The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Metal Recycling Technologies from Fly-Ashes by the Metal Mining Agency of Japan

Kazuyuki Kikuta, Nobuyuki Masuda, Nobuyuki Okamoto, Eiichi Arai, Junichi Kobayashi
Metal Mining Agency of Japan, Japan

In Japan, the municipal solid waste, which amounts to 50 million tons, is generated every year and most of it is incinerated. The bottom and fly ashes are disposed to the registered disposal areas under the provisions of The Waste Disposal and Public Cleaning Law. Especially, as the fly ash from the municipal waste incineration (the primary fly ash) contains heavy metals (lead, zinc, etc) and dioxins, it cannot be disposed directly without decontamination, such as melting, cementation, chelating and dissolving processes provided in the law. However, these procedures for decontamination, except melting, are not enough for dioxins. Even in case of melting, the fly ash from the process (the secondary fly ash) contains high concentration of heavy metals (e.g., Zn; 1-20%, Pb; 1-10%). For these reasons, Metal Mining Agency of Japan (MMAJ), a governmental organization, started a four-year project to develop the treatment technologies of these fly ashes in 1999. The purpose of the project is to establish the integrated technologies to recover the valuable metals from, and to decontaminate, the primary and secondary fly-ashes in the practical scale by utilizing the existing metallurgical processes and facilities, along with the energy saving and the reduction of the environmental impact.
Keywords: municipal waste, metal recovery, segregation, flotation, MF, dioxins

Introduction

The annual generation of the municipal solid waste amounts about 50Mt in Japan. Most of it is incinerated and the bottom ash is landfilled at the registered disposal areas. As the fly ash from the municipal waste incineration (the primary fly ash) contains heavy metals (lead, zinc, etc.), chlorine and dioxins, it cannot be landfilled without the stabilization like melting, cementation, chelating or dissolving according to The Waste Disposal and Public Cleaning Law. The fly ash from the melting process of the primary fly ash and the bottom ash (the secondary fly ash) also contains higher concentration of heavy metals (e.g., Zn 1-20%, Pb 1-10%) and chlorine. The annual generation of the primary and secondary fly ash is estimated to be more than 500 thousand tons, which is one of the national issues in Japan that is densely populated.

Metal Mining Agency of Japan (MMAJ) started the four-year project in 1999, to establish the technology for the decontamination of the primary and secondary fly ashes, the decomposition of dioxins, and the recovery of the valuable heavy metals utilizing the existing technologies and facilities for the non-ferrous metals production along with the energy saving.

The basic concept of the project is shown in Fig.-1. The project is financed by Ministry of Economy, Trade and Industry and carried out at Hosokura and Miike Smelter as shown in Fig.-2, entrusting Mitsubishi Materials Corporation and Mitsui Mining & Smelting Co., Ltd. which are the share-holders of these smelters, respectively. The project is also supported by University of Tokyo, Tohoku University and related organizations. The flow sheet of the primary fly ash treatment at Hosokura is shown in Fig.-3.

The segregation technology is applied to the primary fly ash treatment. The ash is heated and chlorinated in the externally heated rotary furnace in which copper etc. could be reduced to metal on the carbon particles. After segregation and flotation of the carbon particles, chloric acid leaching and neutralization, copper, lead and zinc are recovered as metals or compounds selectively. Dioxins in the primary fly ash are decontaminated. The furnace gas is planned to utilize for the heat decomposition of the waste plastics to recover the fuel oil and the carbon particles for the segregation.

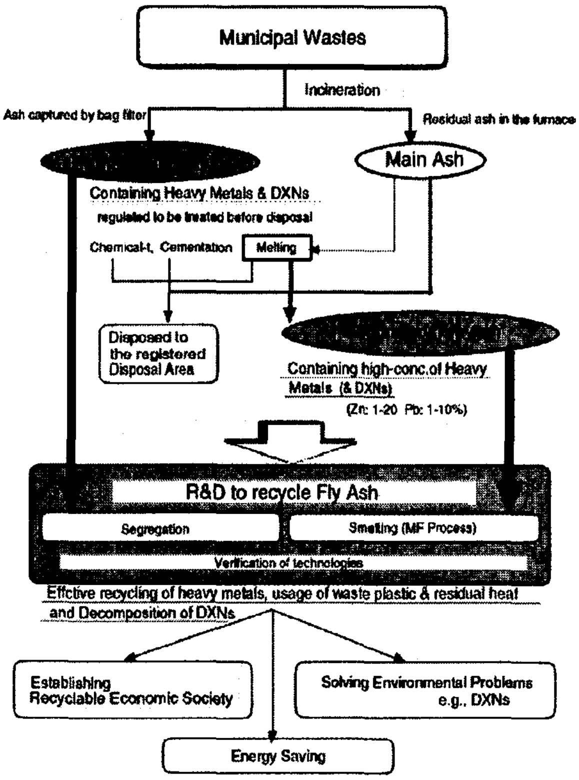

Fig.- 1 Basic concept of R&D to recycle fly ash

The flow sheet of the secondary fly ash treatment at Miike is shown in Fig.-4. The secondary fly ash is treated with MF (Mitsui-type blast furnace) Process after the chlorine removal to recover the heavy metals in the ash. MF is a relatively small blast furnace developed to recover zinc from the residue of the Vertical Retort Process, a traditional zinc production method. Mainly oxide materials of zinc like the electric arc furnace dust are mixed with coal, as fuel and reductant, and sulfite liquor, as the binder, and briquetted to be fed to MF. Zinc and lead are reduced and vaporized in the furnace and recovered to the furnace dust after re-oxidization at the furnace top, which is sent to the zinc/lead smelter with Imperial Smelting Process as a raw material. Waelz Process also could be utilized for this purpose, as MF Process. Waste plastics will be also utilized as the reductant to save coal.
A part of the results of the downsized and the practical scale studies are introduced in this paper, and the further information will be shown in the next opportunity.

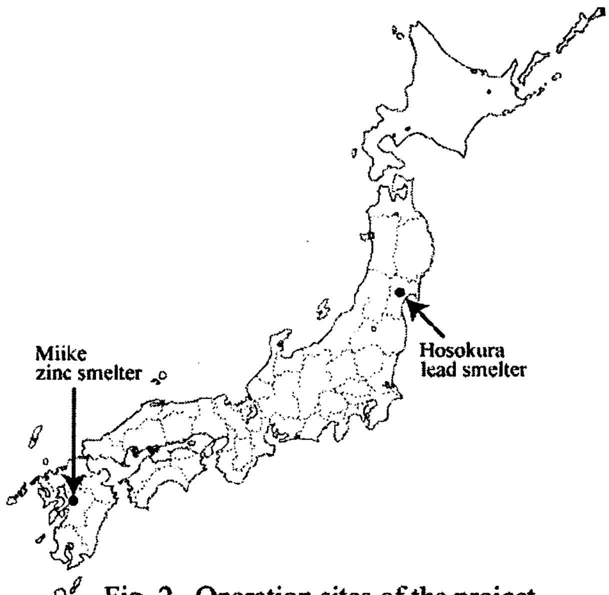

Fig.-2 Operation sites of the project

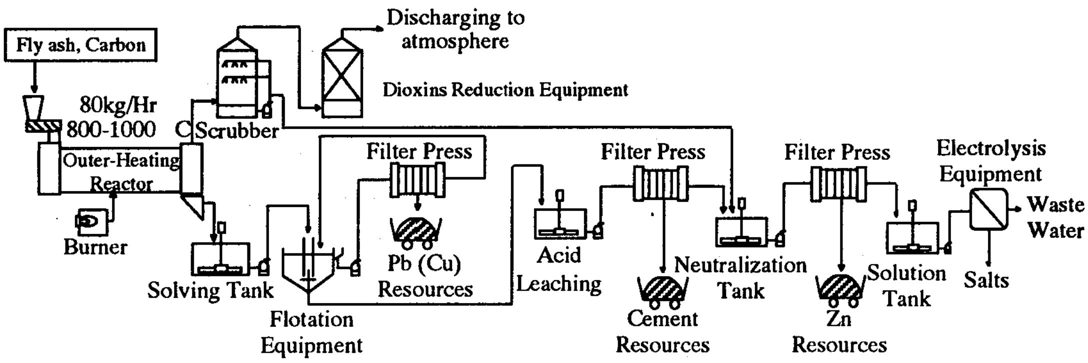

Fig.-3 – Flow sheet of primary fly ash treatment

Experiment

Segregation and flotation processes have been applied to the primary ash at the small-scale test for the selective recovery of the metals. On the other hand, the secondary ash has been tried to feed to the downsized Mitsui Furnace (MF) after the chlorine removal with the alkaline solution, mixed with the other materials to recover zinc and lead to the furnace dust which is expected to use as an raw material for zinc production with Imperial Smelting Process (ISP).

Treatment of the primary fly ash

Two kinds of the primary fly ash were used for the segregation and flotation. The segregation was carried out in the downsized rotary furnace, (220mm ID), which was heated externally at 800 or 900C, for the mixture of the ash, activated carbon or oil coke fly ash and water. As chlorine and SiO2, which are necessary for the segregation, are contained enough in the primary fly ash originally, they were not added in the experiments. After the segregation, the flotation was carried out for the ashes at the bench scale test using two kinds of pine oil as frother.

Treatment of the secondary fly ash

The chlorine removal with alkaline solution was done batch-wise in series of two stages in the actual scale tank, (10m3), keeping pH at 11 to prevent from the operation problems at MF. The slurry density was set at 203 or 133g/l for the first stage, and about 30g/1 for the second. The time for a batch was 30min. After the chlorine removal, (washing and filtration), the ash was mixed with the raw materials of MF, (mixing ratio 1/10), and fed to the downsized MF to recover zinc and lead to the furnace dust and to find any effect to the MF operation and the characteristics of the furnace dust.

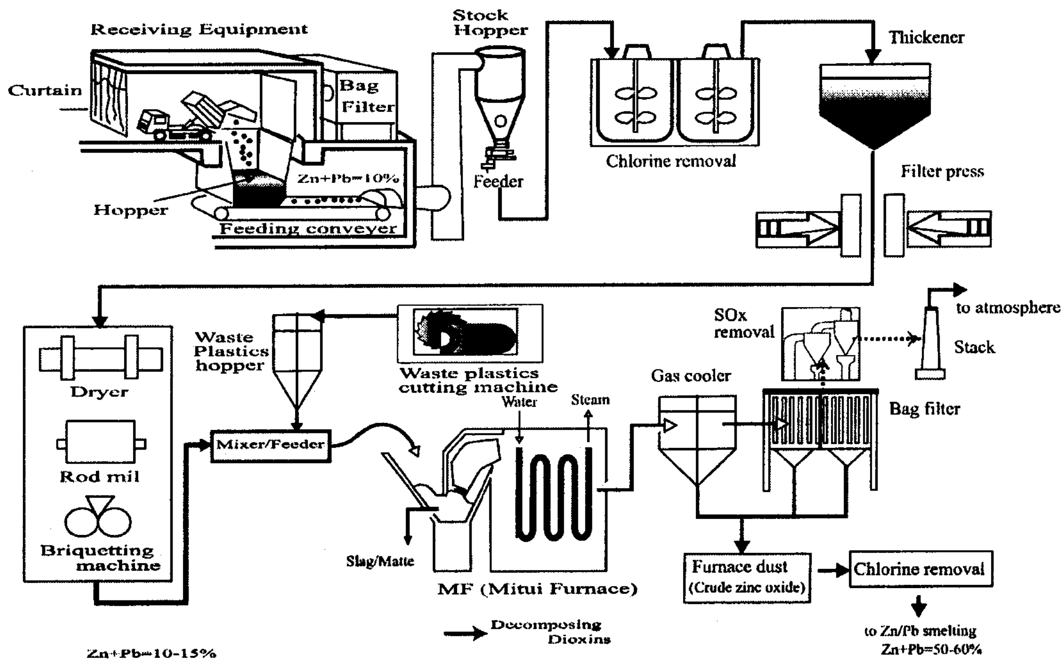

Fig.-4 Flow sheet of secondary fly ash treatment

Results and Discussion

Treatment of the primary ash

The composition of six primary ashes is shown in Table-1. The distinct difference between them is clear. Three

Table-1. Typical composition of the primary ash (%)

No	Na	Cl	SiO_2	Fe	Zn	Pb	Cu
1	6.84	13.7	19.3	0.95	0.66	0.14	0.07
2	3.51	7.3	18.9	1.10	0.26	0.04	0.04
3	3.58	27.0	10.0	0.27	1.24	0.41	0.07
4	4.60	4.8	18.8	1.35	0.48	0.30	0.94
	6.70	16.6	15.1	0.76	0.51	0.48	1.04
5	5.58	7.8	18.7	4.10	1.58	0.56	0.16
	5.34	12.6	18.9	0.98	1.36	0.49	0.11
6	4.76	8.1	18.5	5.85	0.49	0.10	0.07
	3.89	10.9	19.0	3.54	0.57	0.12	0.06

of six were sampled again one month later, and the difference was not so high except chlorine as shown in Table-1. The results of the segregation and flotation are shown in Table-2. Concentration of copper was found only in cases where the oil coke fly ash was used as reductant, and lead and zinc seem not to be concentrated. The poor efficiency in the cases using activated carbon could be improved by the optimization of the frothing condition. Though there could be possible for lead to be recovered to the froth after the segregation / flotation, the behavior of lead in segregation has not been found yet in our study, and the further study will be carried out.

Table-2. Results of segregation / flotation

No	Temp (C)	Carbon (%)	H2O (%)	Recovery (%)		
				Cu	Pb	Zn
1	800	AC 20	30	19.0	13.9	13.4
2	900	AC 20	30	9.3	28.2	14.0
3	800	OC 20	30	61.1	23.9	15.8
4	900	OC 20	30	68.2	20.1	14.0

AC : Activated carbon OC : Oil coke fly ash

Treatment of the secondary ash

The typical composition of the secondary fly ash is shown in Table-3. Heavy metals and chlorine content is higher than the primary one, and there is s ignificant difference among them.

Table-3. Typical composition of the secondary ash (%)

No	Cl	Fe	Zn	Pb	Cd
1	17.4	0.31	4.80	1.43	<0.0
	17.0	0.20	5.55	1.07	<0.0
2	34.1	0.25	10.8	2.48	0.09
	17.3	0.88	16.7	4.85	0.12

The results of the chlorine removal are shown in Table-4. The residual chlorine content of the ashes after the preliminary study of the chlorine removal was higher than expected. The formation of Pb(OH)Cl was detected by X ray diffraction, which can be considered to disturb the chlorine removal. For the purpose of the improvement of the chlorine removal efficiency, the two-stage reaction in series has been introduced.

Table-4. Ash composition after chlorine removal

No	Slurry density(g/l)	Cl(%)	Zn(%)	Pb(%)
1st stage				
1	203	5.85	33.9	8.68
2	133	7.83	35.6	10.2
2nd stage				
1	31	1.98	37.6	9.41
2	32	4.73	38.4	10.8

Zinc and lead in the secondary fly ash are remained and concentrated after the chlorine removal, which means that their loss in these stages can be negligible. The secondary fly ash after chlorine removal was mixed with other raw materials for MF and fed to it to recover zinc and lead to the furnace dust. The composition of the furnace dust of MF is shown in Table-5.

Table-5. Composition of furnace dust (%)

No	Cl	Fe	Zn	Pb	Cd
1	6.21	1.13	58.5	8.78	0.36
2	7.30	0.98	56.9	9.76	0.41
ref.	4.20	2.35	54.85	7.35	0.24

ref.: Actual furnace dust of MF in commercial operation

The chlorine content of the furnace dust is higher than the actual, meaning the necessity of improvement of the efficiency at the chlorine removal. Both the modification of the chlorine removal condition and the additional removal of chlorine from the furnace dust will be studied. A photograph of the downsized MF extracting the molten slag is shown in Fig.-5. The slag composition of the downsized MF is shown in Table-6. Zinc, lead and cadmium contents in slag are higher than the normal by the addition of the ashes, meaning that the operating condition was not stable enough. Modification should be done in the following studies.

Table-6. Composition of MF slag (%)

No	Fe	Zn	Pb	Cd
1	32.3	6.3	0.20	0.03
2	33.6	9.8	0.26	0.03
ref.	36.0	3.0	0.08	ND

ref.: Practical MF slag

The recovery rates of zinc and lead from the secondary fly ash to the furnace dust are 58-78% and 74-94%, respectively, and further improvement can be expected in the following studies.

Fig.-5 Slag extraction from downsized MF

The slag from the ash treatment process is expected to be environmentally sound to utilize to the construction materials, etc. The chemical stability (leachability) of MF slag in this study is found to be conformable enough to the national regulation (The Environmental Standard on Soil) in Japan, as shown in Table-7.

Table-7. Results of leaching test of slag (mg/l)

Element	Regulation	No.-1	No.-2
T-Hg	0.0005	<0.0005	<0.0005
Cd	0.01	<0.001	<0.001
Pb	0.01	<0.01	<0.01
Cr6+	0.05	<0.01	<0.01
T-CN	ND	<0.01	<0.01
As	0.01	<0.01	<0.01
Se	0.01	<0.01	<0.01
Cu		<0.01	<0.01
Zn		0.06	0.02

Energy saving

To make both primary and secondary fly ash treatment processes more practical, the energy saving should be a main subject of the following study. In the primary fly ash treatment process, the furnace gas of the segregation furnace is planned to utilize to the heat-decomposition of waste plastics to recover fuel oil and carbon particles used at the segregation process as reductant. Waste plastics are also utilized in the secondary fly ash treatment process to save coal for MF. 60% of heat recovery from the furnace gas of MF is also planned, which would be utilized to the onsite power generation.

Summary

The segregation / flotation process has been applied to the primary fly ash from the municipal waste incineration to recover copper, lead and zinc selectively. It was found that copper and zinc can be recovered selectively, and the behavior of lead will be found. Further study is continued to establish and optimize the operating conditions of the segregation / flotation and following chemical treatment to make the products of this process useful to each metal production.

The secondary fly ash from the municipal waste melting and/or the primary fly ash melting has been treated with MF Process after the chlorine removal to recover zinc and lead. Even the chlorine removal and the zinc/lead recovery rate should be improved a little, it seems to be able to treat with MF Process. The chemical stability (leachability) of the slag has been found to be conformable to the national regulation (The Environmental Standard on Soil) in Japan.

The energy saving with utilization of waste plastics is also planned to make the total process of this study more practical.

Acknowledgment

The authors would like to thank Ministry of Economy, Trade and Industry, Japan for the financial support for this project, Mitsubishi Materials Corporation and Mitsui Mining & Smelting Co., Ltd. for the cooperation to carry out the experiments and trials and the members of the advisory committee of this project for the effective and helpful suggestion.