LATEST TECHNOLOGICAL EXPERIENCE OF THE REMOVAL OF MERCURY IN FLUE GAS AND THE MANAGEMENT OF FLY ASH FROM MSW INCINERATOR

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ABSTRACT

Recently, mercury emissions from municipal solid waste incineration plants became of concern. As a result, several mercury removal systems have been developed and installed in the flue gas stream of incineration plants in Japan. Both a liquid chelating agent injection system and a sodium hypochlorite injection system at the wet scrubber have achieved more than 90% removal of mercury.

Fly ash from MSW incinerators contains volatile heavy metals such as cadmium, lead and arsenic and leaches these materials to the ground water. Three fly ash management technologies have been established. These are solidification of fly ash with cement, neutralization by flue gas and electric vitrification systems. The purpose of this paper is to describe the status of mercury emission control and fly ash management technologies in Japan.

INTRODUCTION

The continuous measurements of mercury in the flue gas from waste incineration plants showed that the mercury level normally ranges from 0.05 to 0.15 mg/ Nm^3 with a peak of high concentration of 1–2 mg/ Nm^3 detected. This peak was experimentally confirmed to be attributed to mercury in waste mercury batteries and thermometers. This fact, particularly combined with rapidly increased production of dry batteries (Table 1), has caused waste mercury to become a social problem.

TABLE 1 CHANGES IN DOMESTIC CONSUMPTION OF MERCURY (Unit: kg)

	1982	1983	1984	1985	1986
Caustic soda	1,386	269	494	380	88
Amalgam	9,545	3,306	3,895	3,119	2,780
Inorganic chemicals	85,120	61,040	54,843	24,914	33,080
Electric equipment	6,449	7,138	6,554	6,706	5,172
Measuring devices	43,446	41,450	34,652	17,460	22,838
Battery materials	109,248	110,803	121,730	122,714	154,331
Others	5,121	5,449	3,541	3,843	3,570
Total	260,315	230,505	225,709	179,136	221,859

The countermeasures taken to cope with this problem include the following:

(a) Control on use of mercury batteries, reduction in mercury content of dry batteries to one third in 3 years and to one sixth in 5 years, and research for development of mercury-free substitute for dry battery

(b) Classified recovery of waste dry batteries, fluorescent lights and other products containing mercury is adopted, and mercury is regenerated at the Japan's only mercury recovery plant.

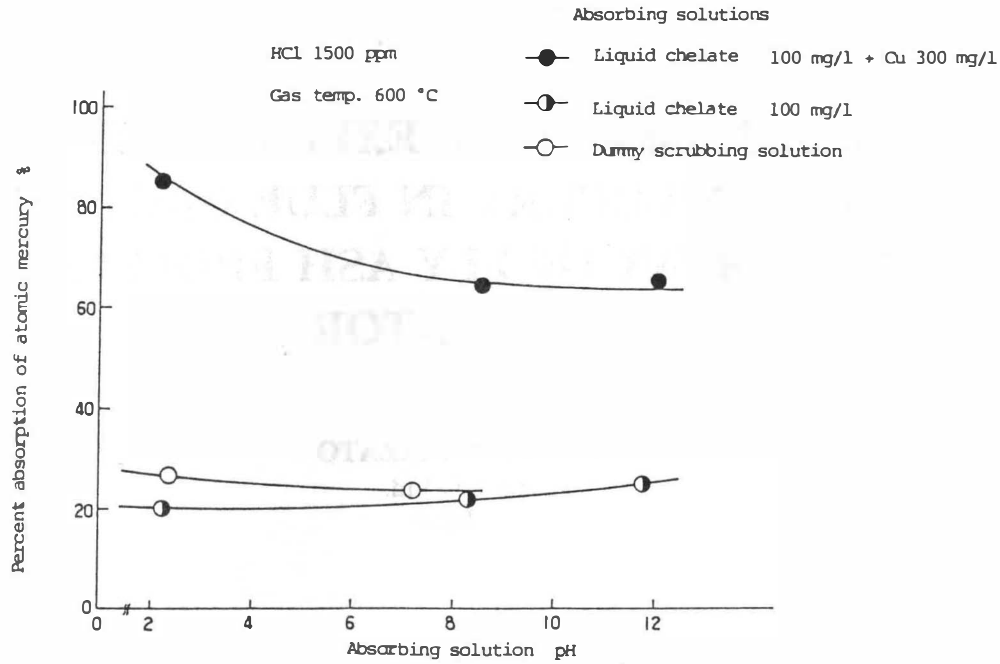

FIG. 1 ABSORBING SOLUTION pH AND ABSORPTION OF ATOMIC MERCURY

(c) Development of technology for removal of mercury in the flue gas.

In major cities and their surrounding cities, toward which the gravitation of population has occurred heavily, it has become very difficult to secure sites for dumping of incineration ash and fly ash. To cope with the situation, several plants for vitrification of incineration ash are now in operation, while there has been an increasing demand for development of technology for stabilization of fly ash containing a high percentage of heavy metal.

MERCURY REMOVAL

Most of waste incineration plants built in major cities and their surrounding cities, where HCl and SO_x emission have been significantly controlled, have been conventionally equipped with a wet scrubber. Investigation of the wet scrubber for its mercury removal efficiency, however, showed that the efficiency level is only in the range of 30–70%. Research for increasing this mercury removal efficiency level to more than 90% led to the development of the following technologies:

LIQUID CHELATING AGENT INJECTION SYSTEM

This system is designed with a caustic soda-based gas scrubbing line, into which a liquid chelating agent and cupric chloride are injected for absorption of atomic mercury contained in the flue gas.

In general, mercury in the flue gas at the wet scrubber entrance occurs in three forms: water soluble mercury, slightly water soluble mercury, and atomic mercury in the approximate ratio of 8:1:1. Water soluble mercury is assumed to be identified as $HgCl_2$ formed by reaction between atomic mercury and HCl in the flue and electrostatic precipitator. Therefore, this form of mercury can be absorbed even in a conventionally-used wet scrubber, which, however, is not capable of absorbing the other two forms of mercury: atomic and slightly water soluble mercury.

Figure 1 shows the relationship between the pH of various absorbing solutions and the percent absorption of atomic mercury in the solutions.

The scrubbing waste water containing mercury is subjected to coagulating sedimentation with the addition of liquid chelating agent at a concentration several times the amount of copper, followed by fixation in the sludge.

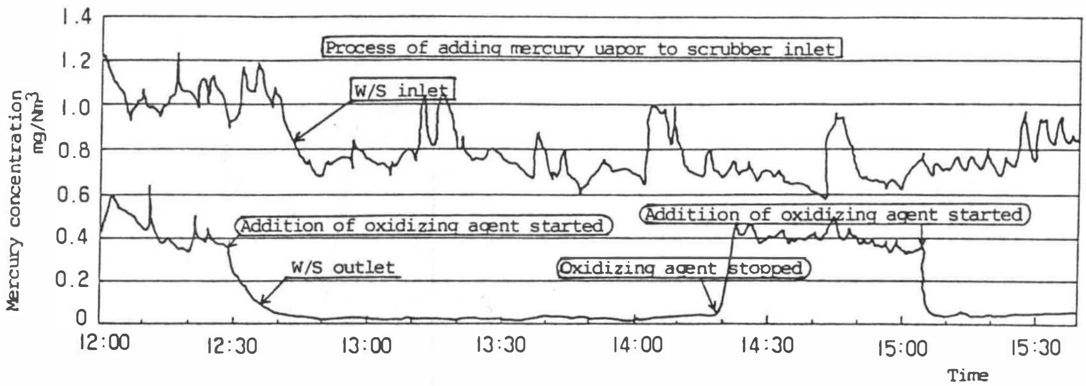

FIG. 2 CONTINUOUS MEASUREMENT OF MERCURY

TABLE 2 CHEMICAL COMPOSITION OF FLY ASH FROM MSW INCINERATOR (Unit: %)

Components	Analyses	Components	Analyses
SiO_2	16.8	V_2O_5	0.1
Al_2O_3	9.5	MnO	0.2
Fe_2O_3	3.3	NiO	0.1
CaO	10.2	CuO	0.4
MgO	3.1	SnO	0.7
Na_2O	11.5	ZnO	4.2
K_2O	6.5	PbO	1.3
P_2O_5	1.7	Cl^-	14.3
TiO_2	1.1	Ignition loss	8.6

TABLE 3 RESULT OF SOLUBILITY TEST ON FLY ASH FROM MSW INCINERATOR

Components	Content mg/kg	Elution mg/ℓ
Hg	5.5	< 0.0005
Cd	335	14.3
Pb	12200	2.1
T-Cr	544	0.20
Cr^{6+}	< 0.01	< 0.01
As	30.2	< 0.001
T-CN	1.8	< 0.001

SODIUM HYPOCHLORITE INJECTION SYSTEM

This system is designed with a wet scrubber, to which sodium hypochlorite is injected at a concentration of several tens of ppm for reaction with mercury to form mercuric chloride for absorption. The system provides for a mercury removal efficiency of 90–95%.

Also, the system features concurrent removal of nitrogen oxides achieved by addition of bromine at an efficiency of 30–50%. Figure 2 shows the reaction of mercury concentration with the addition of oxidizing agent.

FLY ASH MANAGEMENT

Fly ash collected in the electrostatic precipitator contains various types of chlorides, as well as harmful heavy metals, among which lead and cadmium occur in a state where they are subject to elution. Table 2 shows the typical chemical composition of fly ash from MSW incinerator, and Table 3 shows the relation between heavy metal content in fly ash and the elution rate by solubility test.

The following describes various technologies developed for treatment of this fly ash into a stabilized state.

Cement Solidification

This system is designed with the following process for treatment of fly ash: cement is added to the fly ash at a concentration of approximately 15% and the mixture is fed to a mixer with the addition of water, followed by molding into pellets or blocks with a molding machine. The pellets or blocks are cured by storage in a pit prior to dumping. Figure 3 shows system flow diagram of cement solidification.

Heavy metals contained in the fly ash stabilized by this system have their elution prevented by the crystal lattice of the cement.

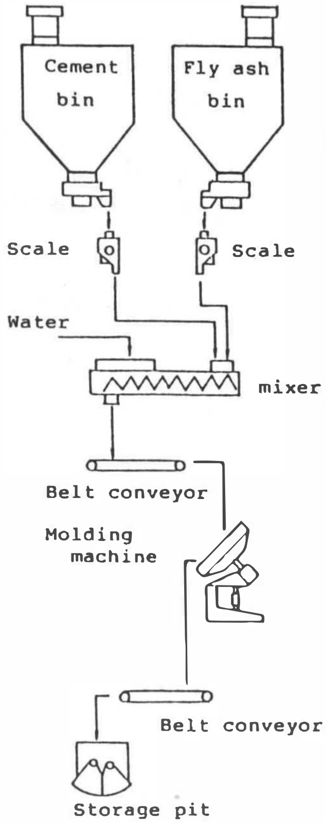

FIG. 3 SYSTEM FLOW DIAGRAM OF CEMENT SOLIDIFICATION

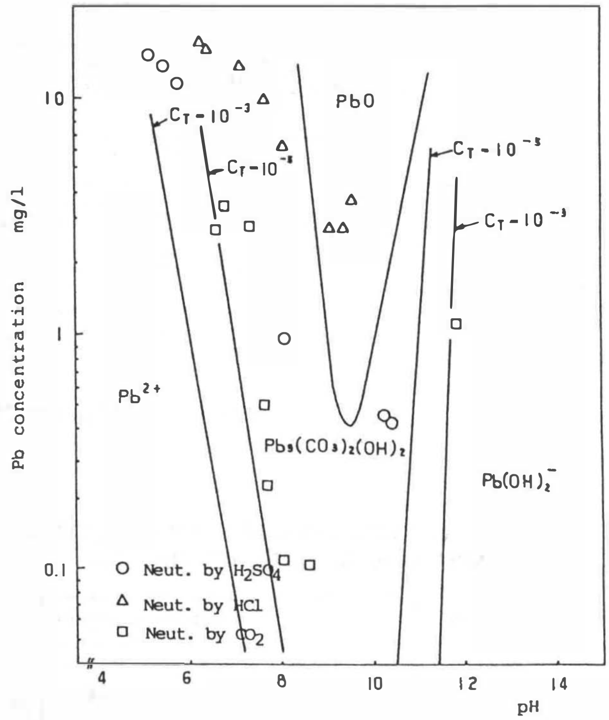

FIG. 4 EFFECTS OF TYPES OF NEUTRALIZING ACIDS AND pH ON Pb SOLUBILITY

It should be noted, however, that a low mixing ratio of cement to fly ash may lead to failure in its stabilization.

FLUE GAS NEUTRALIZATION SYSTEM

This system is designed with the following process for fly ash stabilization: fly ash is dissolved in ash-quenching water and the waste water is then neutralized with CO_2 in waste combustion exhaust gas to transform heavy metals contained in the fly ash into inactive carbonates for stabilization. Figure 4 shows changes in the lead concentrations of the filtrates obtained from the ash-quenching water upon its neutralization with H_2SO_4, HCl and CO_2, indicating that CO_2 induces lowest Lead concentration in liquid, and SO is superior to H_2SO_4 and HCl as a neutralizing agent for Lead treatment.

The system flow diagram is illustrated in Fig. 5, where the Fly Ash Solution Tank is subjected to pH control at 10, followed by reduction to pH 8 by CO_2

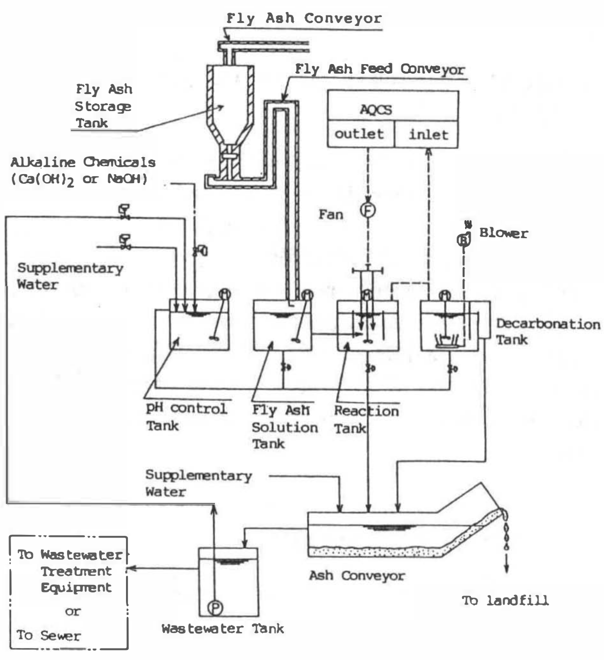

FIG. 5 SYSTEM FLOW DIAGRAM

TABLE 4 RESULT OF SOLUBILITY TEST ON FLY ASH WITH NEUTRALIZATION

Item	Sample	before neutralization		with after neutralization	
	Unit	#1	#2	#1	#2
Cd	mg/ℓ	<0.01	<0.01	<0.01	<0.01
Pb	〃	120	71	0.4	1.7
T-Hg	〃	0.0027	0.0033	<0.0005	<0.0005
As	〃	0.03	0.05	<0.01	<0.01
Cr^{6+}	〃	<0.05	<0.05	<0.05	<0.05
CN	〃	<0.01	<0.01	<0.01	<0.01
Org-P	〃	<0.05	<0.05	<0.05	<0.05
A-Hg	〃	<0.0005	<0.0005	<0.0005	<0.0005
PCB	〃	<0.0005	<0.0005	<0.0005	<0.0005

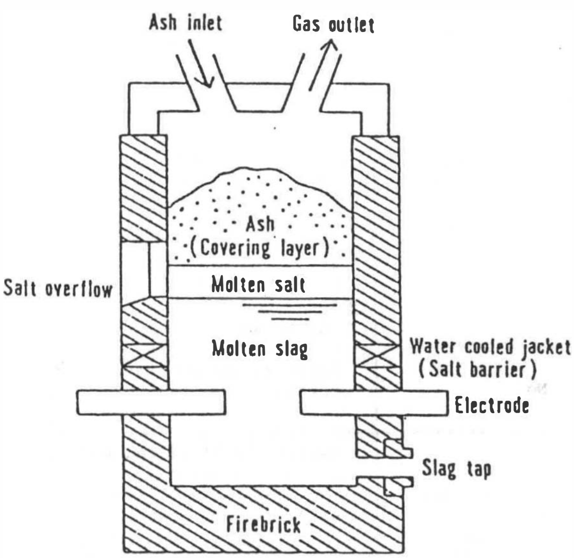

FIG. 6 FLY ASH MELTER

gas for stabilization of Lead in form of basic lead carbonate.

After the dissolution of fly ash in the ash-quenching water, the resultant fly ash solution is fed to the ash conveyor for sedimentation of its solid portion before being fed as ash-quenching water to the wastewater treatment equipment for fixation of heavy metals in coagulation-sedimented sludge. Table 4 shows the differential concentration in waste water on fly ash with neutralization.

Electric Vitrification System

This system is designed with the use of a metal electrode embedded in molten slag, through which al-

TABLE 5 HEAVY METAL CONTENT OF VITRIFIED FLY ASH

	Cr %	As %	Pb %	Zn %	Cd %	Hg mg/kg
Case 1 Without slaked lime injection	0.5	0.003	0.56	15	0.010	0.80
Case 2 With slaked lime injection	–	0.003	0.01	0.5	0.001	0.18

TABLE 6 RESULTS OF ELUTION TEST ON VITRIFIED FLY ASH

	Cr mg/ℓ	As mg/ℓ	Pb mg/ℓ	Zn mg/ℓ	Cd mg/ℓ	Hg mg/ℓ
Case 1	< 0.1	< 0.1	0.1	0.1	< 0.1	0.0001
Case 2	< 0.1	——	< 0.1	< 0.1	< 0.01	<0.0001
Standard by the Prime Minister's office for Dumping	< 1.5	< 1.5	< 3.0	——	< 0.3	< 0.005

ternating current is applied to form a molten layer on the molten slag, for treatment of fly ash. Specifically, the fly ash is fed from the furnace top so that it is piled up on the top of the molten layer to form a cold filter layer (covering layer) for collection of low-boiling heavy metal to melt it while preventing its volatilization. The fly ash thus vitrified was tested for elution with the results shown in Tables 5 and 6, which show that the elution level is below the standard specified by the Prime Minister's Office for dumping, although approximately 10% of the fly ash fed forms a molten salt, which requires treatment for disposal.

Table 7 shows a comparison of the above described three systems.

CONCLUSIONS

Effective countermeasures against waste mercury are to reduce the consumption of mercury in the field of production and to recover waste products containing mercury for regeneration. It should be noted here, however, that there is also a forecast for an annual increase of approximately 10–20% in the production of dry batteries and other products containing mercury, indicating a great need for development of tech-

TABLE 7 COMPARISON OF VARIOUS FLY ASH MANAGEMENT SYSTEMS

Item \ Management system		Cement Solidification System	Flue Gas Neutralization System	Electric Vitrification System
Advantages		① Cement is less expensive, more easily available and safer in handling than any other solidifying material. ② Simple equipment and easy maintenance. ③ No measures required for control of fire, odor and exhaust gas. ④ Excellent in capability of fixing heavy metal for stabilization. ⑤ Volume reducing effect (approx. 1/2)	① Utilization of flue gas, thus eliminating the need for use of chemicals necessary for neutralization. ② Greatly effective in antiscaling in ash-contained waste water system. ③ Formation of water insoluble carbonate, thus reducing the elution of heavy metal from sludge. ④ Reduction in BOD and COD of ash-contained waste water. ⑤ Large volume reducing effect (sludge volume ratio: approx. 1/4 based on sludge with water contents of 50%)	① Slow melting by Joule heating with formation of a covering layer, which is effective in fixing 70 to 80% of most of low-boiling heavy metals in slag, to make them harmless. ② Formation of stable slag, which causes no elution of heavy metal. ③ Separation of salts in ESP ash as molten salt (in solid state). ④ Large volume reducing effect (approx. 1/10). ⑤ Reuse of slag as backfill
Disadvantages		① Weak in strength just after molding, thus requiring curing equipment. ② Molding are vulnerable to acid. ③ Special design of working environment required.	① Rise in temperature of ash-contained waste water due to the use of flue gas (approx.200℃)	① Transfer of part of heavy metal in ESP ash to gas system, thus requirering cooling in the gas system for recovery of the heavy metal and treatment to make it harmless. ② Separate treatment of molten salt required.
Volume reducing effect		Small in volume reducing effect due to addition of cement.	NO	Large in volume reducing effect
Possibility of effective use		Small	NO	Yes(for backfill and road-bed material)
Ease of operation		Easy	Easy	Slightly complicated
Utility	Power consumption	30kw/t of waste to be treated	40kw/t of waste to be treated	800 ～1,200kw/t of waste to be treated
	Additive	Cement: approx. 150kg/t of waste to be treated	Effective use of incinerator flue gas	Electrode: 20 ～30g/t of waste to be treated
	Cooling water	50ℓ/t of waste to be treated	0.4m³/t of waste to be treated	Not required
Others	Consumables	Small amount of money required (for wear-resistant plate, etc.)	Small amount of money required (for packing, etc.)	Large amount of money required (for repair of refractories, etc.)
	Behavior of harmful materials during treatment	No fly of harmful materials due to treatment at room temperature.	No fly of harmfull materials	Transfer of part of heavy metal in ESP ash in gas system, thus requiring cooling in the gas system for recovery of the heavy metal and treatment to make it harmless.
Actual applications		Many	Few	Demonstration level

nology for removal of mercury in the flue gas. A wet scrubber, when designed with the above-described system, is capable of achieving a mercury removal efficiency of more than 90%. However, research for further improvement in the mercury removal efficiency is required.

A fly ash management system should be selected according to its overall rating based on the assessment of its various aspects including dumping site management and environmental impact. The cement solidification system, flue gas neutralization system and electric vitrification system have both advantages and disadvantages. Therefore, continued research is required for the optimization of the management systems.

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Key Words: Fly Ash; Heavy Metals; Mercury; Scrubber; Vitrification