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Vitrification of Simulated Combustible Dry Active Wastes in a Pilot Facility

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Abstract

In order to evaluate and finally optimize the vitrification condition for combustible dry active waste (DAW), dust and gas generation characteristics were investigated for PE, cellulose, and mixed waste. Tests were conducted by varying the operation variables such as melter configuration, excess oxygen amount, and waste feeding rate. Results showed that dust generation characteristics were affected by the operation parameters and the melter's configuration is the dominant one. For all tested DAWs, dust generation was reduced by increasing the waste feeding rate and the excessive oxygen amount in the melter. Among waste types, dust amount was decreased by the order of mixed wastes, PE, and cellulose. Other parameters such as temperature variation and operation time have also affected the dust generation. The optimum condition for the DAW vitrification was determined as the melter's configuration equipped for minimizing the waste dispersion with 20 kg/h of waste feeding rate and 100% of excessive oxygen supply. CO gas concentration in the off-gas was immediately influenced by the combustion state in the melter, but showed similar trend as the dust generation. For the NOx production during the vitrification process, thermal NOx, which is generated from the Post Combustion Chamber (PCC), rather than fuel NOx was assumed to be dominant. The gas cleaning of efficiencies of the PCC, wet scrubber, and Selective Catalytic Reduction system (SCR) were found to be high enough to keep the concentration of pollutants (CO, NOx, SOx, HCl) in the stack below their relevant emission limits.

Key Words : vitrification, dry active waste, dust generation ratio, off-gas, cold crucible melter

1. Introduction

Pilot scale vitrification facility was established by NETEC (Nuclear Environment Technology Institute)/KEPCO to treat low- and intermediate-level radioactive wastes (LILWs) from nuclear power plants. A series of pilot tests has been conducted with simulated wastes to produce design data for the establishment of a commercial plant.

In our vitrification process, organic wastes including ion exchange resin and combustible dry active waste (DAW) are combusted and vitrified in a Cold Crucible Melter (CCM) and non-combustible wastes are treated by a Plasma Torch. Through the vitrfication, organic bulk wastes are converted to an stable glass form suitable for safe disposal. Regarding the environmental and economical aspects as well as the safety of the process, optimizing the vitrification conditions in the melter will be the essential matter because it is the main source of the secondary wastes, hazardous gases and a waste glass. Adjustable parameters which may affect the vitrification condition include melter configuration, waste feeding rate, melter temperature, negative pressure, oxidative condition, etc.

During the operation of the melter, airborne radionuclides, aerosols and hazardous gases are generated and would be dispersed to the environment unless appropriate off-gas treatment systems (OGTS) have been established. This system is important, as the OGTS is the ultimate barrier to the emission of radioactivity to the atmosphere. Therefore, evaluating the performance and finding the optimum configuration of the OGTS will be main purpose to be accomplished in the pilot scale tests. In addition, operational experience with the pilot plant leads to technical solutions of problems such as equipment life time and reliability, maintenance, and corrosion of components.

Among LILWs, DAW represents about 41 % of the total waste volume and is composed of various materials such as paper, clothes, plastics, and so on. Their vitrification characteristics are varied depending on the physical and chemical properties of treated material. Therefore, DAW tests were performed in the pilot plant mainly focused on the optimization of the vitrification condition and the evaluation of the performance of the OGTS. In this paper, characteristics of the particulate and gas generation were evaluated on the operating conditions and the gas cleaning efficiencies of the OGTS were analyzed.

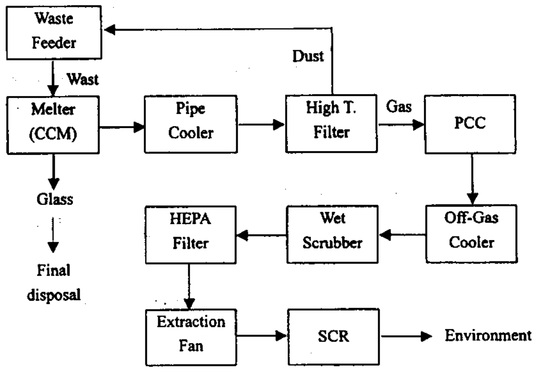

Fig. 1. A Schematic Diagram of the Pilot Scale Vitrification Process

2. Experimental

2.1. Vitrification Process

NETEC's vitrification process with a CCM is to incinerate and vitrify combustible low-level wastes in a single operation: waste is combusted and the remained ash is vitrified simultaneously in a melter. The induced current created by the High Frequency Generator heats the CCM. The melter employs oxygen/air bubbling to promote mixing and to increase the melting rate. The top of the melter is equipped with a waste feeding pipe in the center and six oxygen injectors surrounding the waste feeding pipe.

DAWs are cut into 5×5 mm of nominal size by a Shredder and then fed into the CCM continuously through a screw type feeder. The gases produced by the various reactions (combustion, pyrolysis, oxidative pyrolysis, etc.) in

Table 1. Physical and Chemical Characteristics of DAW [2]

Waste	Composition (wt%)	Ash content (wt%)	Heat of combustion (kcal/kg)	Major elements
Cellulose	47.4	0.3 ~ 0.5	~3900	C, H, O
PVC	18.6	6.8	4300	C, H, Cl
PE	14.5	0.4	11000	C, H
Rubber	10.7	2.4	10700	C, H
Others	8.8	-	-	-
Average composition	100	~1.9	~5900	-

the melter are drawn to OGTS and cleaned by several steps as shown in Fig. 1.

At first, particles included in the gas flow are removed in the High Temperature Filters (HTF). The main function of it is to protect the following system from the radioactive contamination by the dust deposition. The periodical air pulse declogs the accumulated dusts on the outside surface of the filters with a 2 bar pressure. The dusts are recovered in the drum of the HTF bottom and then recycled into the vitrification process. A Post Combustion Chamber (PCC) is installed downstream of the HTF. Temperature of the PCC is maintained at 1100℃ to completely oxidize the products of incomplete combustion and destroy dioxins. In general incinerators, if there is enough air and the burning temperature is above 950℃, all dioxins and other organic stuff are effectively destroyed[1]. Off-gases from the PCC are cooled below 500℃ in the Off-Gas Cooler (OGC). The following Jet and Pack Scrubbers cool the gas temperature and absorb the acid gases such as HCl and SOx by spraying the NaOH solution. The pH of the scrubbing solution is maintained about 7 ~ 10. After the scrubber, the gases pass through a HEPA filter in which any remaining radioactive aerosols are trapped. The gases are heated up then to about 300℃ and enter the DeNOx system (SCR ; Selective Catalytic Reduction system) in which NOx and NH_3 react catalytically to nitrogen and water. Finally, gases are released to stack, where CO, HCl, SOx, O_2, and NOx concentrations were monitored by the on-line Continuous Emission Monitoring System (CEMS). Important process parameters such as gas flowrate, temperature, and pressure are measured by on-line and the values are recorded every 10 seconds.

2.2. Waste

Material composition of DAW and the characteristics of each material are shown in Table 1. Cellulose is the major constituent (47.4 %) of DAW and the others are PVC (18.6 %), PE (14.5 %), rubber (10.8%), etc.

Three types of wastes were tested in the pilot plant; cellulose, PE, and mixed waste (50% of cellulose, 20% of PVC, 20% of PE, and 10% of rubber). The composition of the mixed waste was determined on the basis of average material composition data in Table 1[2].

2.3. Operation Parameters

In order to optimize the DAW vitrification process, three operation parameters were selected: configuration of the melter, wastes feeding rate, and excessive oxygen amount. Detailed operation conditions are indicated in Table 2. Pilot tests were performed at various conditions combining these three operation

Table 2. Operation Parameters for the DAW Vitrification

Waste	Parameter	Cond. 1	Cond. 2	Cond. 3	Cond 4	Cond. 5	Cond. 6
PE	Feeding rate (kg/h)	5	10	10	10	15	20
	Excess O_2 (%)	70	70	100	100	100	100
	CCM configuration	Type I : High waste feeding pipe Low oxygen injectors			Type III : Med. waste feeding pipe High oxygen injectors		
Cellulose	Feeding rate (kg/h)	5	10	15	20	-	-
	Excess O_2 (%)	100	100	100	100	-	-
	CCM configuration	Type II : Low waste feeding pipe Low oxygen injectors				-	-
Mixed Waste	Feeding rate (kg/h)	10	15	20	20	20	-
	Excess O_2 (%)	100	100	100	70	50	-
	CCM configuration	Type III : Medium waste feeding pipe High oxygen injectors					-

parameters. Operation time for each condition was about 1 to 3 hours.

2.4. Analysis

Dust In order to evaluate the dust amount, dust concentration was measured at an outlet of the CCM according to the Korean Standard Sampling and Analysis Methods. This method is to collect particulate at a filter in the sampling equipment by the isokinetic off-gas sampling. The dust collected at the bottom drum of the HTF was also used for the analysis of the dust generation characteristics. As the air pulse clear clogged dusts in the HTF at a constant frequency, mass of the collected dust can give information about the dust generation amount. The dust deposited onto the internal surface of the Pipe Cooler and escaped from the HTF was ignored from the consideration because the accumulated amount was not so significant and the HTF has 99.99 % of removal efficiency for 1-micrometer particle.

The weight of the dust collected in the HTF drum was measured with a time interval of about one-hour. And it was normalized for each condition in order to exclude the effects of waste feeding rate and feeding time. That is, total dust amount was divided by waste feeding rate and feeding time. It was called here as "dust generation ratio" of which unit is 'g/kg'. It implies the ratio of the generated dust weight to the supplied waste weight. For the compositional analysis of dust, ICP-AES and CHNS analyzer were used.

Off-Gas Gas concentration was analyzed using a

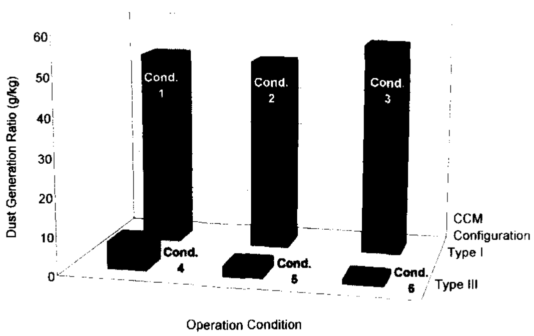

Fig. 2. Dust Generation Ratios on the Operating Conditions for PE Waste Vitrification

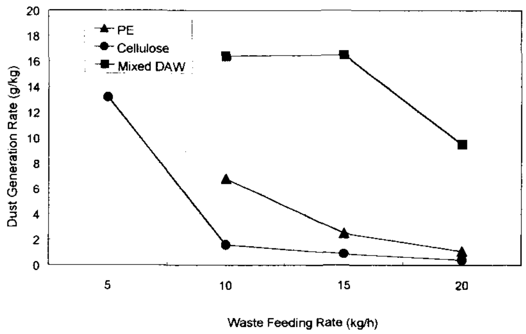

Fig. 3. Dust Generation Ratios for Three Waste Types on the Waste Feeding Rates

portable gas analyzer (PGA) for NOx, SOx, and CO gases. Also, NOx analyzers were installed at the inlet pipe of SCR and stack and the concentration was measured by on-line.

3. Results and Discussion

3.1. Dust Generation

Vitrification tests for PE waste were carried out for six operating conditions by varying three parameters; CCM configuration, waste feeding rate, and excessive oxygen amount. Fig. 2 shows the dust generation ratios for each operating condition. A remarkable difference was found in the results between two groups; condition 1/2/3 and condition 4/5/6. The first group, which was operated at melter's configuration type I, produced about 10 times more dust than those of the second group operated at configuration III. It implies that melter's configuration is the most dominant parameter to influence the combustion condition inside the melter. Configuration I type of the melter was equipped with a higher waste feeder and the lower oxygen injectors than that of configuration III. The reason why the configuration I condition generates more dust is judged that shredded PE with a low bulk-density is more easily blown off by the flow caused by oxygen injection flow and extraction fan force. That is, the effects of off-gas and oxygen flows on waste dispersion may be more vehement in configuration I because the distance between the injector outlet and accumulated waste surface is shorter than that of configuration III. Consequently, it may be difficult for wastes to be stably accumulated on the molten glass surface and to have a sufficient retention time for a complete oxidation in the configuration I condition. It is assumed that oxygen flow induce some disturbance in the combustion process inside the CCM in the configuration I condition.

At the same CCM configuration type I, dust generation ratios were not changed significantly by the waste feeding rates (Cond. 1, 2 in Fig. 2). On the other hand, as shown in Cond. 4/5/6 in the Fig. 2, the dust generation ratios decreased with the increase of waste feeding rate in the configuration III. Therefore, it is thought that the fed waste is stably accumulated on the glass surface as the waste feeding rate increases, and then, the thick layer of accumulated waste blocks the escape of the particulates to the OGTS penerating through the layer. Mason in VECTRA Technologies, Inc. reported that deep waste bed on top of the glass functioned as a cold-cap to efficiently remove particulate and condense volatile radionuclides and heavy metals by reincorporating them into the glass[3].

Carbon contents in dusts also indicated the combustion efficiency. HTF ash were containing about 75 % of carbon when the test was performed at the CCM configuration type I, whereas carbon contents were reduced to 14~19 % in the configuration III.

Fig. 3 shows the dust generation ratios on the waste feeding rates for PE, cellulose, and mixed waste. All tests were carried out at the 100 % of excessive oxygen condition. The melter was operated at the configuration III for PE and mixed waste and with the configuration II for cellulose waste. A similar trend was observed on the relationship between the dust generation ratio and the waste feeding rate irrespective of waste types: dust generation ratio decreased as the waste feeding rate increased.

However, there was a significant difference depending on the waste types. While the mixed waste was treated, produced dust amount was much larger than the case of PE and cellulose. Mixed waste contains 20 % of PVC and 10 % of rubber. It was experimentally measured that ash contents were 6.8 % for PVC and 2.4 % for rubber, while those of PE and cellulose were 0.3 ~ 0.5 % [2].

The major elements composing the ash were analyzed to be B, Na, Si, and C, which were common in all types of waste ashes. However, the mixed waste ash contained the significant amount of metal and inorganic components such as Pb and Zn. They are known to be the components of specific additives (plasticizer, filler, and pigment, etc.) of PVC and rubber[4]. The additives are added during the manufacturing process for easy handling of raw material or providing specific properties of the final product. Therefore, high ash contents of PVC and rubber are assumed to be one of reasons causing the high dust

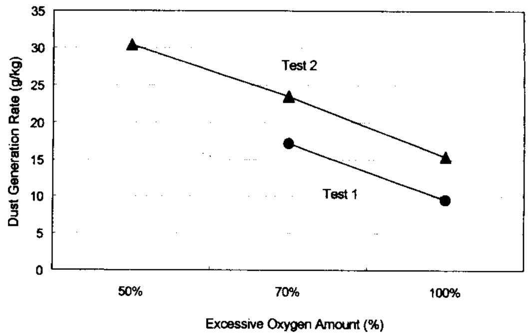

Fig. 4. Dust Generation Ratios on the Excessive Oxygen Amounts for the Mixed DAW Vitrification Tests

generation ratio.

In addition, glass temperature variation is suspected to contribute to the high dust generation ratio. It was observed in the previous tests that a sharp change in the glass temperature resulted in an instant increment of CO concentration and off-gas flowrate. It means that temperature variation is one of parameters causing the incomplete combustion. During the cellulose tests, glass temperature was maintained almost constantly (about 1200℃), while the temperature variations were 60 ~ 80℃ and 90 ~ 180℃ for PE and mixed waste, respectively. The dust generation ratio of each waste type tends to be increased with the temperature change of molten glass.

During the mixed waste treatment, dust generation ratio was investigated at the 20 kg/h of feed rate by varying the excessive oxygen amount. The results showed that dust generation ratio is inversely proportional to the excessive oxygen amount (Fig. 4). However, absolute dust generation ratios were different between the two tests while the decrease tendency on the excessive oxygen amount was similar. In the Test 1, glass bath temperature was maintained stable in the range of 1150℃ ~ 1200℃ compared to the 1090 ~ 1250℃ of the Test 2. In general, proper

Table 3. CO Concentration in the Off-Gas Measured after the HTF

Waste	Operation Condition	CO concentration (ppm) Average	Max.	CxHy (%)
PE	Cond. 1	3800~5000	8000	0.03
	Cond. 2	2000~8000	10000	~ 0.22
	Cond. 3	~ 2000	6000	
	Cond. 4	~ 200	1000	0.02
	Cond. 5	~ 200	2500	~ 0.05
	Cond. 6	~ 100	600	
Cellulose	Cond. 2	~ 50	1500	0.01
	Cond. 3	~ 50	4500	~ 0.06
	Cond. 4	~ 50	1500	
Mixed DAW	Cond. 1	~ 1000	4500	0.02
	Cond. 2	~ 800	2000	~ 0.06
	Cond. 3	< 300	-	
	Cond. 4	300 ~700	3500	0.01
	Cond. 5	< 700	-	~ 0.07

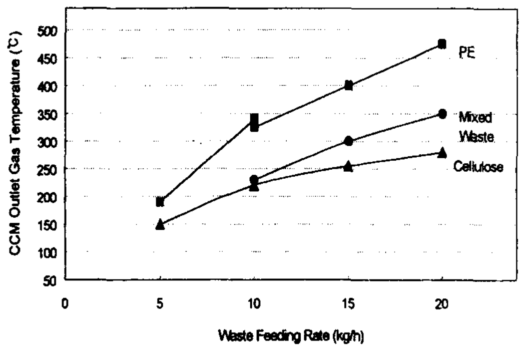

Fig. 5. Off-Gas Temperature Measured at the Outlet of CCM

oxygen amount and temperature controls are essential for suppressing the generation of hydrocarbons during thermal treatment. Ultimately, it is expected that temperature variation influenced on the dust generation ratios in the two mixed waste tests.

3.2. Performance of OGTS

Off-gas temperature measured at the outlet of the CCM was changed mainly depending on the waste types and feeding rates (Fig. 5). It was increased near to 500℃ while vitrifying PE with 20 kg/h of rate. Temperature data showed that it is almost proportional to the combustion enthalpy of each material even though the temperature of the molten glass in the CCM was changed from test to test. It is assumed that low gas temperature is caused from the water-cooling of the melter wall.

Temperature of the gas affects the design criteria and performance of the following equipments. Low gas temperature may enhance the condensation of the vapor or aerosol phase radioactive species, and, thereby, reduce the contamination of the following system and the radioactive secondary waste generation. However, it needs to be controlled to an optimum range considering the filtration efficiency of the HTF especially for volatile radionuclides, dioxin reformation, etc.

CO concentration in the off-gas from the CCM was very sensitive to the change in the glass temperature. However, the average concentration was varied by the waste types and operation parameters. As shown in Table 3, CO concentration data showed similar trends as the results of the dust generation ratios. For PE waste, CO concentration was increased up to about 10,000 ppm when operated at the configuration I condition and decreased to about 200 ppm after the CCM configuration was changed from Type I to III. Among waste types, vitrification of cellulose was favorable than the other wastes in teams of CO gas and dust production.

Although the CO concentration was increased to several thousands ppm during the waste treatment, emitted value to the environment was less than 30 ppm (emission limit : 600 ppm) and remains almost constantly regardless of the variation of the produced CO concentration. From these data, CO removal efficiency in the PCC was estimated to be over 99.8 %.

While vitrifying the mixed DAW including the 20% of PVC with a 20 kg/h of feeding rate, HCl gas concentration was estimated to be around 10000 ppm supposing that all the chlorinated gases were present as HCl form. Whereas, emitted HCl concentration to the stack was lower than 0.1 ppm through the test. It indicates that the HCl removal efficiency of the scrubber is sufficient. However, further tests are needed to evaluate the exact performance of the scrubber and to regulate the Cl_2 gas emission because the ratio of the HCl and Cl_2 concentration is varied by temperature, pressure, and the concentration of H_2O and O_2 in the gas[5].

Chlorinated gases are very corrosive to equipment, as well as produce volatile and corrosive metal chlorides. It was reported that Cs volatility was increased by the presence of chlorine[6]. Generally, maintaining the temperature below 350℃ can minimize the high temperature corrosion by acid gases and the lower temperature is limited by vapor condensation which makes more corrosive chloride ion[7]. After the PVC vitrification, pitting corrosion was examined in the inside wall of the Off Gas Cooler due to the vapor condensation. The means for solving the corrosion problem should be settled in the future. By these reasons, PVC content in the DAW will be one of important considerations in the design and operation of the commercial plant in the point of the emission regulation and the system corrosion problems.

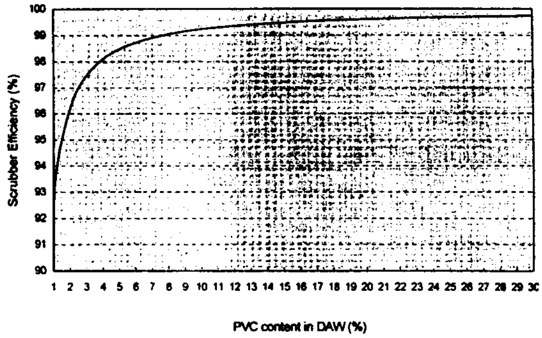

Fig. 6. HCl Removal Efficiency of the Scrubber on the PVC Content in DAW to Meet the 50 ppm of HCl Emission Limit

In order to estimate the performance criteria of the scrubber, the scrubber efficiency to meet the 50 ppm of emission limit was calculated on the PVC content in the DAW in the case of 30 kg/h of waste feed rate (Fig. 6). Based on this estimation, if we tend to treat the average composition of DAWs containing the 20 % of PVC, HCl gas removal efficiency of the scrubber should be higher than 99.6 %. Although the removal efficiency of the wet scrubber for HCl gas is known to be very high, the PVC content in the feed materials has to be controlled in the commercial system by considering the actual efficiency.

NOx data showed that the concentration was

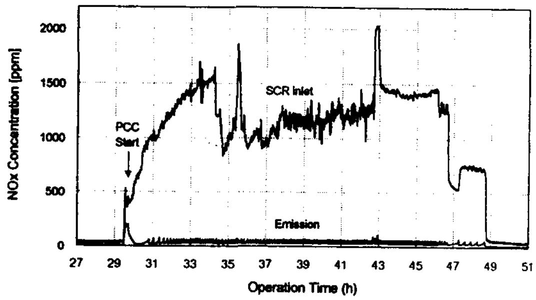

Fig. 7. NOx Concentration in the Off-Gas Analyzed at the Inlet of SCR and Stack During the PE Vitrification

not related with the operation variables such as waste type, feeding rate, etc. For all types of wastes, NOx concentration before the SCR was in the range of 500 ~ 2000 ppm. The major source of NOx generated during the vitrification were supposed to be the PCC by considering the following four results: (1) Nitrogen is not a major element composing the DAW, (2) NOx produced in the resin treatment (N content of the treated resin is about 2.7 %) was almost same as during the DAW tests, (3) when the PCC and the CCM was being operated not feeding the wastes, the concentration was similar to the data during the wastes feeding, and (4) NOx concentration was increased very sharply at the time when the PCC started heating.

It is known that thermal NOx is produced as a result of the reaction of nitrogen with the molecular oxygen over 1000℃[8]. From these results, it is assumed that PCC generates most of thermal NOx even though it destroys hydrocarbon, CO, and dioxin species. Therefore, the methods to suppress the generation of thermal NOx should be investigated because it makes possible to reduce the size of SCR and the operational cost. Reducing the air-inleakage or lowering the operation temperature of the PCC can be probable methods.

Figure 7 shows the SCR performance during the PE test. NOx removal efficiency of it was above 93% and maintains the NOx emission below the regulatory limit of 200 ppm.

4. Conclusions

The dust characteristics generated from the melter were analyzed to derive the optimum conditions for the vitrification of the DAWs by varying the three operating parameters; melter configuration (configuration I, II, III), excessive oxygen amount (50%, 70%, 100%), and waste feeding rates (5, 10, 15, 20 kg/h).

The test results showed that the dust generation characteristics have a close relationship with the operation variables. Among the tested parameters, the melter configuration was found as the dominant one to affect the DAW vitrification process. Dust generation ratio was minimized as the waste feeding rate was increased for all waste types. It implies that large amount of waste can be treated with less dust generation. There was a significant difference in the dust generation ratio depending on the waste type. The dust amount was decreased by the order of mixed wastes, PE, and cellulose. The dust generation ratio was inversely proportional to the excessive oxygen amount and minimized at the 100 % of excessive O_2 condition. Other parameters such as temperature variation and operation time have also affected the dust generation.

CO gas concentration was directly influenced by the combustion state in the melter, but showed similar trend as the dust generation ratio. On the other hand, NOx concentration was not varied depending on the operation parameters. It was assumed that thermal NOx rather than fuel NOx was dominant on the NOx generation and the PCC was the main source of the thermal NOx. The gas cleaning efficiency of the PCC, scrubber, and SCR was found to be very high and, therefore, criteria pollutants (CO, SOx, NOx, and HCl) were well below the Korean environmental regulatory limit through the tests.

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