of dioxins contained in the melting fly ash, dissolution residue, recovered materials, effluent sludge and effluent are illustrated in Fig. 4. The concentrations of dioxins are indicated by TEQ in the figure. Since 97% or more of the dioxins contained in the melting fly ash migrate to the dissolution residue and effluent sludge, they are thermally decomposed by remelting to make harmless.

The concentrations of dioxins in the recovered materials containing Cu and (Pb plus Zn) are approximately 0.03 ng-TEQ/g in total and those in the untreated effluent are below 0.1 pg-TEQ/ ℓ . If necessary, an optical decomposition process by ozone treatment, etc. is applied.

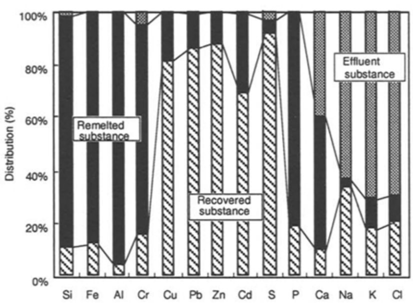

Figure.3 Distribution of elements in molten fly ash

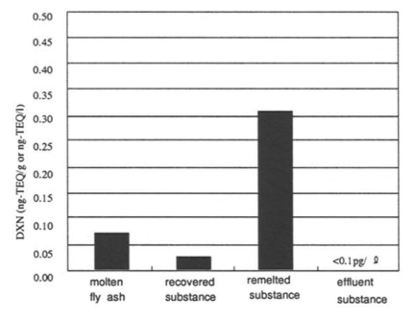

Fig.4 Balance of Dioxins for the process of heavy metals

4. CONCLUSIONS

1)Acid extraction sulfide process (AES Process) of fly ash

The stabilization of fly ash, the recovery of salts and the circulation of water without discharge of the scrubbing waste water were demonstrated by treating the fly ash and scrubbing waste water together in a full-scale plant.

Not only stabilizing the heavy metals contained in the fly ash but also utilizing the heavy metals contained in the stabilized cake as well as the salts to use as the resources will be investigated in the future.

2)Separating recovery process of heavy metals from melting fly ash

It was confirmed that the each useful heavy metal is separately recovered from the melting fly ash and these recovered materials have so high quality levels that they are able to be used as the raw materials for nonferrous metals.

The effects of the properties of the melting fly ash as on the process conditions and the quality levels of the recovered materials and the behaviors of trace components in the melting fly ash will be investigated in the future.

Acknowledgements

The authors acknowledge the very special assistance received from Unitika LTD. in the development of the acid extraction process of fly ash (AES Process) and Kobe Steel LTD. in the development of the separating recovery process of heavy metals from the melting fly ash.

Also, special thanks are given to the officers and staffs concerned in the guidance and cooperation for those developments.

5. PREFERENCES

1. M.Fujiwara,Treatment manual for special controlled general waste,fly ash,Japan Waste Research Foundation,Vol.4,No.1,P68,1993
2. H.Katsuura,T.Inoue,H.Hiraoka,S.Sakai,Full-scale Plant Study on Fly Ash Treatment by the Acid Extraction Process,Seminar on Cycle and Stabilization Technologies of MSW Incineration Residue,P137,1996
3. M.Hiraoka,S.Sakai,Review on properties of fly ash from incineration plants and its treatment technologies,Waste Management Research,Vol.5,No.1,P9,1994
4. H.Kawabata,H.Kinari,M.Katayama, Seperating Recovery Process of Heavy Metals From Melting Fly Ash ,Waste Management Research,Vol.7,No.1 ,P488,1996
5. Japan Waste Research Foundation,Annual report of WI21C"Slim-Waste" Research , P67,1996
6. T.Itou,Vitrification of Fly Ash by Swirling-Flow Furnace,Seminar on Cycle and Stabilization Technologies of MSW Incineration Residue,P66,1994