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Kawasaki Steel Thermoselect Waste Gasification and Melting Process

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Synopsis:

The Thermoselect process, a completely new solid waste treatment process which achieves pollution-free recycling of municipal wastes by gasification melting technology, was developed by the Swiss company Thermoselect S.A. Kawasaki Steel introduced this world's leading technology in 1997, and built a 300t/d (150t/d ×2 lines) plant in Chiba Works, Kawasaki Steel. The Chiba Plant was put into operation in September 1999 and has completed demonstration run and treated 15000 t of municipal solid wastes. By using the plant, an industrial waste disposal business started in April 2000.

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1 Introduction

The Kawasaki Steel Thermoselect process was developed to construct a system in which the impact of waste disposal on the environment is minimized and by which even wastes that have so far been considered difficult to recycle can be recycled and used as resources¹⁾. In 1989, a Swiss company, Thermoselect S.A. started the development of the process. In 1992, it constructed a demonstration plant of an 100 t/d·furnace in Fondotoce, Italy, and brought the plant into operation. In Germany, a plant in Karlsruhe (240 t/d·furnace × 3 lines) has been operating since March 1999.

In November 1997, Kawasaki Steel concluded a contract with Thermoselect S.A. to receive this technology and constructed a plant of 150 t/d · furnace × 2 lines at Chiba Works as a demonstration plant that serves also as a commercial industrial waste treatment facility. In accordance with the Ministry and Health and Welfare's 1999 "Ordinance for the Amendment of Part of the Rules for the Enforcement of the Laws concerning the Disposal and Cleaning of Wastes (Ordinance No. 14)²¹," implemented this process is classified under incineration facilities of gasification and gas reforming method to be covered by the ordinance.

Through the use of this Chiba Plant, from September 1999 to March 2000, Kawasaki Steel conducted tests on

Chiba City municipal solid wastes (household waste, pulverized waste residue, and incinerator ash treatment) as joint research with Chiba Pref. and Chiba City, and demonstrated that stable treatment is possible on a commercial production scale. In this period, continuous operations of not less than 90 d and operations for a total of not less than 130 d were completed. Based on the results of this demonstration for municipal waste treatment, the company was awarded a Technical Inspection Certificate by the Japan Waste Management Association.

Since fiscal year 2000, the company has been commissioned to treat industrial wastes, and has been producing fuel gases from the wastes and supplying them to the Works.

This report describes the features and basics of the Kawasaki Steel Thermoselect Waste Gasification and Melting Process³⁻⁵).

2 Features and Overview of Kawasaki Steel Thermoselect Waste Gasification and Melting Process

2.1 Features of Process

The process flow of the Kawasaki Steel Thermoselect process is shown in **Fig. 1**. The features of this process are summarized as follows.

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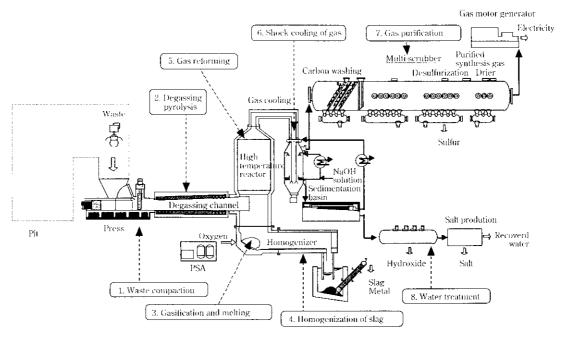


Fig. 1 Kawasaki Steel Thermoselect process

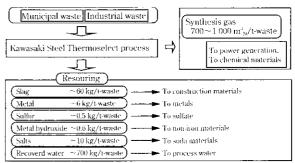
(1) Suppression of Generation of Dioxins

In conventional incincration plants, waste is burned and dioxins contained in the exhaust gas are removed after the recovery of heat. In contrast, in the Kawasaki Steel Thermoselect process, waste is pyrolyzed and melted at high temperatures and organic substances are sufficiently decomposed. At the same time, the gas generated by pyrolysis is kept at high temperatures of approximately 1 200°C then reformed. After that, it is rapidly cooled to under 70°C, thereby keeping the generation of dioxins to a minimum and recovering the gas as a fuel. During the treatment, useful by-products such as metal hydroxides can be recovered without generating fly ash, which is a difficult-to-treat residual.

It is possible to lower the dioxin concentration of the recovered fuel gas to a minimum value. The dioxin concentration of exhaust gas after power generation using the recovered gas is much lower than 0.1 ng-TEQ/m³_N, which is the new regulation set by the Ministry of Health and Welfare, and is not more than 1/100 of the regulatory standard value for exhaust gas after gas power generation using the recovered gas.^{6,7)}

(2) Complete Resource Recycling from Waste

In this process, waste is converted to purified gas, slag, metals, metal hydroxides, sulfur, mixed salt and reusable water, and almost complete resource recycling is achieved (Fig. 2). Slag can be used as construction materials such as roadbed material, metals and metal hydroxides as raw materials for refining nonferrous metals, and sulfur and mixed salt can be used as raw materials in the chemical industry. Further, reusable water is used as the process cooling



Quantities are based on the typical value for Japanese municipal waste.

Fig. 2 Resourcing of by-products

water.

(3) Clean Gas Recovery by Gas Cracking

In this process, with the gasification and high-temperature reforming of waste, energy is converted to a very clean combustible gas equivalent to natural gas and is recovered (gasification and gas reforming²). This purified gas, which is mainly composed of H₂ and CO, can be used not only as a fuel for high-efficiency gas power generation and for industrial use, but also as a chemical raw material for the synthesis of methanol, alcohol, acetic acid, ammonia, etc.

In the case where this synthesis gas is used as a fuel, there is little production of toxic substances such as HCl and SO_X in the combustion exhaust gas and the generation of NO_X can also be suppressed. For this reason, a large stack becomes unnecessary. In the cases where the synthesis gas is used as a fuel for power generation, an optimum method of power generation suited to the scale of equipment, site conditions can be selected from power generation using a

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gas motor, power generation using fuel cells. Power generation using fuel cells, in particular, generates little NO_X and the effect on the environment can be minimized.

(4) Space Savings and Cost Minimization

There are several reasons for the compactness. First, the degassing channel and the high temperature reactor are integrally manufactured, and a large stack is not necessary. Furthermore, pure oxygen is used for gasification, and the gas is purified before using the gas for combustion, which can reduce the volume of the gas for treatment to 1/6 or less of the exhaust gas volume of an ordinary incinerator. Therefore, the plant is compact and the construction space can be reduced to about 70% in comparison with the conventional incineration plus ash melting process. Furthermore, the melting treatment by use of the energy reclaimed from waste enables running costs to be reduced compared to the conventional incineration plus ash melting process.

2.2 Outline of Process

This process comprises the following four steps:

- (1) Press and degassing channel ((a)waste compaction, (b) drying and pyrolysis)
- (2) High-temperature reactor and homogenizer ((c) gasification and melting, (d) homogenization of slag, (e) gas cracking)
- (3) Gas purification ((f) rapid gas cooling (shock cooling, acid washing and alkali washing), (g) gas purification (dedusting, desulfurization and dehumidification))
- (4) Water treatment ((h) water treatment and salt production)
- (1) Press and Degassing Channel
 - (a) First, waste is compacted to approximately 1/5 of the initial volume by means of a press. This makes the distribution of moisture in waste uniform and removes air, thus improves the degassing efficiency.
 - (b) Next, the compacted waste is degassed (evaporation of moisture, generation of volatile matter by pyrolysis) in the degassing channel, which is an indirect heating furnace. It is further pyrolyzed by the radiation heat from the high-temperature reactor, etc. Examples of pyrolysis reactions of the hydrocarbons and cellulose contained in the waste are shown below, and pyrolysis carbon is obtained through these reactions:

$$C_nH_m \rightarrow xCH_4 + yH_2 + zC \cdots (1)$$

 $3C_6H_{10}O_5 \rightarrow 8 H_2O + C_6H_8O + 2CO_2 + 2CO + CH_4 + H_2 + 7C \cdots (2)$

- (2) High-temperature Reactor and Homogenizer
 - (c) The gas generated in the degassing channel flows into the high-temperature reactor. Pyrolyzed substances are pushed out by charged new compacted waste and accumulate in the lower part of the high-

temperature reactor. Carbons in the pyrolyzed substances react with oxygen blown at the bottom of the reactor, leading to the maximum temperature of about 2 000°C at the center. The extremely high temperature allow metals and ash component in the waste melt in the reactor.

$$C + O_2 \leftrightarrows CO_2 + \Delta Q \cdots \cdots (3)$$

$$C + 1/2O_2 \Rightarrow CO + \Delta Q \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (4)$$

The carbon remaining in the lower part of the high-temperature reactor and O₂ undergo an exothermic reaction to form CO₂. The CO₂ thus produced is reduced to CO while it passes through the pyrolyzed substances containing carbon.

$$C + CO_2 \rightleftharpoons 2CO - \Delta Q \cdots (5)$$

When excessive high-temperature steam molecules are present, a reaction proceeds to form combustable gases. In this case, carbon and water are converted to CO and H_2 .

$$C + H_2O \rightleftharpoons CO + H_2 - \Delta Q \cdots (6)$$

Organic substances react with H₂O to form CO, H₂.

- (d) The melt flows from the high-temperature reactor into the homogenizer kept at approximately 1600°C and small amounts of carbon, etc., are gasified. Because the metal portion of the melt (metal) in the homogenizer has a high density, it segregates under the molten ash (slag). The melt flows over an overflow weir and down into a slag granulating system, where it is cooled and solidified. The mixture thus recovered is separated into slag and metal by magnetic separation.
- (e) The gas generated in the lower part of the high-temperature reactor and the pyrolysis gas generated in the degassing channel join and remain for not less than 2 s at approximately 1 200°C in the cracking section of the high-temperature reactor. Under these conditions, the tar portion, dioxins and their precursors are completely decomposed and reformed into a crude synthesis gas which contains H₂, CO, CO₂ and H₂O as main components. At temperatures of about 1 200°C, the equilibrium of Eq. (8) shifts to the right-hand side and the only trace amount of methane gas remains.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \cdots (8)$$

- (3) Gas Purification
 - (f) The crude synthesis gas cracked in the high-temperature reactor is rapidly water-cooled by the quench scrubber from approximately 1 200°C to under 70°C and the reformation of dioxins by *de novo* synthesis is prevented. After that, heavy metals are removed by acid washing and acid gas is

removed by alkali washing. Heavy-metal components such as Zn and Pb of low evaporating temperature are transformed into a gaseous state in the high-temperature reactor. The chlorine contained in the waste is present mainly as HCl in the synthesis gas. The acid water which washes the synthesis gas absorbs the HCl and heavy metal components in the gas. In this system, the chlorine portion in the waste is effectively utilized. The washing liquid is fed to a sedimentation basin, where carbon particles are removed. After indirect cooling with a heat exchanger, the washing liquid is recirculated and used again for the rapid cooling of gas. Water coming from the waste becomes excessive water in the sedimentation basin and is fed to the water treatment process, where it is treated. Examples of reaction in the acid washing system are shown below:

$$Zn + 2HCl \rightarrow H_2 + ZnCl_2 \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (9)$$

$$Pb + 2HCl \rightarrow H_2 + PbCl_2 \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (10)$$

Owing to this acid washing, fly ash is not generated in this process. The synthesis gas washed in the acid is then washed in an alkaline liquid and acid gases such as hydrogen chloride are neutralized and removed.

$$HCl + NaOH \rightarrow NaCl + H_2O \cdot \cdot \cdot \cdot \cdot (11)$$

The NaCl thus generated is eventually recovered as mixed salt in the salt production system.

- (g) Furthermore, the dedusting, desulfurization, and drying of the gas are conducted and a clean fuel gas (purified synthesis gas) is finally obtained.
- (4) Water Treatment and Salt Production System
 - (h) The H₂O gas generated in the high-temperature reactor condenses in the gas rapid cooling and purification steps, and all the heavy metals and chroline that are contained in the exhaust gas as fly ash in the conventional incineration system, move into the washing water. For this reason, fly ash is not generated, and the water contains metals such as Fe, Zn, Pb, Na and K. However, the metals are recovered as useful substances such as hydroxides and mixed salt in the water treatment process. Because the Chiba Plant is situated in a coastal region, it has no salt production system. However, the water is subjected to ion exchange that makes it capable of being discharged into the sewer system. In a standard equipment makeup (as in the Fondotoce and Karlsruhe plants), the installation of salt production enables water having the quality that permits reuse as the process water for cooling and mixed salt to be obtained, thus providing a closed system.

2.3 Mechanism for Suppressing the Generation of Dioxins

In the conventional incineration plus ash melting

equipment, reductions in the concentrations of dioxins at the exit of an incinerator have been attempted by improving the combustion portion, improving three T's (combustion temperature, residence time of burned substances, and turbulence, i.e., the mixed condition of air and burned substances), etc.⁸¹.

However, with the conventional system it is impossible to prevent the reformation of dioxins, because heat is recovered by a steam boiler and hence rapid cooling cannot be performed. There must be a low-temperature bag filter to remove dioxins. Exhaust gas is then reheated and discharged to the air after reducing dioxins in this manner. Fly ash captured in the bag filter contains large quantities of dioxins that had reformed in the steam boiler. Although it is necessary to decompose this fly ash by melting it, fly ash is also generated from ash melting equipment and this fly ash from melting furnaces also contains dioxins.

In general, it is said that the dioxins will reform under the following conditions:

- (1) Presence of precursors of dioxins (example, aromatic compounds such as benzene)
- (2) Residence time at *de novo* synthesis temperatures (example, 200–500°C)
- (3) Presence of *de novo* synthesis catalyzers (Cu compounds)
- (4) Presence of oxygen gas
- (5) Presence of gases containing chlorine
- In the Thermoselect process, reformation conditions (1) to (4) are avoided. In other words, the reformation of dioxins is prevented for the following reasons:
- (1) The precursors of dioxins are almost all decomposed in the high-temperature reactor.
- (2) The residence time at *de novo* synthesis temperatures is extremely short (not more than 0.1 s) because of the rapid cooling system.
- (3) Cu compounds, etc. that act as *de novo* catalyzers are melted in the high-temperature reactor in a reducing atmosphere and are discharged to outside the system. Therefore, there are few such compounds in the cooling process.
- (4) Oxygen is not contained in the crude synthesis gas.

3 Results of Demonstration Tests at the Chiba Plant

3.1 Results of Treatment

From September 9, 1999 to March 7, 2000, the plant with a treatment capacity of 150 t/d furnace × 2 lines constructed at Chiba Works, treated approximately 15 000 t of municipal solid waste. In this period, continuous operations for 30 d and a total of not less than 130 d were completed for one furnace. Continuous operations for not less than 90 d were also conducted and it was demonstrated that the plant can be operated in a stable manner on a commercial scale⁹⁾. The composition of the municipal solid waste (combustible waste) is shown

Table 1 Characteristics of combustible waste

F			Minimum	Maximum	Average
3 components	Moisture content	(%)	37.8	55.5	47.7
	Ash content	(%)	4.2	9.2	6.7
	Volatile solid content		38.4	57.2	45.6
Measured lower hea	at value (k	J/kg)	6 400	12 500	8 500

Table 2 Characteristics of synthesis gas (at the Chiba Plant)

Component	<u> </u>	Concentration
CO	(%)	32.5
H_2	(%)	30.7
CO_2	(%)	33.8
N_2	(%)	2.3
Dioxins	(ng-TEQ/m³)	0.00039
Dioxins (O ₃ : 12%)	(ng-TEQ/m³)	0.000 09

Table 3 Leaching test of slag (at the Chiba Plant)

Items	Slag (mg/ℓ)	Soil standard (mg/ℓ)
Total-Hg	< 0.000 5	≦ 0.000 5
Cd	< 0.01	≨ 0.01
Pb	< 0.01	≤ 0.01
Crit	< 0.05	≦ 0.05
As 1	< 0.01	≦ 0.01
Se	< 0.01	≤ 0.01

in Table 1.

An example of recovered fuel gas (purified synthetic gas) is shown in **Table 2**. The fuel gas containing H₂ and CO as main components was fed into a by-product gas pipe at Chiba Works where the demonstration plant is situated and was eventually used as an industrial fuel in the power generation equipment, etc. at the Works. The dioxin content of the fuel gas was 0.000 39 ng-TEQ/m³_N (0.000 09 ng-TEQ/m³_N, O₂: 12% after conversion¹⁰). This value is not more than 1/1 000 of 0.1 ng-TEQ/m³_N (O₂: 12% after conversion¹⁰), which is the regulatory standard value set by the Ministry of Health and Welfare.

3.2 Some Properties of Recovered Substances

As shown in **Table 3**, the slag obtained in the Chiba Plant meets the elution standard contained in the "Guidelines for the Recycling of Melted Solid Matter

from Municipal Waste¹¹, set by the Ministry of Health and Welfare. The slag is used in asphalt concrete, roadbed materials, etc. as primary products and in street drains, heat insulators and wall materials as secondary products, and a follow-up survey of temporal changes is at present being conducted.

The principal metal component is iron and contains high concentrations of copper. Therefore, with some copper contents it is possible to use the metal as a raw material for nonferrous metal refining. In the demonstration conducted using combustible waste from Chiba City, the metal contained 17.5% copper on average and was therefore used as a raw material for copper refining.

Metal hydroxides contain not less than 30 - 40% zinc (average: 39.6%) on a dry basis and can be effectively used as a raw material for nonferrous metal refining. Furthermore, because the sulfur portion contains 67.8% sulfur on average, the recovered sulfur portion was used as a raw material for sulfuric acid.

Table 4 shows the dioxin content of by-products in the Chiba Plant and their total emission. The dioxin content of the treated water is 0.01 pg-TEQ/ℓ, which is lower than 1 pg-TEQ/ℓ — the regulatory value set by the Standards for Water Pollution by Dioxins in Japan. The dioxin content of the purified gas is also lower than 0.6 pg-TEQ/m³— the regulatory value set by the Standards for Ambient Air Pollution in Japan. Furthermore, the dioxin content of the slag, sulfur and metal hydroxides is lower than 1 000 pg-TEQ/g— the regulatory value of Standards for Soil Pollution by Dioxins¹².

The total emission of dioxins in the by-products in the Chiba Plant is about $0.000 \, 69 \, \mu g$ -TEQ/t-waste. This value is much lower than the $5 \, \mu g$ -TEQ/t-waste^[3] which is estimated to be achievable with conventional incineration technology. At present, it is said that the content of dioxins contained in Japanese municipal solid waste is about $10 \, \mu g$ -TEQ/t-waste^[4] and it was demonstrated that this process is capable of strongly decomposing dioxins (Fig. 3).

Table 4 Total dioxins emitted (at the Chiba Plant)

By-products	Dioxins contents	Recovered quantities	Dioxins output (ug-TEQ/t-waste)
Synthesis gas	0.00039 ng/TEQ/ni _N	722 m³ _N /t-waste	0.000 28
Slag	0.000 7 ng-TEQ/kg dix	62.5 kg/t-waste	0.000 04
Sulfur	0.35 ng-TEQ/kg day	0.52 kg/t-waste	0.000 18
Metal hydroxide	0.29 ng-TEQ/kg do	0.63 kg/t-waste	0.00018
Recovered water	0.000 01 ng-TEQ/ℓ	680 ℓ/t-waste	0.000 01
	Total dioxins emitted		0,000 69

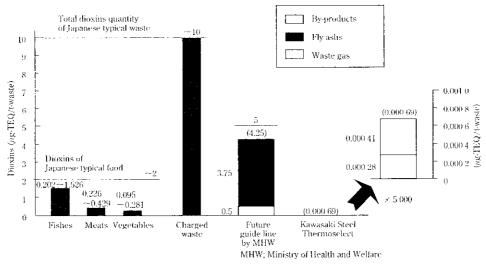


Fig. 3 Resolution property for dioxins by Kawasaki Steel Thermoselect process

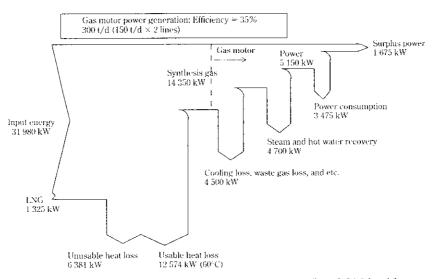


Fig. 4 Energy balance (waste caloritic value 9.2 MJ/kg (2 200 kcal/kg))

3.3 Example of Heat Balance

From the heat loss obtained in the demonstration experiment, heat balance was estimated for a standard equipment make-up of 150 t/d·furnace × 2 lines. The lower calorific value of waste was assumed to be 2 200 kcal/kg (9.2 MJ/kg) and it was assumed that power is obtained by a gas motor generator and is consumed in the oxygen production equipment and the plant. An example of heat balance is shown in Fig. 4. When the plant has a 300 t/d treatment scale, both surplus power and, a large amount of excess heat are generated.

4 Conclusion

Through the use of the plant with a treatment capacity of $150 \text{ t/d} \cdot \text{furnace} \times 2 \text{ lines}$ constructed at Kawasaki

Steel's Chiba Works, continuous operations of not less than 90 d and operations for a total of not less than 130 d were completed in fiscal year 1999 with cooperation from Chiba Pref. and Chiba City for the demonstration prescribed in the "Guideline for Waste Disposal Performance." This was the first demonstration in Japan as municipal solid waste treatment in melting equipment by gasification and gas reforming on a commercial production basis (150 t/d·furnace). It was demonstrated that this process can minimize emissions of dioxins to outside the system and almost completely recycle resources from wastes.

In fiscal year 2000 at this plant within Chiba Works, the company started to produce a fuel gas from the consigned industrial waste and utilizing the gas as a fuel for power generation at Chiba Works, etc. (the company had already acquired official authorization based on the stip-

ulations under Clause 1, Article 8 of the Law concerning Special Measures for the Promotion of Utilization of New Energy). The authors believe that the technology of this process can play an important role in a waste-recycling society which does not rely on final disposal sites.

The authors would like to extend their sincere thanks to Chiba Pref. and Chiba City for their great support in conducting the demonstrations of the gasification and melting furnaces using the Kawasaki Steel Thermoselect process.

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