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Application Expansion of Incineration Ash Melting Technology and Development of Incineration Ash Recycling Technology

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Abstract:

Established in 1991, coke-bed incineration ash melting technology was developed by taking advantage of a wealth of experience in municipal solid waste direct melting furnaces and by conducting basic experiments with demonstration furnaces. In 1992, an order was received from Tokai City, Aichi Prefecture for two commercial 15-t/d-capacity furnaces. The increasing difficulty of acquiring final disposal landfill sites has been raising the expectations placed on municipal solid waste melting furnaces. To further the use of coke-bed incineration ash melting technology under these circumstances, research and development work was initiated to expand its applications to embrace shredded noncombustible residue and incinerator fly ash, among other things. The behavior of low-boiling point substances such as heavy metals that impede the recycling of molten slag and fly ash was also studied. The research and development results confirmed the suitability of the coke-bed melting furnace for processing a variety of ashes and clarified that exposure to the high-temperature and reducing atmosphere of the coke-bed melting furnace process would volatilize heavy metals. This means that the coke-bed incineration ash melting technology is very effective in rendering the molten slag harmless, concentrating the heavy metals in the fly ash, and promoting the reuse of recovered heavy metals.

1. Introduction

In 1979, Nippon Steel constructed a municipal solid waste direct melting furnace by making use of its high-temperature melting technology developed over many years in the ironmaking field. It also took the initiative in reducing the volume of rendering harmless, and recycling municipal solid waste. Tapping this experience, in 1987 Nippon Steel started the research and survey of the technology for melting incineration ash by using coke as a heat source and carried out basic research using an experimental furnace with a capacity of 2 to 3 t/d for about 2 years from 1988. In 1991, a demonstration furnace with a capacity of 7 to 10 t/d was operated for about one year, thereby establishing the associated technology[1].

In 1992, Nippon Steel commenced research to expand the

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scope of the technology to cover such types of ashes as shredded noncombustible residue, and it scaled up the demonstration furnace to a large furnace with a capacity of 20 t/d[2]. The ash discharged from municipal solid waste incineration plants (incinerator fly ash) was specified as specially regulated general waste under these circumstances. In fiscal 1994, Nippon Steel started joint research with the Tokyo Metropolitan Government concerning the melting of incinerator fly ash[3]. The company also pushed ahead with research into the recycling of molten slag and fly ash discharged resulting from the melting.

The findings obtained from these recent research activities are reported here.

2. Outline and Principle of Melting Furnace

Fig. 1 shows the equipment flow sheet of a test melting furnace. The incinerator ash stored in the ash pit is fed by the crane to the vibrating screen to remove lumps too large to be properly handled by the above-furnace charging equipment. These are charged by a hoisting bucket into the above-furnace ash hopper. Coke and limestone are charged by a hoist into their respective above-furnace hoppers. The incinerator ash, coke, and limestone in the above-furnace hoppers are weighed for each charge and dumped into the furnace at a signal indicating a drop in the burden level of the melting furnace.

The melting furnace is a packed bed of inverted conical shape, as shown in **Fig. 2**. The incinerator bottom ash, coke and limestone are charged through the center of the furnace, and coke is also charged through the periphery of the furnace. This is to ensure gas permeability and to stabilize the descent of the burden. The coke is burned at high temperatures by the preheated air blown through the tuyeres, and a red-hot coke bed at 1,700 to 1,800°C is formed over a wide area in the lower part of the furnace. The descending burden is dried and preheated by the coke combustion waste gas, melted, dripped and heated to about 1,500°C as it passes through the coke bed, and is finally dis-

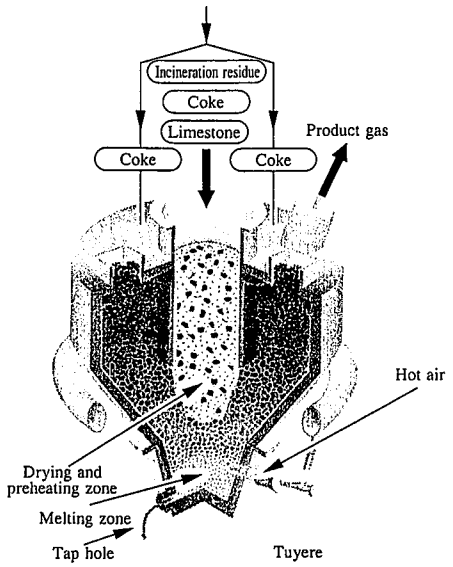

Fig. 2 Cross-sectional view of melting furnace

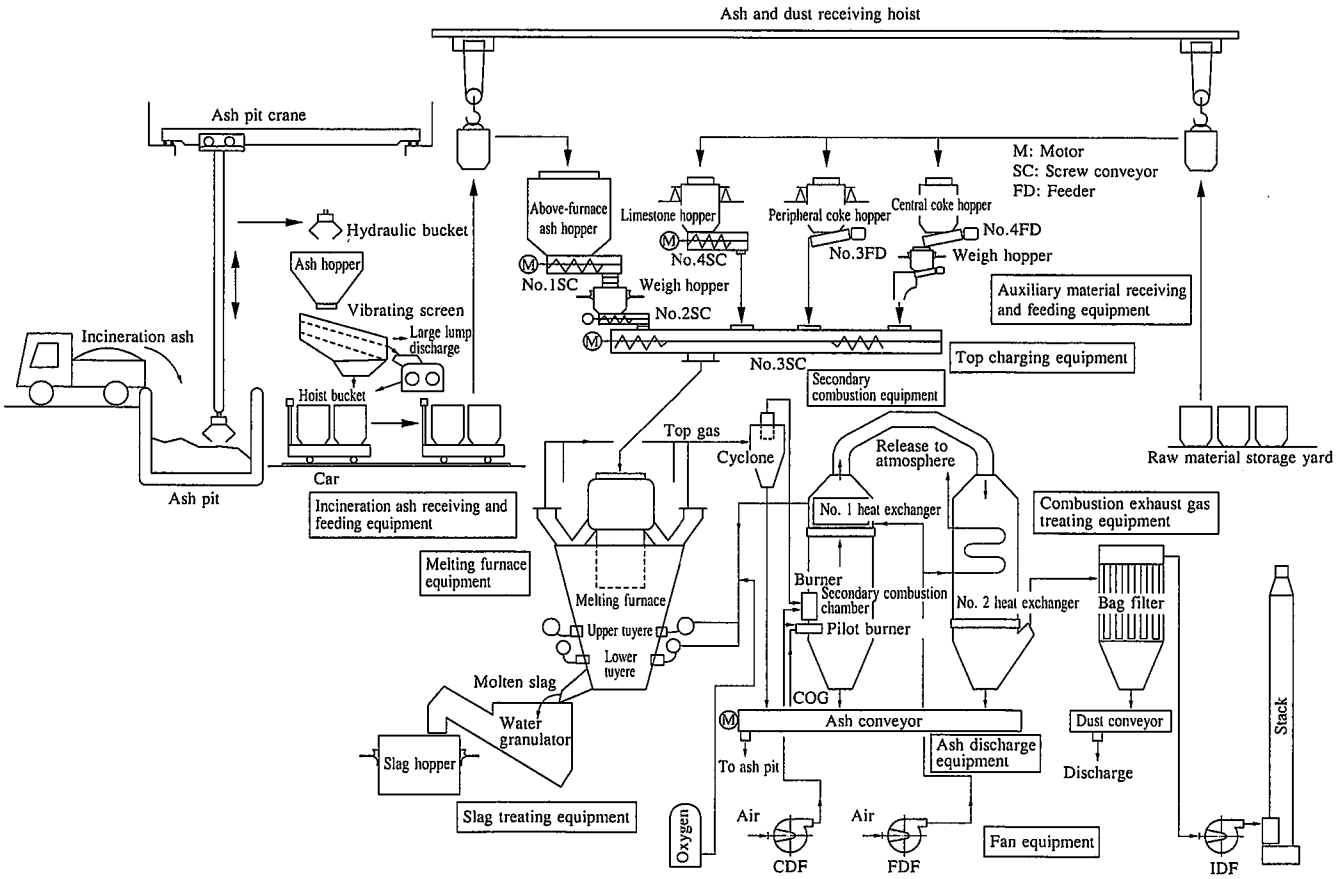

Fig. 1 Flow sheet of incineration residue melting test plant

charged from the furnace through the tap hole. The melt is rapidly cooled by dumping into a water tank, then separated and recovered as slag and metal.

The gas produced in the furnace contains combustible components. This gas is drawn through the furnace top and completely burned in the secondary combustion chamber. The combustion waste heat is utilized for preheating the blast air, among other things. The combustion waste gas is cooled in the gas cooling chamber to 180-200°C, dedusted by the bag filter, and released through the stack.

3. Applicable Ash Type Expansion Tests

3.1 Purpose of tests

The incineration ash melting technology was initially designated for incinerator bottom ash as the principal type of feed material to be handled. The high volume of shredded noncombustible residue currently dumped in landfills needs to be reduced, and melting is regarded as an effective technology to dispose of the incinerator fly ash designated as general waste for special regulation. To meet these needs, tests were run to confirm the possibility of incinerator bottom ash being mixed and treated with the shredded noncombustible residue and incinerator fly ash. Since the salts and low-boiling point heavy metals that pose a problem in the melting of the incinerator fly ash have an impact on the properties of molten slag, their behavior was clarified by thermodynamic analysis as well as by the melting tests.

3.2 Shredded noncombustible residue mixture melting test[2]

The bottom ash of a continuous stoker incinerator was mixed with shredded noncombustible residue and was melt tested. **Table 1** shows the three components of the shredded noncombustible residue used in the test. The combustible fraction accounts for as much as about 35%. This means that the shredded noncombustible residue contains relatively large amounts of combustible substances. **Table 2** lists the chemical analyses of the incinerator bottom ash and shredded noncombustible residue.

The test methods and results are follow. The feed materials to be melted were incinerator bottom ash only and it mixed with the shredded noncombustible residue at a weight ratio of 7:3. **Table 3** gives some of the melting test results. The incinerator bottom ash and the mixture of the incinerator bottom ash and shredded noncombustible residue were stably melted and exhibited no significant differences. The incinerator bottom ash was treated at a rate of 12.1 t/d. The mixture of the incinerator bottom ash with the shredded noncombustible residue was treated at a slightly lower rate of 10.7 t/d. Since coke consumption was almost constant, the amount of coke required to melt one ton of the incinerator bottom ash/shredded noncombustible residue mixture was somewhat greater than that required to melt one ton of the incinerator bottom ash/alone.

The heat balance of the melting furnace when treating the incinerator bottom ash/shredded noncombustible residue mixture is shown in **Table 4**. The increased coke rate and the combustible fraction of the shredded noncombustible residue increased the heat input. The increased heat input resulted in a greater temperature and heating value of the gas discharged from the furnace. The sensible heat and latent heat of the gas are high enough for the gas to be stably burned in the secondary combustion chamber.

3.3 Incinerator fly ash mixture melting test[3]

The bottom ash of the continuous stoker incinerator was mixed with fly ash and melt tested. The fly ash was mixed at

Table 1 Three fractions of shredded noncombustible residue (wt%)

Moisture	Combustible	Noncombustible	Total
14.5	35.1	50.1	99.7

Table 2 Chemical composition of incinerator bottom ash and shredded noncombustible residue to be melted in furnace (wt%)

		Incinerator bottom ash	Shredded noncombustible residue
Chemical composition of noncombustible fraction	SiO_2	35.0	39.7
	CaO	13.8	4.4
	Al_2O_3	15.3	2.3
	MgO	1.9	0.8
	MnO	0.2	0.3
	Na_2O	4.4	6.1
	K_2O	1.5	1.1
	TiO_2	0.8	0.2
	FeO	5.7	1.0
	Fe_2O_3	14.9	0.7
	M-Fe	0.9	0.9
	Pb	0.1	0.2
	Zn	0.3	0.3
	Cu	0.7	0.1
	SO_4	0.5	0.2
	S	0.1	0.1
	Cl	1.3	0.2
Combustible fraction		1.1	41.2
Total		98.5	99.8

Table 3 Melting test results

			Incinerator bottom ash	Incinerator bottom ash mixed with shredded noncombustible residue
Proportion	Incinerator bottom ash	wt%	100	70
	Shredded noncombustible residue	wt%	0	30
Operating performance	Treatment rate	t/d	12.1	10.7
	Coke consumption	kg/h	153	151
	Gas production	Nm^3/h	688	707
	Product gas temperature	°C	340	430
	Stack gas emission rate	Nm^3/h	2,715	3,584
	Molten matter production rate	kg/h	508	408

Table 4 Heat balance of melting furnace (%)

		Incinerator bottom ash	Incinerator bottom ash mixed with shredded noncombustible residue
Proportion	Incinerator bottom ash (wt%)	100	70
	Shredded noncombustible residue (wt%)	0	30
Heat input	Heat generated by coke	89.3	77.1
	Heat generated by carbon in feed	3.7	16.6
	Sensible heat of preheated blast air	7.0	6.3
Heat output	Latent heat of gas produced in furnace	41.2	49.0
	Sensible heat of gas produced in furnace	5.8	6.9
	Heat of evaporation of moisture in feed	5.8	5.1
	Heat of decomposition of limestone	6.5	4.4
	Heat of dissolution of slag and metal	20.6	13.8
	Latent heat of gas emitted through tap hole	9.6	10.1
	Heat radiation from furnace, etc.	10.5	10.7

ratios of 15% and 30%. The chemical analyses of the mixtures are listed in **Table 5**.

The melting furnace was test operated at a rate of about 15 t/d for four days and was held in a steady state for two days to gain a better grasp of its material balance.

The material balance results of the furnace when the incinerator bottom ash/fly ash mixture was melted follow. The percentage of fly ash in all of the solids discharged out of the furnace during melting is defined as the fly ash distribution coefficient. The distribution coefficients of heavy metals and salts are shown in **Fig. 3**. Of the heavy metals, lead and zinc exhibited high distribution coefficients of over 96% and 80%, respectively.

Table 6 shows the chemical analyses of slag. The content of lead that becomes a problem in the slag leaching test was held low at about 60 ppm despite its high proportion in the fly ash. **Table 7** lists the chemical analyses of fly ash. Slag components such as SiO_2 and CaO are small, and the volatile components such as sodium, potassium, lead and zinc are concentrated.

4. Behavior Analysis of Low-Boiling Point Substances during Melting

4.1 Discussion of volatile matter in furnace

The volatilization and concentration of low-boiling point substances observed in the melting process in the incinerator bottom ash/fly ash mixture melting test is important in evaluating the melting function of the melting furnace. To recycle slag and reuse heavy metals, it is ideal that the slag should contain no heavy metals and that the heavy metals should transfer to the fly ash and should be concentrated in the fly ash. This chapter focuses on the volatile substances (heavy metals) in the furnace and discusses the behavior of each element from a thermodynamic equilibrium standpoint.

4.2 Behavior at high-temperature dissolution plane in melting furnace

When a metal in ash is heated, it progresses from the condensed phase (solid or liquid phase) to the gas phase, volatilizes, and separates from the ash. When various reactions in the melting furnace are observed, chlorine and sulfur are found to be present in relatively large amounts. This points to the need for considering chlorides and sulfides in addition to oxides. **Fig. 4** shows the vapor pressure of the main volatile elements and their compounds. Chlorides and sulfides of metals are generally lower in boiling point and more volatilizable than their oxides. This favors their separation from the ash.

The high-temperature melting zone in the lower part of the coke-bed melting furnace is held at a high temperature of more than 1,500°C, and under the reducing atmosphere produced by the combustion of coke. Metallic compounds in various ashes are reduced in this melting zone.

Fig. 5 shows an Ellingham diagram of oxides in which the

Table 5 Chemical composition of feed to be melted

	Incinerator bottom ash mixed with 15% fly ash	Incinerator bottom ash mixed with 30% fly ash
SiO_2	35.55	35.65
CaO	14.94	16.22
Al_2O_3	16.77	13.38
MgO	2.11	2.48
MnO	0.19	0.17
Na_2O	4.36	4.38
K_2O	1.84	2.30
TiO_2	0.68	0.82
FeO	5.56	4.69
M-Fe	0.77	0.64
Pb	0.19	0.18
Zn	0.45	0.54
Cu	0.65	0.55
S	0.68	1.07
Cl	1.61	2.42

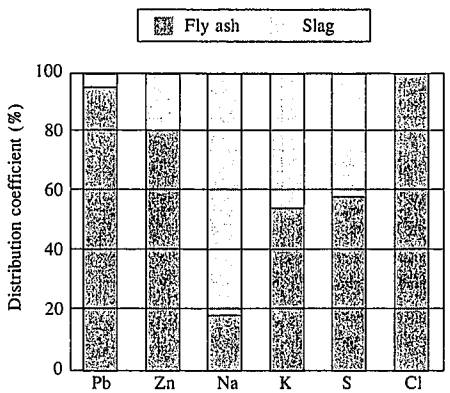

Fig. 3 Distribution coefficients of elements

Table 6 Chemical composition of slag (%)

	Incinerator bottom ash mixed with 15% fly ash Average of 2 samples	Incinerator bottom ash mixed with 30% fly ash Average of 2 samples
SiO_2	36.00	33.90
CaO	32.80	33.90
Al_2O_3	13.35	15.20
MgO	1.90	2.70
MnO	0.17	0.14
Na_2O	3.30	2.95
K_2O	0.77	0.78
TiO_2	1.00	1.06
FeO	5.49	4.13
Fe_2O_3	0.15	0.12
M-Fe	0.56	0.57
Pb	0.0065	0.0063
Zn	0.0925	0.0674
Cu	0.1070	0.1339
S	0.23	0.36

Table 7 Chemical composition of fly ash (%)

	Incinerator bottom ash mixed with 15% fly ash Average of 4 samples	Incinerator bottom ash mixed with 30% fly ash Average of 3 samples
SiO_2	3.93	5.03
CaO	1.53	1.47
Al_2O_3	0.75	1.73
MgO	0.35	0.69
MnO	0.04	0.05
Na_2O	17.13	17.10
K_2O	18.85	22.03
TiO_2	0.03	0.07
FeO	3.11	0.15
M-Fe	0.31	0.10
Pb	5.69	5.06
Zn	8.32	5.61
Cu	0.13	0.23
S	5.77	5.62
Cl	27.70	24.69

stability of individual metals is plotted against the furnace gas atmosphere and temperature. The melting furnace has a reducing atmosphere with a CO/CO_2 ratio of more than 1/1 as indicated by curve C.

Since curve A, indicating the formation of lead oxide, lies above curve C at all temperatures, the lead oxide to be reduced to metallic lead is constantly present. Similarly, zinc oxide (curve B) is reduced to metallic zinc above the temperature of 1,300°C at the intersection of curve B with curve C. If sulfur and chlorine are present in sufficient amounts in the melting furnace, metallic lead and zinc in the reduced condition are considered to form low-boiling point sulfide and chloride and to volatilize out of the furnace.

4.3 Thermodynamic equilibrium relations between oxides and chlorides

To evaluate the stability of oxides and chlorides of the metals lead, zinc, sodium, potassium and calcium introduced into the melting furnace, their standard free energies of formation are calculated by the following reaction equations:

$PbO + 2HCl\ (g) = PbCl_2 + H_2O\ (g)$ ……(1)

$ZnO + 2HCl\ (g) = ZnCl_2 + H_2O\ (g)$ ……(2)

$Na_2O + 2HCl\ (g) = 2NaCl + H_2O\ (g)$ ……(3)

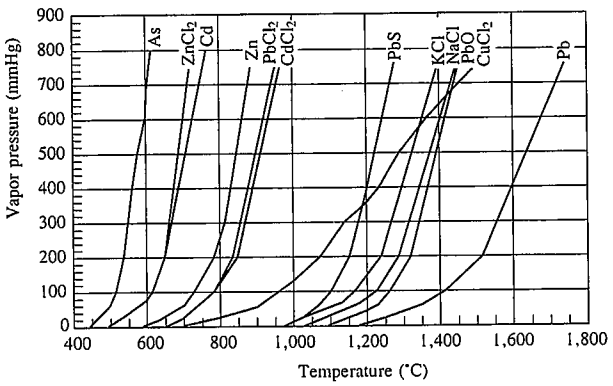

Fig. 4 Vapor pressure of main volatile elements and their compounds

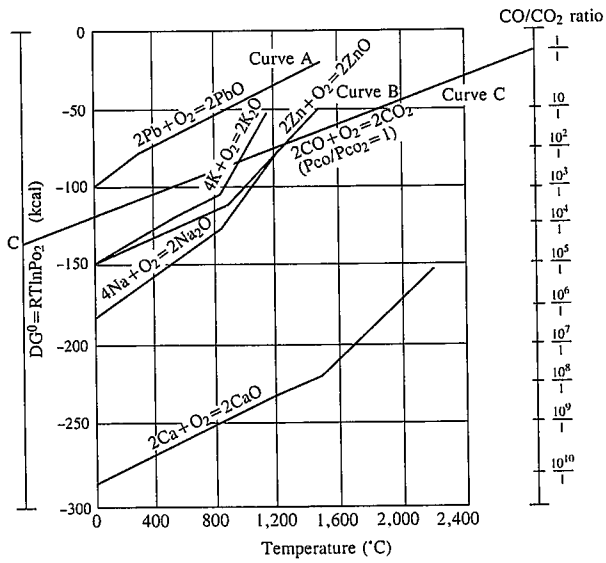

Fig. 5 Ellingham diagram of oxides

$K_2O + 2HCl\ (g) = 2KCl + H_2O\ (g)$ ……(4)

$CaO + 2HCl\ (g) = CaCl_2 + H_2O\ (g)$ ……(5)

When their reaction equilibrium constants are obtained from the above reaction equations, the elements most likely to form chlorides are ordered as K > Na ≫ Ca ≈ Pb > Zn. Sodium and potassium are stabilized as the chlorides NaCl and KCl.

4.4 Thermodynamic equilibrium relations between chlorides and sulfides

To evaluate the stability of chlorides and sulfides of the metals lead, zinc and calcium introduced into the melting furnace, their standard free energies of formation are similarly calculated by the following reaction equations:

$PbCl_2 + H_2S\ (g) = PbS + 2HCl\ (g)$ ……(6)

$ZnCl_2 + H_2S\ (g) = ZnS + 2HCl\ (g)$ ……(7)

$CaCl_2 + H_2S\ (g) = 2CaS + 2HCl\ (g)$ ……(8)

When their reaction equilibrium constants are obtained from the above reaction equations, the elements most likely to form sulfides are ordered as Zn > Pb > Ca.

When HCl and H_2S coexist in the reducing atmosphere of the melting furnace, the waste gas is presumed to contain PbS and ZnS as stable sulfides and NaCl and KCl as stable chlorides.

4.5 Form analysis of dust collected at melting furnace outlet

The dust in the waste gas at the melting furnace outlet in the incinerator bottom ash/fly ash mixture melting test was collected with filter paper and form analyzed by the X-ray diffraction technique. The results appear in **Table 8**. The compounds NaCl, KCl, PbS, and ZnS were detected in the collected dust. The analyzed results agree well with the results estimated from thermodynamic equilibrium theory.

5. Research on Slag and Fly Ash Recycling[3)]

5.1 Slag leaching test results

Table 9 shows the leaching test results of slag obtained from the incinerator bottom ash and incinerator bottom ash/fly ash mixture melting tests. The levels cleared set soil environmental standards. This is probably influenced by a low lead content of about 60 ppm. Melting at high temperatures in the reducing atmosphere has the effect of accelerating lead volatilization.

5.2 Slag material test results

Slag resulting from the direct melting of municipal solid wastes is already sold as aggregate for interlocking blocks, among other things. Slag from the melting of incinerator bottom ash was evaluated for its suitability as fine aggregate (sand substitute) for asphalt mixtures. Types of slag produced in the incinerator bottom ash and incinerator bottom ash/fly ash mixture melting tests were tested to confirm their properties.

Table 8 Form analysis results of collected dust by X-ray diffraction

	Compound form of element
Compounds highly likely to be present	NaCl,KCl,PbS,ZnS
Compounds likely to be present	ZnS,SiCl4,FeS,CaO

Table 9 Slag leaching test results

	Incinerator bottom ash mixed with 15% fly ash	Incinerator bottom ash mixed with 30% fly ash	Lower limit
Pb	ND	ND	0.01
Cd	ND	ND	0.001
Cr^{6+}	ND	ND	0.04
T-Hg	ND	ND	0.0005

ND : Non-detected

Table 10 presents the general property test results of slag as fine aggregate for asphalt mixtures. Each slag type satisfies the stability standard of the Manual for Design and Construction of Asphalt Pavements and the hardness criterion of Company N and is confirmed as a substitute for sand.

5.3 Recovery of heavy metals from fly ash

The incinerator bottom ash/fly ash mixture melting test results show that melting treatment increased the lead and zinc contents of the fly ash from about 0.2% and 0.5% to 5-6% and 5-8%, respectively. Recovering these heavy metals is extremely important as a means of recycling resources. Tests were conducted to verify this possibility.

The process involved is illustrated in **Fig. 6**. It consists of alkali separation and chloride volatilization from the fly ash, using an existing blast-furnace pellet plant. Pellets have the maximum limit content of zinc, sodium, potassium, and copper specified as quality constraints. Sodium and potassium, which are contained in high amounts in fly ash, are extracted in the alkali separation step. In the chloride volatilization step, the heavy metals are volatilized as chlorides from the extraction residue.

To confirm the effect of water washing in removing alkalies from the fly ash, a one-hour water extraction test was conducted under the conditions of one part fly ash to 10 parts water. About 80-90% of the sodium and potassium were extracted. The extraction residue was mixed with the pellet feed and calcium chloride, agglomerated with a small amount of water, and tested for chloride volatilization in an annular electric furnace. Over 95% of the lead and zinc were volatilized. The heavy metals dissolved in the water extract solution are also recovered and sent together with the extraction residue to the chloride volatilization step. The above-mentioned test results confirmed that a high amount of lead, zinc, and other heavy metals can be recovered from the fly ash without adversely affecting pellet quality.

6. Conclusions

To accomplish the volume reduction, harmless treatment, and recycling of incineration ash by making effective use of the incineration ash melting technology, it is important to flexibly accommodate a wide variety of feed materials and to appropriately control the properties of slag and fly ash as products from the melting furnace. The results of tests and analyses show that the high-temperature reducing atmosphere created by the combustion of coke promotes the volatilization of low-boiling point heavy metals, renders molten slag harmless, and concentrates the heavy metals in the molten fly ash. This is an extremely important finding for making effective use of the slag and for promoting the future recycling of heavy metals in fly ash.

The coke-bed melting technology is a process ideal for the issues discussed above. Two 15-t/d furnaces ordered as the first commercial incineration ash melting furnaces by Tokai City in Aichi Prefecture were completed and put into operation in November 1995. The authors will work further to popularize the coke-bed melting furnaces as one solution to the problem of municipal solid waste disposal.

Table 10 Properties of slag as asphalt aggregate

Item		Incinerator bottom ash	Incinerator bottom ash mixed with 30% fly ash	Quality standard
Specific gravity	Saturated surface-dry	2.89	2.90	
	Apparent	2.934	2.91	
	Bulk	2.868	2.89	
Water absorption (%)		0.78	0.24	
Stability (%)		1.2	2.1	≤ 12
Unit weight (t/m³)	Packing method	1.467	1.506	
	Rodding method	1.617	1.639	
Hardness (FDR)		1.507	1.529	≤ 1.6

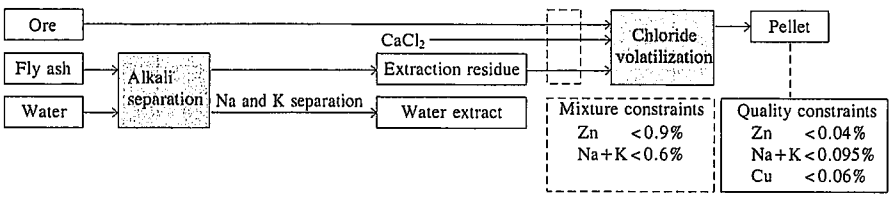

Fig. 6 Fly ash treatment process

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