

Pilot-scale Test for Vitrification of Simulated Ion Exchange Resin

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ABSTRACT

Vitrification pilot plant had been constructed in Taejon, Korea to overcome, in advance of the future commercial plant, any difficulties which may occur when treating various types of low-level radioactive waste (LLW) generated from nuclear power plants (NPPs) in Korea. As a part of this project, Nuclear Environment Technology Institute (NETEC) has completed its pilot-scale test for vitrification of simulated resin as well as performance test of the pilot plant. This paper presents the test results of utilizing selected glass frits to vitrify the resin by analyzing the compositional distribution in the glass material or the dust deposited on the melter wall and its downstreams. B and Na in the base glass consisting of Na, B, Al and Si were found to be selectively lost during the glass melting. In the separate phase above the glass melt surface, sodium sulfate appears to be major compound with sulfates or chlorides of potassium or lithium present, if any. Particularly, in both the dust samples deposited on the horizontal inner surface of Pipe Cooler and the dust declogged from ceramic filters, sodium and boron oxides were present in higher concentration. It showed that more boron condenses on the cooler surface of Pipe Cooler while more sodium condenses on the warmer surface of ceramic filters.

INTRODUCTION

Vitrification pilot plant had been constructed in Taejon, Korea under cooperation of Nuclear Environment Technology Institute (NETEC), SGN and Hyundai Mobis Inc. for treating various types of low-level radioactive waste (LLW) generated from nuclear power plants (NPPs) in Korea. The LLW generated from routine operation of NPPs include mainly, the DAW (combustible and non-combustible), spent resin, and evaporator bottom (borate liquid waste).

As a part of this project, NETEC has planned its pilot-scale tests using ion exchange resin as well as combustible Dry Active Waste and borate concentrates. The pilot plant will be the basis for the development and establishment of an industrial scale vitrification installation in Korea.[1] NETEC has been developing product control scheme which can maximize waste loading into final glass forms for different waste streams.

A series of the tests would focus on observation and measurement of off-gas generated during the combustion of resin. Therefore, the melter operating condition is differently setup such as the height of the oxygen feeder from the melt surface and the oxygen feeding direction and amount, until an optimum configuration of melter is reached by comparing off-gas characteristics.

As preliminary study, we focus on the compositions of glass in the melter and glassy material or the dust, which is deposited on inner wall of Pipe Cooler and retrieved from High Temperature Filter candles. Also, the entrainment and volatility of elements have been studied when vitrifying the ion exchange resin.

VITRIFICATION PROCESS

NETEC's vitrification process with a Cold Crucible Melter (CCM) is to incinerate and vitrify combustible low-level waste in a single operation: waste is combusted and the produced ash is vitrified simultaneously in a melter. The induced current created by the high frequency generator heats titanium ring immersed in the raw glass and then it melts the glass in 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 and several oxygen injectors.

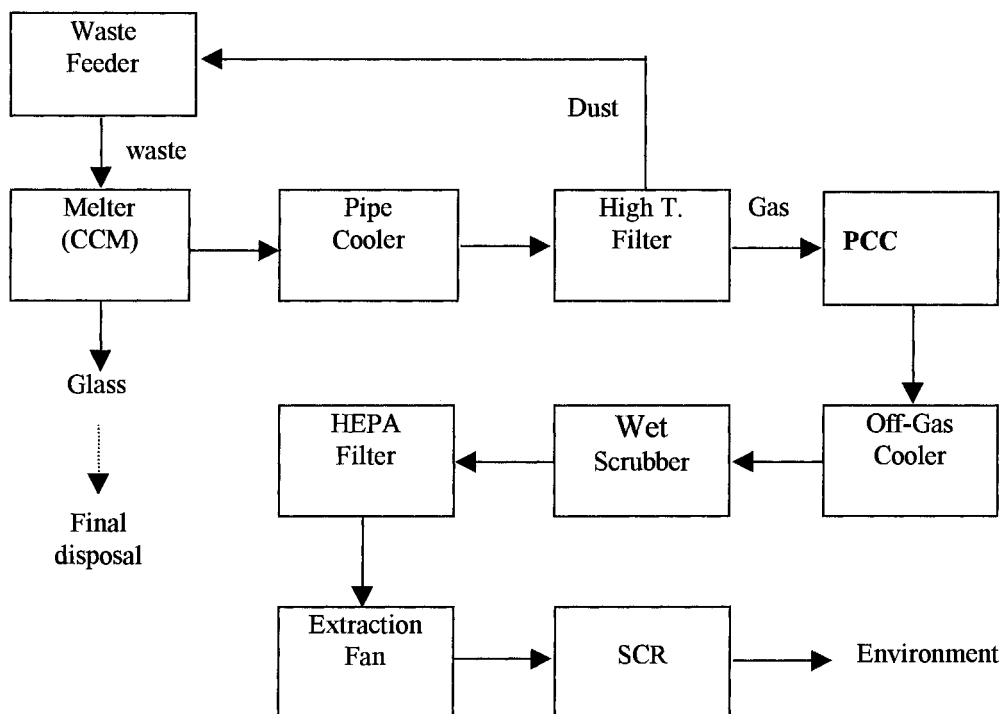


Fig. 1. A schematic diagram of the pilot scale vitrification process

DAWs are cut into 5x5 mm of nominal size by a Shredder and then fed into the CCM continuously through the screw type feeder. The gases produced by the various reactions (combustion, pyrolysis, oxidative pyrolysis, etc.) in the melter are drawn to the off-gas treatment system (OGTS) and cleaned by several steps as shown in Figure 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. Post Combustion Chamber (PCC) is installed downstream of the HTF to completely oxidize the products of incomplete combustion (PICs) and destroy dioxins. Gas temperature is maintained at 1100°C and residence time is at least 2 seconds. Off-gases from the PCC are cooled below 500°C 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 SO_x by spraying the NaOH solution. The pH of the scrubbing solution is always maintained about 7 ~ 10. The gases possibly containing small particles are cleaned in the HEPA filter. Then NO_x gases produced by the oxidation of waste nitrogen (fuel NO_x) and in-leaked air (thermal NO_x) are removed in the Selective Catalytic Reduction Reactor (SCR) where NO_x is converted to N₂ gas by the ammonia injection. Finally, gases are released to stack and monitored by the on-line Continuous Emission Monitoring System.

Important process parameters such as flowrate, temperature, pressure of off-gas, etc are measured by on-line and the values are recorded by the interval of 10 seconds.

TEST PROCEDURES

Waste

As first phase of study, fresh wet resin has been selected as waste simulant to investigate its off-gas behavior under oxygen supply into molten glass. The moisture content is about 56 to 59% and impurity of inorganics such as Na, K, Fe, Ca, and Mg is between 20 to 50 ppm. However, it is assumed that unburned carbon and sulfur, as residues of the resin, can be retained as separate phases in glass.

Operation Parameters

In order to optimize the resin vitrification process, three operation parameters were selected as follows: configuration of the melter, wastes feeding rate, and excessive oxygen amount. Pilot plant tests were performed with the combinations of these three operation parameters.

Operating Condition

Each test run was designed for isolating some effects from others. Major objectives of the tests are to optimize the off-gas characteristics while feeding directly the mixed (50% cation+50% anion) ion exchange resin onto the molten glass. Moreover, glasses as well as ashes are examined for their elemental analysis.

Table 1: Test Conditions

	unit	Test Number	
		#2	#3
Resin Feed	kg/h	20	30
Total Resin	kg	187	107
Glass Feed	kg/h	0	0
Glass Fed (80 kg)	kg	Neph-BF1	Neph-BF2
Glass Surface Temperature	deg-C	1050-1170	1100-1400
Center O2 Feed	Nm3/h	8~13	13
Periph. O2 Feed	Nm3/h	12	18
Bubbler O2 Feed	Nm3/h	2	2

Table 2: Compositions of Base Glasses

Oxides	Nepheline	#2 (Neph-BF1)	#3 (Neph-BF2)
SiO2	54.00	47.76	47.92
Na2O	28.00	24.77	24.85
Al2O3	18.00	15.92	15.98
Fe2O3		1.3	1.25
B2O3		10.25	10
SUM	100	100	100
Melting Temp. at viscosity=50 poise	1390	1266	1269

Two tests had been performed by feeding the resin into the melter under different configurations: 1) upper oxygen feeder tips, 2) bottom bubbler position, both in relation to the level of glass melt. About 80 kg of the glass Neph-BF1 or Neph-BF2 (Table 2) was initially melted. As the surface temperature reached about 1200°C, a sample of base glass was collected for each test run. Then, the resin was fed onto the glass melt with oxygen feeding configuration as described in Table 1. In test runs #2 and #3, total amount of the resin fed was 187 and 107 kg, respectively. At 20 or 30 kg/h of resin feedrate, they were fed for about 9 and 4 hours, respectively. In test #2, the oxygen was supplied 20~50% in excessive amount for the 20 kg/h resin feedrate while in test #3, the oxygen was supplied 25% in excessive amount for the 30 kg/h resin feedrate. After completing the combustion, three samples of the glass melt as well as glassy material or dust deposited in various positions (Fig. 1) were collected and analysed for its elemental composition.

On the cooled wall of off-gas plenum, a glassy material was sampled above the glass surface (CCM-P1). At the entrance of off-gas line a glassy material was sampled (CCM-P2). On the cooled wall of oxygen feeder, another glassy material was collected (CCM-P3). Also, the dust deposited in the cooling pipe directly connected from CCM to High Temperature Filter (HTF) was separately collected near CCM (PCR-D1) and near HTF (PCR-D2). Finally, the dust declogged from HTF candles was collected in HTF bottom (HTF-B1).

Analysis

Dust or Glass 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 away clogged dust 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 the particles larger than 1-micrometer.

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 time and feeding rate. 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. Dust size distributions were measured with a Cascade Impactor equipped with ten impactor stages. Sampling method was identical to the dust concentration measuring method. For the compositional analysis of dust, ICP-AES and CHNS analyzer were used.

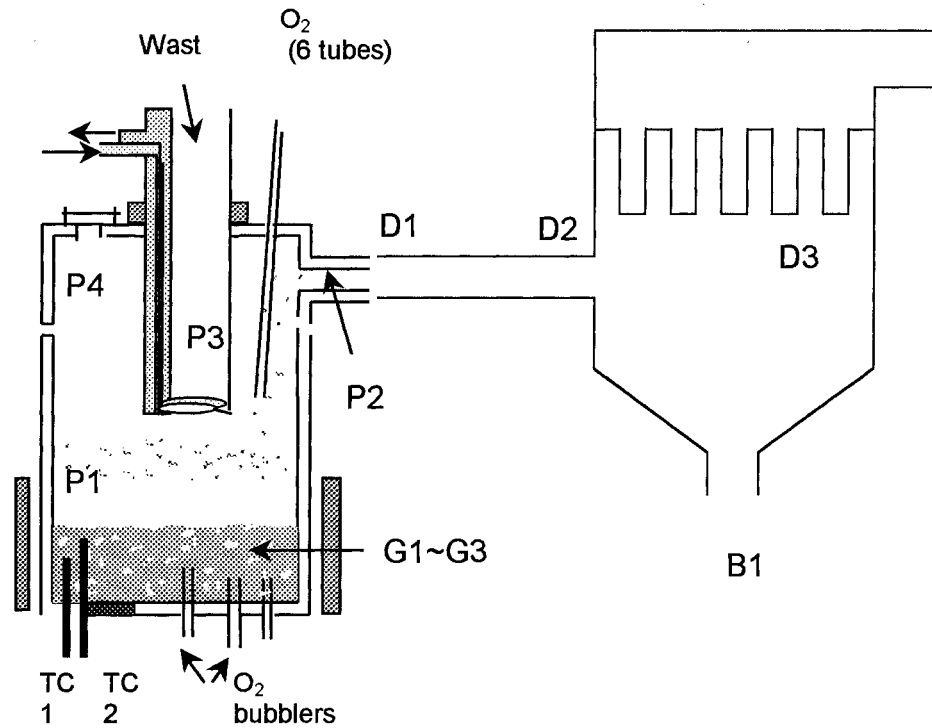


Fig. 1: Sampling Positions

For compositional analysis of inorganic elements, the glass or dust samples were ground and fused in crucibles. After making clear solution, some was analyzed by inductively coupled plasma spectrometry (ICP) for the concentration of several main glass components, such as B, Ca, Mg, and Al, etc. Others were analyzed by ICP-Mass for the concentration of several components such as Cs, if necessary.

For the C, H, N and S analysis, samples are oxidized at 900°C under pure oxygen environment that produce a gaseous mixture of carbon dioxide, carbon monoxide, water, elemental nitrogen and oxides of nitrogen. After 2 to 6 min in the oxygen environment, the products are swept with a stream of helium through a 750°C tube furnace where hot copper reduces the oxides of nitrogen to the element and removes the oxygen as copper oxides. Additional copper oxide is also present to convert carbon monoxide to the dioxide.

There is a gravimetric analysis used for analysis of SiO₂. Samples containing more than 0.5 g are fused as clear melt with addition of Na₂CO₃+ K₂CO₃+Lithium borates. The melt is dehydrated and separated into the precipitate as insoluble SiO₂.

RESULTS AND DISCUSSIONS

Table 3: Glass compositions in Resin Test #2

Oxides	Bottom	Middle	Top
Al ₂ O ₃	14.83	14.75	14.84
B ₂ O ₃	10.39	10.81	10.72
BaO	0.15	0.15	0.15
CaO	0.1	0.09	0.1
Fe ₂ O ₃	0.96	1.16	0.98
K ₂ O	0.18	0.19	0.18
MgO	0.03	0.03	0.02
Na ₂ O	23.84	23.25	24.26
SiO ₂	46.03	45.95	46.04
TiO ₂	0.32	0.33	0.33
ZrO ₂	0.16	0.16	0.18

Table 4: Compositions of Dust or Glassy Material deposited in Resin Test #2

Oxides	CCM-P1	CCM-P2	HTF-B1	PCR-D1	PCR-D2
Al ₂ O ₃	1.04	0.63	0.06	0.29	0.43
B ₂ O ₃					
BaO	0.02	0.01	0.00	0.01	
CaO	4.02	0.83	0.02	0.07	
Fe ₂ O ₃	0.73	2.47	0.42	1.92	
K ₂ O	1.31	0.56	0.95	0.55	
MgO	2.28	0.34	0.01	0.02	
Na ₂ O	43.80	23.06	39.69	23.42	14.84
SiO ₂	0.50	0.60	0.35	0.89	2.91
TiO ₂	0.03	0.05	0.01	0.02	0.061
ZnO	0.03	0.02	0.14	0.03	
S	59000	124000	96000	101000	30660
C	54000	233000	19000	95000	38770

Compositions of the glasses which were collected at different levels were analyzed (Table 3 and 5). Na, K, Li, Cs and B are most common volatile components even though it is dependent of feed method and melter technology [3]. In test run #2, the bath was at the glass temperature below 1170°C, while in test run #3 the bath was operated at the temperature between 1000 and 1400°C for more than 16 hours. The components such as B, Na and Fe as well as the less volatile components such as Al and Si have shown some mass loss during the melting.

Table 5: Glass compositions in Resin Test #3

Oxides	Bottom	Middle	Top
Al ₂ O ₃	16.46	15.55	15.49
B ₂ O ₃	8.45	8.45	8.55
BaO	0.17	0.15	0.16
CaO	0.13	0.08	0.08
Fe ₂ O ₃	1.04	0.86	0.95
K ₂ O	0.09	0.16	0.16
MgO	0.03	0.03	0.03
Na ₂ O	22.73	23.02	22.7
SiO ₂	49.99	47.87	47.78
TiO ₂	0.4	0.36	0.36
ZrO ₂	0.18	0.16	0.16

In both test runs #2 and #3, the material condensed from the plenum space (CCM-P1) contains mostly Na₂O and SO₃, which can be complexed as sodium sulfate. There are also some calcium and potassium sulfates present. In the horizontal cooling pipe, off-gas exits around 300°C and high Fe condensed on the cold surface (CCM-P2 and PCR-D1). At the entrance or bottom of HTF, the gas was cooled down to less than 200°C. The dust retrieved from the bottom contains mostly Na₂O, SO₃ and C which can react into sodium sulfate. Unburned carbon concentration was highest in the dust scrapped from the walls close to combustion chamber (CCM-P1 & P3). Sulfur concentration is as high as 5 to 6 wt% around surface of the molten glass. (CCM-P1, Table 4 and 6) However, in test #2, it showed about 10 to 12 wt% in the dust from the pipe cooler and HTF. (Table 4) Larger amount of the resin fed as well as its more reduced condition in test #2 may have caused the higher deposition of sulfur. Usually sulfate-containing material should be carefully sampled because both glass and salt phases can be distributed even in small samples. [4]

Table 6: Compositions of Dust or Glassy Material deposited in Resin Test #3

Oxides	CCM-P1	CCM-P2	CCM-P3	HTF-B1	PCR-D1	PCR-D2
Al ₂ O ₃	0.41	0.41	0.05	0.043	0.14	0.2
B ₂ O ₃						
CaO	0.03	0.06	0.02			
Fe ₂ O ₃	0.22	1.22	0.26			
K ₂ O	0.93	0.38	0.87			
MgO	0.00	0.00	0.00			
Na ₂ O	35.37	14.84	31.53	39.25	28.3	16.83
SiO ₂	0.15	1.53	0.29	0.17	0.52	0.58
TiO ₂	0.02	0.06	0.01	0.003	0.009	0.029
ZnO	0.05	0.01	0.03			
S	66100	11480	19620	25830	46090	6420
C	131100	484900	120800	16500	49540	79550

CONCLUSIONS

NETEC focused on optimizing the operating conditions based on test results accumulated from off-gas characteristics. At this stage of research, Nepheline mixed with boron and iron oxides (Neph-BF1) was used as start-up materials to prepare the glass bath. On the two test runs, melter configuration was kept in same manner as described earlier. However, elemental composition data of the material deposited in the melter and its downstreams under various conditions could be analysed for improving the process.

B, Na and Fe in base glass were selectively lost during the glass melting. On the wall above the glass melt surface, sodium sulfates appears to be major compound with sulfates of potassium and calcium present. Particularly, in the dust samples on the horizontal cooler surface, the sulfur as well as the carbon unburned from the organic resin was present in higher concentration. It is expected that boron and iron would condense on the cooler surface, while sodium and lithium condense on warmer surface. However, this phenomenon is complicated and should be investigated more in details. Larger amount of the resin fed as well as its more reduced condition in test #2 may have contributed to the higher deposition of sulfur.

It has been reported that the metallic phase is usually found around the area of resin accumulation due to this reduced condition caused by resin combustion. With the resin loaded with Fe and Ni , a series of tests will be designed to clarify the effect of sulfur on the formation of metallic phase in the glass and then to drive the effect of experimental tools such as bubbling flowrate and position of the bubblers in order to make more oxidized environment in glass melt.

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