

## **Evaluation of Off-gas Characteristics in Vitrification Process of Ion-Exchange Resin**

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### **Abstract**

The properties of off-gas generated from vitrification process of ion-exchange resin were characterized. Theoretical composition and flow rate of the off-gas were calculated based on chemical composition of resin and its burning condition inside CCM. The calculated off-gas flow rate was  $67.9\text{Nm}^3/\text{h}$  at the burning rate of  $40\text{kg}/\text{h}$ . And the composition of off-gas was evaluated as  $\text{CO}_2(41.4\%)$ , steam( $40.0\%$ ),  $\text{O}_2(13.3\%)$ ,  $\text{NO}(3.6\%)$ , and  $\text{SO}_2(1.6\%)$  in order. Then, actual flow rate and composition of off-gas were measured during pilot-scale demonstration tests and the results were compared with theoretical values. The actual flow rate of off-gas was about 1.6 times higher than theoretical one. The difference between theoretical and actual flow rates was caused by the in-leakage of air to the system, and the in-leakage rate was evaluated as  $36.3\text{Nm}^3/\text{h}$ . Because of continuous change in the combustion parameters inside CCM, during demonstration tests, the concentration of toxic gases showed wide fluctuation. However, the concentration of CO, a barometer of incompleteness of combustion inside CCM, was stabilized soon. The result showed quasi-equilibrium state was achieved two hours after feeding of resin.

**Key Words** : vitrification process, resin combustion, resin treatment, resin vitrification, off-gas characteristics, off-gas treatment

### **1. Introduction**

For the much higher volume reduction and safer treatment of low- and intermediate-level radioactive wastes, NETEC-KEPCO has developed a pilot-scale vitrification plant. A series of spent resin vitrification tests has been successfully performed in the plant. A schematic diagram of

the pilot-scale vitrification plant is shown in Fig. 1.

The pilot plant is consisted of a cold crucible melter(CCM) and an off-gas treatment system (OGTS). Simulated spent resin is introduced through central feeder to the upper chamber of CCM. The resin is thermally decomposed beneath the cold cap formed on the surface of glass melt to ash and pyrolysis gas at the

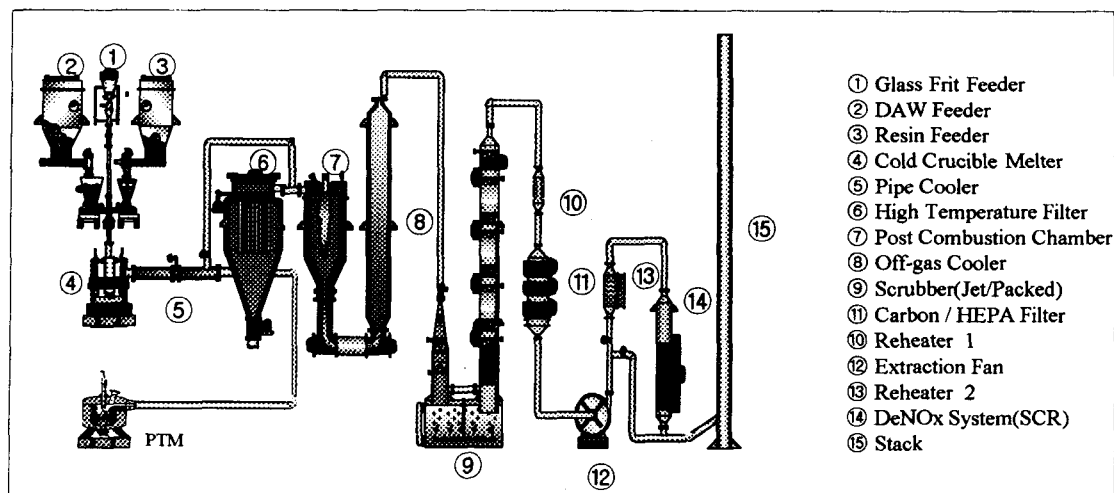


Fig. 1. Schematic Diagram of Pilot-Scale Vitrification Plant of KEPSCO-NETEC

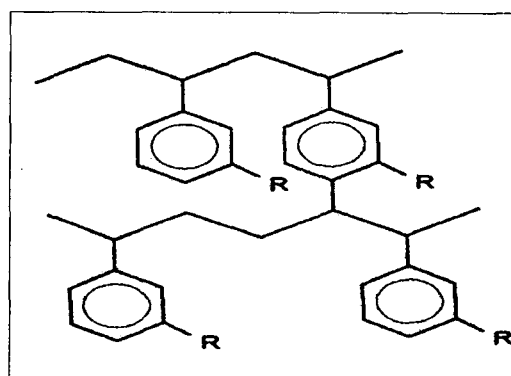
temperature range of 1150~1350°C. The residual ash is incorporated within the glass melt by forced convection of glass melt. While the decomposed gas is burnt under excess oxygen atmosphere inside CCM and discharged into the OGTS as off-gas. The OGTS is designed to treat the off-gas according to the national emission standards at stack.

In this study, the off-gas generation characteristics from resin burning process of the pilot plant were evaluated in order to verify the performance of the OGTS. And the theoretical composition and the flow rate of off-gas were calculated based on the fresh resin composition and combustion inside CCM. Then, the theoretical values were compared with the values measured during the demonstration tests.

## 2. Theoretical Characterization of Off-gas

### 2.1. Structure of Ion-Exchange Resin

Fig. 2 shows the chemical formula of ion-exchange resin commonly used in NPP. Cation



Cation Exchange Resin :  $R = SO_3^+H^+$

Anion Exchange Resin :  $R = CH_2N^+(CH_3)_3OH$

Fig. 2. Chemical Formula of Ion-Exchange Resin

and anion resins have the same chemical base structure of polystyrene DVB but the different functional groups. In the figure, the functional group, R represents sulfonic group( $-SO_3$ ) for cation exchange resin, and trimethylammonium group( $-CH_2N^+(CH_3)_3$ ) for anion exchange resin.

The spent resin generated as half and half mixture of cation resin and anion resin on the basis of ion exchange capacity in the nuclear power plants. Thus, in this study, the mixture of

**Table 1. Moisture Content in Fresh Resins**

	Resin	2h Drying	16h Drying	18h Drying	20h Drying	Remark
Fresh Resin	NRW-100(Cation)	-	57.4 wt%	-	57.5 wt%	1.8eq/g
	NRW-600(Anion)	-	58.9 w/t%	-	59.1 wt%	1.2eq/g
	NRW-36LiLC(Mixed)	-	58.4 wt%	-	58.6 wt%	Cation(40%) Anion(60%)
Simulated Resin	NRW-100/NRW-600 (50% / 50%)	54.4 wt%	-	55.5 wt%	-	0.1wt% of Co <sup>2+</sup> , Cs <sup>+</sup> , B <sup>-</sup>

fresh cation resin(NRW-100, Purolite™) and fresh anion resin(NRW-600, Purolite™) was used for the demonstration tests.

## 2.2. Moisture Content in Resin

The spent resin was introduced to CCM as wetted form. And because of it's negative effect on the OGTS, the moisture content in off-gas is very important characteristic in vitrification process. The moisture content in off-gas could be calculated based on evaluation of the moisture in the resin. In this study, ASTM D644-55 was adopted as a standard method for the measurement of moisture in the resin.

Following the standard, each 100g of the resin were sampled from the four different kinds of resins and dried for about 20 hours in oven under the temperature of 105°C. While drying, the samples were periodically taken out and weighed until their weight change is sufficiently small. Then, the moisture content in the resin was calculated base on the weight loss of the samples. The moisture contents measured in the drying test were shown in Table 1. As show in the table, the moisture contents in the resins were in between 57~59wt%. Due to the bigger granular size of cation resin, the moisture content in cation resin was a little higher than that in the anion resin. Also, the moisture content in loaded resin was

about 2~3wt% below than the others.

## 2.3. Analysis of Atomic Composition of Resin

The composition of theoretical off-gas could be simply calculated on the basis of chemical formula of resin. But because of impurities in the resin, the chemical analysis of the resin is needed also. In this study, the elemental inorganic analyzer(CE EA-1108) was utilized for the atomic analysis of the resin structure. In the analyzer, major atoms such as carbon, nitrogen, sulfur, hydrogen in the resin structure were thermally decomposed under pure oxygen atmosphere, exceptionally under nitrogen atmosphere for the oxygen, and the temperature of 1020°C. Then, the compositions of atoms were evaluated based on the each concentrations of gases analyzed by the thermal conductivity. The atomic compositions acquired by calculation and analysis are shown in Table 2, and they are well coincided each other.

## 2.4. Evaluation of Theoretical Off-gas Composition

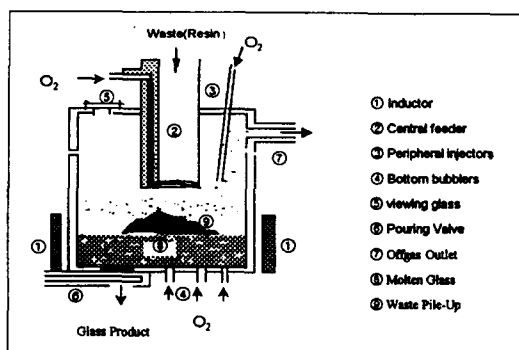
Conceptual diagram of the pyrolysis and combustion of the resin in CCM is shown in Fig. 3. In the figure, the is consisted of a lower chamber and an upper chamber. The lower

**Table 2. Atomic Composition of Fresh Resin**

		Unit : wt%						
Resin	Data	C	H	O	N	S	H <sub>2</sub> O	Total
NRW-100 (Cation Bed)	Analyzed	29.25	2.44	11	-	7.3	50	100
	Calculated	26.6	3.7	11.8	-	7.9	50	100
NRW-600 (Anion Bed)	Analyzed	39.7	4.6	3	2.7	-	50	100
	Calculated	36.8	6.15	3.75	3.3	-	50	100
NRW-36LiLC (Mixed Bed)	Analyzed	34.48	3.52	7	1.35	3.65	50	100
	Calculated	31.7	4.93	7.78	1.65	3.95	50	100

**Table 3. General Operation Conditions of CCM**

Operation Parameters	Condition	Operation Parameters	Condition
Inductor Power	80 kw/kg resin	Resin Feeding	40 kg/h
Combustion Atmosphere	125% O <sub>2</sub>	Glass Frit Feeding	4 kg/h
Combustion Temperature	> 1250 °C	Feeder gas(N <sub>2</sub> )	1.5 Nm <sup>3</sup> /h
Glass Bubbling(O <sub>2</sub> )	0.5Nm <sup>3</sup> × 4	Negative Pressure	-30 mmH <sub>2</sub> O
Viewing Glass Air(O <sub>2</sub> )	3 Nm <sup>3</sup> /h	In-leakage(Air)	< 15 Nm <sup>3</sup> /h

**Fig. 3. Conceptual Diagram of Resin Combustion in Upper Chamber of CCM**

chamber is used as a container of molten glass and the upper chamber is used as a combustion space of pyrolysis gases. The combustion of thermally decomposed gas is taken place in-between the waste pile-up and the glass melt. And the gases produced from the pyrolysis of the resin are burnt in the upper chamber under the oxygen atmosphere. Because the wetted resin was

introduced without any pre-treatment, the process of the resin burning in CCM could be explained like below sequence.

- Evaporation of water exist in the pore of the resin
- Pyrolysis of the resin structure to ash and simple pyrolysis gases
- Combustion of pyrolysis gases

Among above steps, the first two steps are endothermic reaction but the final step is exothermic reaction. These three step reactions are sensitively influenced by feed rate of resin, heating speed of CCM, negative pressure inside CCM, and configuration of oxygen supply and so on. The governing operating parameters that could influence to the composition of off-gas are summarized in Table 3. The theoretical composition of off-gas, shown in Table 4, was evaluated under assumption of ideal combustion and below parameters.

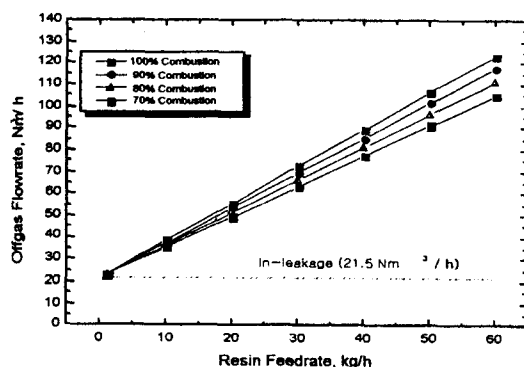
**Table 4. Theoretical Composition of Off-gas**

	CO <sub>2</sub>	NO	SO <sub>2</sub>	Steam	Excess O <sub>2</sub>	Total
Resin 20 kg/h	14.05 Nm <sup>3</sup> /h	1.23 Nm <sup>3</sup> /h	0.56 Nm <sup>3</sup> /h	13.58Nm <sup>3</sup> /h	4.52 Nm <sup>3</sup> /h	33.94 Nm <sup>3</sup> /h
Composition(%)	41.4	3.6	1.6	40.0	13.3	100

**Table 5. Test Condition of Resin in Pilot-Scale Vitrification Plant**

Test No	Resin (kg/h)	Glass Bath1) (°C)	Pressure (mmH <sub>2</sub> O)	off-gas Temp. (°C)	Glass Frit (kg/h)
NET-R01	20	1200±50	-30/-40/-50	210/180/220	-
NET-R02	20/30	1250±20	-20/-20/-20/-20/-20	225/230/190/220/265	-
NET-R03	30/20	1200±10	-30/-30	230/230	-
NET-R04	30	1420±10	-30/-30	280/275	-
NET-R06	40	1400±100	-30/-30	300/315	-
NET-R07	40	1300±100	-30/-30	300/380	4
NET-R08	20/40	1300±100	-30/-30/-30/-30	200/240/240/320	4

Note) 1. Temperature of Surface Part of the Bath.



**Fig. 4. Effect of Negative Pressure on Off-gas Flow Rate at the Resin Burning Rate of 20kg/h**

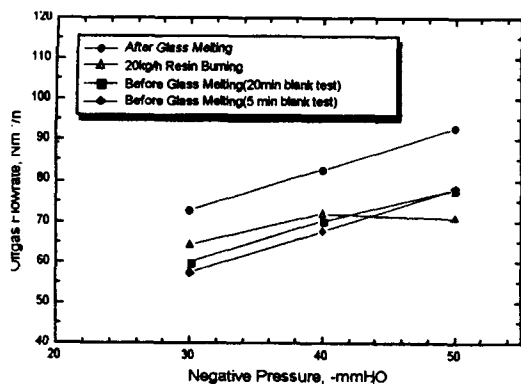
- Feed rate : 20kg/h of mixed resin
- Oxygen supply : 25% excess than stoichiometrically needed
- No retention of sulfur within glass product
- Only CO<sub>2</sub> formation from CO-CO<sub>2</sub> system
- Only NO formation from the NO-NO<sub>2</sub> system

From the Table 4, CO<sub>2</sub>(41.4 vol %) and

steam(40.0 vol %) were identified as the major compositions of off-gas. In due to the sulfur in the cation resin and the nitrogen in the anion resin, the concentrations SO<sub>x</sub>, and NO<sub>x</sub> were also very high in the theoretical composition of off-gas. However, in practical resin burning process, the volume off-gas generation could be reduced by the incomplete combustion. Therefore, the composition of off-gas could be changed a little based on the degree of incomplete combustion. Fig. 4 shows decrease of the off-gas flow rate with the increase of incompleteness of combustion.

### 3. Off-gas Characteristics from Demonstration Tests

To characterize the properties of off-gas, a series of resin burning demonstration tests was performed in the pilot plant. Table 5 shows the list of tests conducted for the demonstration of the resin burning in CCM and the major parameters setted during the tests.



**Fig. 5. Effect of Negative Pressure on Off-gas Flow Rate at the Resin Burning Rate of 20kg/h**

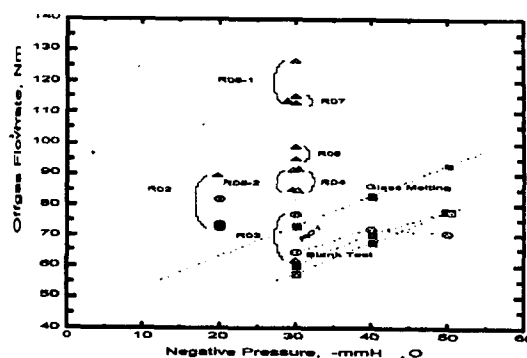
Among the off-gas characteristics, the flow rate of off-gas is the most important parameter in designing the off-gas treatment system. In this regard, the off-gas flow rate could be evaluated based on the theoretical composition of off-gas as mentioned in previous section. However, much portion of off-gas stream, called in-leakage to the system, could be evaluated only at actual tests because these gas streams have nothing to do with the resin burning. In the pilot plant, the in-leakage includes air in-leaked to the system, glass fume, air from the bubbler, air blown to looking glass, nitrogen supplied through feeder, etc.

And among the hazardous gases in off-gas, CO was selected as an indicator of the incompleteness of combustion in CCM because the concentration of CO gas represents well the degree of combustion.

### 3.1. Flow Rate of Off-gas

#### 3.1.1. Effect of Negative Pressure Inside CCM on Flow Rate of Off-gas

For the evaluation of air in-leakage, a series of

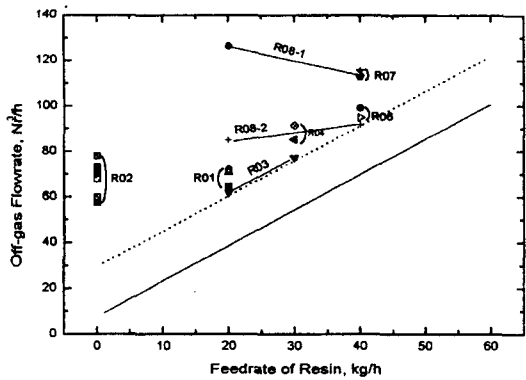


**Fig. 6. Effect of Negative Pressure on Off-gas Flow Rate Under the Condition of 20~40kg/h Resin Burning**

blank tests was performed under the negative pressure of -30, -40 and -50 mmH<sub>2</sub>O each and under without- and with-resin burning condition. The result from the blank tests is shown in Fig. 5 and Fig. 6. In Fig. 5, when negative pressure was -40mmH<sub>2</sub>O, the in-leakage rate was evaluated to be about 70Nm<sup>3</sup>/h. Because of the location of off-gas flow meter, this air in-leakage includes air in-leaked through all the front part of the process such as feeder, CCM, pipe cooler and HTF. After glass melting, in the figure, the flow rate of off-gas was increased as about 13Nm<sup>3</sup>/h more than before glass melting. This is because the increase of glass mixing influenced both to the increase of air bubbling in glass bath and to the increase of glass fume generation. In Fig. 6, the off-gas flow rates are always higher than the in-leakage, the dotted lines in the figure, along the negative pressure. In the tests, the flow rates are measured under the actual test conditions of 20~40kg/h of the resin feeding and -20~-50mmH<sub>2</sub>O of negative pressure. As shown in the figure, the increases of off-gas flow rate is proportion to the increase of negative pressure in the test range of negative pressure.

**Table 6. Evaluation of Air In-leakage to the System**

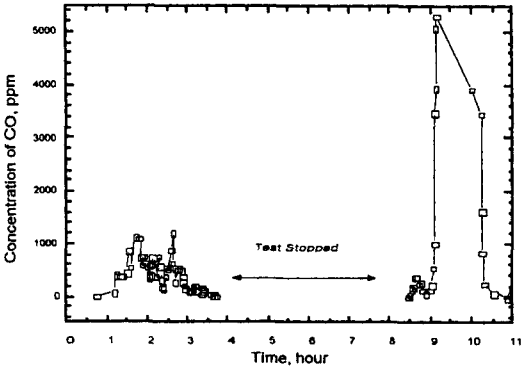
Resin Feed	off-gas Flowrate (Nm <sup>3</sup> /h)		In-leakage (Nm <sup>3</sup> /h)
	Theoretical	Test Result	
20 kg/h	33.9	61.7~81.9(mean 71.3)	37.4
30 kg/h	50.9	77.1~91.2(mean 85.7)	34.8
40 kg/h	67.9	91.6~115.1(mean 104.5)	36.6



**Fig. 7. Effect of Resin Feed Rate on Off-gas Flow Rate**

**3.1.2. Effect of Resin Feed Rate on Flow Rate of Off-gas**

In Fig. 7, the off-gas flow rates obtained from the demonstration tests were plotted again on the basis of the resin feed rate. In the figure, the dashed line is the in-leakage flow rates evaluated in previous section and the other dotted line is just connection line of all the lower flow rates at each feed rate in demonstration tests. The difference between the two lines is considered as the air in-leakage to the system at each feed rate of resin. For more understanding, the off-gas flow rates obtained at the demonstrations tests under the resin burning condition of 20 ~ 40kg/h are shown in Table 6 again. In the table, the in-leakage flow rate is appeared as about 36.3Nm<sup>3</sup>/h. Under the burning rate of 40kg/h of the resin, the off-gas from the demonstration tests



**Fig. 8. Concentration of CO in Off-gas(Test R03)**

was 91.6~115.1Nm<sup>3</sup>/h and it was 1.6 times higher than the theoretical off-gas flow rate of 68Nm<sup>3</sup>/h.

**3.2. Concentration of CO in Off-gas**

The Off-gas characteristics, including the concentration of CO, were analyzed simultaneously through the demonstration tests of Test NET-R03, Test NET-R04, Test NET-R07, and Test NET-R08.

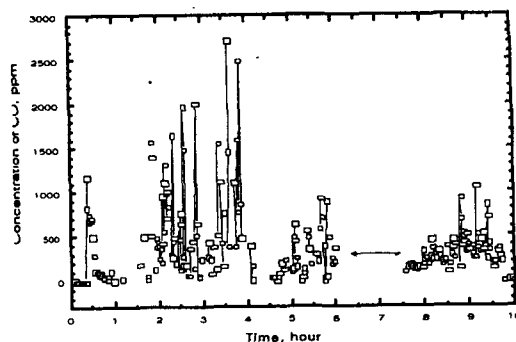
For the analysis of the concentration of the off-gas, PGA(portable gas analyzer, Greenline Mk-2) which is adopting chemical cell type sensor was utilized at the outlet of CCM.

**3.2.1. Test NET-R03**

Evaluation of the necessary time to reach steady

state of the resin burning in CCM was one of the purpose of test NET-R0<sub>3</sub>. The arrival to steady state of the burning was decided mainly by the concentration of CO at the outlet of CCM and the color of ash and dust concentration at the outlet of CCM were also considered as secondary indicators as well. Fig. 8 is showing the concentration of CO analyzed by the PGA in test NET-R0<sub>3</sub>. As shown in figure, when 20kg/h of resin is feeding, the average concentration of CO was stabilized below 1000ppm. In the first part of the test, about 1000ppm of CO peaks were appeared. Unfortunately, due to the unplanned stop of the test, only the two peak was confirmed. It took about 1.7 hour for the arrival of the first peak of CO and the period between the peaks was about one hour. In spite of lack revival, the periodical appearance and collapse of the CO peak considered as the formation and collapse of the cold cap which is a pile of the slag generated from the thermal decomposition of the resin on the surface of glass melt. Upon the assumption of continuous appearance of the CO peaks, the time to reach the steady state of burning could be evaluated as two hours conservatively. When 30kg/h of resin is burning, the concentration of CO increased to up 5200ppm. At the moment, the off-gas flow rate was 77.13Nm<sup>3</sup>/h. This is 4.72Nm<sup>3</sup>/h higher than theoretically expected value under same condition. The superficial resident time of the off-gas in CCM was to be about 7.3 sec. It was calculated based on the flow rate of off-gas and inner volume of upper chamber(about 0.2m<sup>3</sup>) of CCM. Even such a sufficient burning time and excess oxygen(25%) were applied, incomplete combustion gases was observed at the sampling point just after CCM. That could be explained as follows.

- Excess cooling by the local and momentary sensible/latent heat of water in the resin (50wt%)



**Fig. 9. Concentration of CO in Off-gas at Test NET-R04**

- Reducing atmosphere, developed local and momentary around the resin, due to the evaporation of water in the resin
- Lack of turbulence of gas inside CCM due to both the much little off-gas generation than designed and the simple shape inside CCM.

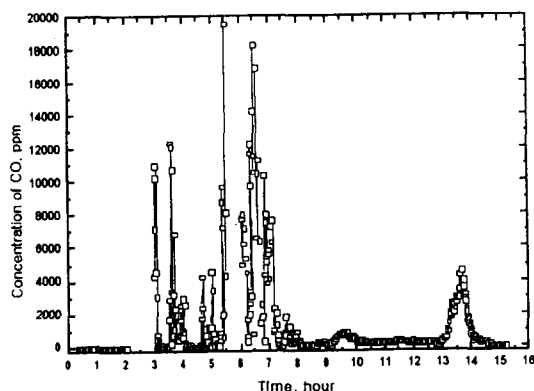
### 3.2.2. Test NET-R04

Test NET-R04 was performed to study the effect of cold cap size which is formed on the surface of melt. In this test, 30kg/h of resin was fed under -30mmH<sub>2</sub>O of negative pressure inside CCM. As shown in Fig. 9, during the test, temperature of off-gas was to be 300~315°C and flow rate of off-gas was in the range of 84~91Nm<sup>3</sup>/h. Superficial resident time of off-gas inside CCM was evaluated as about 4.0 sec. The concentration of CO was very high from the first time, but about four hours after the state of the resin burning become stabilized.

### 3.2.3. Test NET-R07

Test NET-R07 was performed to evaluate the effect of oxygen supplying configuration on combustion of the resin. Heights of the central





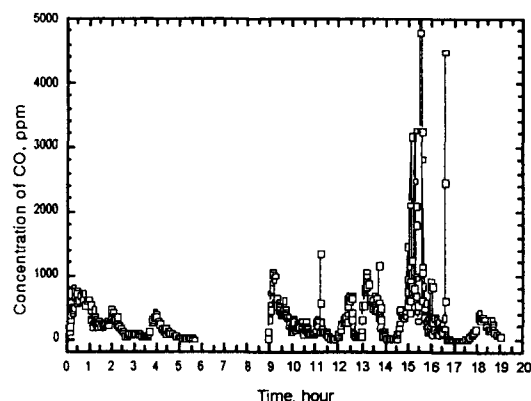
**Fig. 10. Concentration of CO in Off-gas at Test NET-R07**

feeder and 6 peripheral feeders were changed during the test. Also, the volatility behavior of radionuclides inside CCM was tested. To test the volatility of radionuclides, chloride form of inactive cesium and cobalt were loaded to the resin. A 40kg/h of the resin feeding and -30mmH<sub>2</sub>O of negative pressure inside CCM was maintained during the test.

For the test result, off-gas flow rate was reduced from 115Nm<sup>3</sup>/h of first half period of operation to 112Nm<sup>3</sup>/h of at the left operation. On the contrary, temperature of the off-gas was increased from 300°C to 380°C. Superficial resident time was calculated as 2.9~3.2sec. From the first time, as shown in Fig. 10, the concentration of CO was fluctuated sharply and the highest peak of CO was to be about 19600ppm. From this, severe incomplete combustion of resin in CCM was notified.

### 3.2.4. Test NET-R08

Test NET-R08 was carried out to test the effect of bubbling on the homogeneity of the glass melt. The effect of glass frit feeding on the volatility of Cs was evaluated also. In the middle of the test, the resin feeding was increased from 20kg/h to



**Fig. 11. Concentration of CO in Off-gas at Test NET-R08**

40kg/h. And negative pressure inside CCM was maintained as -30mmH<sub>2</sub>O. For the test result, temperature of off-gas was increased from 200°C at the first half of the test to 240°C at the second half of the test. On the contrary, off-gas flow rate was decreased from 126Nm<sup>3</sup>/h to 113Nm<sup>3</sup>/h. The off-gas generation was about 85% of the designed capacity. The superficial resident time of off-gas in CCM was about 3.6sec. In Fig. 11, the concentration of CO was stabilized to under 1000ppm at the first part of test. But in the middle of the test, CO concentration increase to 4800ppm and combustion was unstable.

## 4. Conclusions

The characteristics of off-gas of the vitrification process were evaluated through both the theoretical analysis of the chemical composition of the resin and the demonstration tests conducted in the vitrification pilot plant. From this study, below informations were acquired.

- The resin burning process was analyzed as following 3 steps
- Evaporation of water exist in the pore of the resin(endothermic reaction)
- Pyrolysis of resin structure(endothermic

reaction)

- Combustion of pyrolysis gases(endothermic reaction)
- The theoretical off-gas flow rate was evaluated to be  $67.9\text{Nm}^3/\text{h}$  at  $40\text{kg/h}$  of the resin burning in CCM.
- The composition of off-gas was evaluated in order of  $\text{CO}_2(41.4\%)$ , steam( $40.0\%$ ),  $\text{O}_2(13.3\%)$ ,  $\text{NO}(3.6\%)$ ,  $\text{SO}_2(1.6\%)$  at  $40\text{kg/h}$  of the resin burning.
- The off-gas flow rate from the demonstration tests was 1.6 times bigger than that of theoretically analyzed.
- In-leakage of the air to the system was evaluated about  $36.3\text{Nm}^3/\text{h}$  at  $20\sim 40\text{kg/h}$  of the resin burning rate.
- The concentration of CO were stabilized under 1000ppm in the normal test condition.
- In regard to the incomplete combustion of the

resin in CCM, below items were analyzed.

- Direct introducing of cool and wet resin into CCM and therefore the sensible and latent heat of water causes local and momentary excess cooling.
- The steam evaporated from the resin makes local and momentary reducing atmosphere in CCM
- Lack of turbulence inside CCM causes incomplete combustion.

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