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Pilot-scale Tests to Vitrify Ion Exchange Resin from Korean NPPs

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ABSTRACT

Vitrification pilot plant had been constructed in Taejon, Korea to tackle or 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 finished its pilot-scale tests for ion exchange resin as well as test operation. First phase of the tests would focus on observation and measurement of off-gas characteristics during the combustion of resin. This paper presents the test results of utilizing a selected glass frit to vitrify simulated resin from Korean NPPs by analyzing the compositional change in the glassy material or dust deposited through the melter and its downstreams. B, Na and Fe in base glass were found to be 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 unburnt from the organic resin was present in higher concentration. It is expected that more boron and iron would condensate on the cooler surface. However, the iron analysis was obtained to imply the trend. In more oxydizing condition combined with the larger amount resin fed in the test run R02, more sulfur appears to be oxidized into gaseous phase or to entrain downstream as particles.

INTRODUCTION

Vitrification pilot plant had been constructed in Taejon, Korea under cooperation of KEPCO, SGN and Hyundai Precision Inc. for 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 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.[2] NETEC has been developing product control scheme which can maximize waste loading into final glass forms for different waste streams.[1,2]

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

The LLW generated from routine operation of NPPs include mainly, the DAW (combustible and non-combustible), spent resin, spent filter, and evaporator bottom (borate liquid waste). In this study, fresh wet resin has been selected as waste simulant to investigate its off-gas behavior under oxygen supply on 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 unburnt carbon and sulfur, as residues of the resin, are retained as separate phases in glass.

As preliminary study, we focus on the compositions of glass in the melter and glassy material, the dust deposited on inner wall of Pipe Cooler and the dust retrieved from High Temperature Filter candles

As a part work of vitrification process development, Korea Electric Power Research Institute (KEPRI), and subsequently NETEC had investigated the glass formulation for vitrifying respectively, mixed combustible DAW, borate waste and spent resin from Korean NPPs. However, in this paper, the entrainment and volatility of elements have been studied when vitrifying the ion exchange resin.

TEST PROCEDURES

Operating Condition

Each test run was designed for seperating 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 under different configurations: 1) upper oxygen feeder tips, 2) bottom bubbler position. About 80 kg of the glass Neph-BF1 or Neph-BF2 (Table 2) was initially melted. As the surface temperature (TC1 in Table 1) 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 R02 and R03, total amount of the resin fed was 187 and 107 kg, respectively. At 20 or 30 kg/h of resin feedrate, they were fed over 8 and 4 hours, respectively. In R02, the oxygen was supplied 20~50% in excessive amount for the 20 kg/h resin feedrate while in R03, 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).

Major Inorganic Element Analysis

The 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.

Organic Element Analysis

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.

SiO_2 Analysis

There is a gravimetric analysis used for analysis of SiO_2. Samples containing more than 0.5 g are fused as clear melt with addition of Na_2CO_3+ K_2CO_3+Litium borates. The melt is dehydrated and separated into the precipitate as insoluble SiO_2.

RESULTS AND DISCUSSIONS

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 R02 or R03, by identifying in weight percent the change of major components between the third/fourth column of Table 2 and last three columns Table 3 or 5, the components such as Na, B and Fe are selectively lost during the melting. However, Al and Si have been decreased in test run R02, while not changed in R03. It is not expected that Al2O3 or SiO2 have any significant volatility. This reason is not certain. However, sampling or analysis errors may have contributed this discrepancy.

In both test runs R02 and R03, the material condensed from the plenum space (CCM-P1) contains mostly Na_2O and SO_3, which can be complexed as sodium sulfate. There are also some cacium 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 cooled down to less than 200°C. The dust retrieved from the bottom contains mostly Na_2O, SO_3 and C which can react into sodium sulfate. Unburnt carbon concentration was highest in the dust scrapped from the CCM-P3 which is a coolest surface. Sulfur concentration is as high as 5 to 6 wt% around surface of the molten glass.(Table 6) However, in R02, 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 oxydizing condition in R02 may have contributed to 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]

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 was used as starting 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 unburnt from the organic resin was present in higher concentration. It is expected that boron and iron would condensate on the cooler surface. Larger amount of the resin fed as well as its more oxydizing condition in R02 may have contributed to the higher deposition of sulfur.

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Fig. 1: Positions of Samples

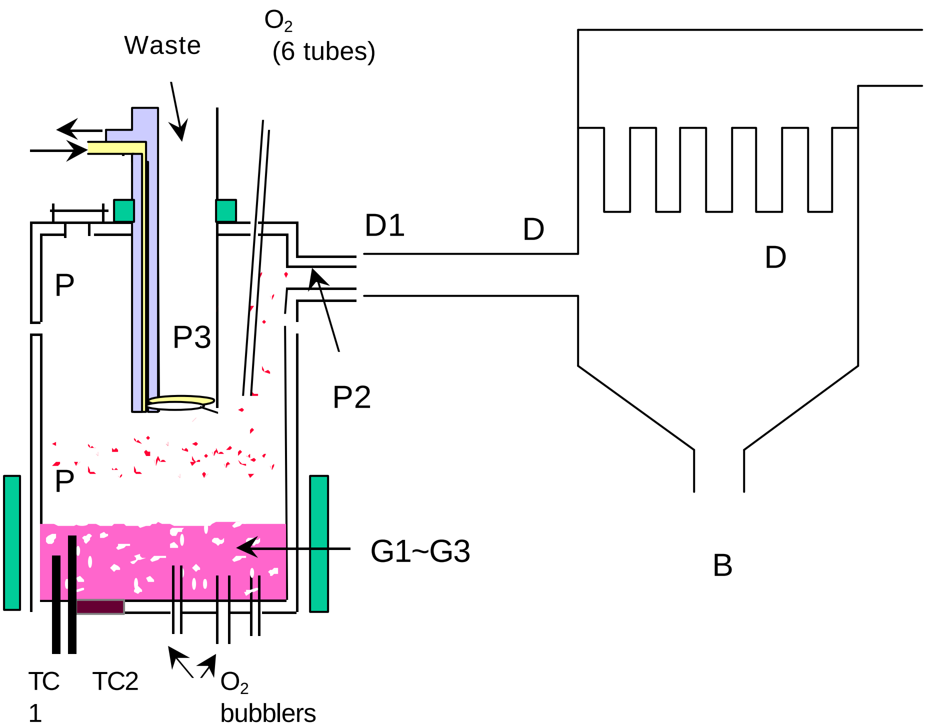

Table 1: Test Conditions

	unit	Test Number	
		R02	R03
Resin Feed	kg/h	20	30
Total Resin	kg	187	107
Glass Feed	kg/h	0	0
Glass Fed	kg		
Center O2 Feed	Nm3/h	8~13	13
Periph. O2 Feed	Nm3/h	12	18
Bubbler O2 Feed	Nm3/h	2	2

Table 2: Composition of the Base Glass

Oxides	Nepheline	Neph-BF	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

Table 3: Glass compositions in Resin Test #R02

Oxides	Bottom	Middle	Top
Al2O3	14.83	14.75	14.84
B2O3	10.39	10.81	10.72
BaO	0.15	0.15	0.15
BeO			
CaO	0.1	0.09	0.1
CoO			
Cr2O3	0	0.01	0.01
Cs2O			
CuO	0		
Fe2O3	0.96	1.16	0.98
K2O	0.18	0.19	0.18
Li2O			
MgO	0.03	0.03	0.02
MnO2	0		
MoO3	0.01	0.03	0.01
Na2O	23.84	23.25	24.26
Nb2O5			
NiO	0		
P2O5	0.01	0.01	0.01
PbO			
SiO2	46.03	45.95	46.04
SrO			
TiO2	0.32	0.33	0.33
ZnO	0		
ZrO2	0.16	0.16	0.18
Cl			
S			
C			
SUM	97.01	96.92	97.83

Table 4: Compositions of Dust or Glassy Material deposited in Resin Test #R02

Oxides	CCM-P1	CCM-P2	HTF-B1	PCR-D1	PCR-D2
Al2O3	1.04	0.63	0.06	0.29	0.43
B2O3	0.00	0.00	0.00	0.00	
BaO	0.02	0.01	0.00	0.01	
BeO	0.00	0.00	0.00	0.00	
CaO	4.02	0.83	0.02	0.07	
CoO	0.00	0.00	0.00	0.00	
Cr2O3	0.00	0.01	0.00	0.01	
Cs2O	0.00	0.00	0.00	0.00	
CuO	0.00	0.00	0.01	0.00	
Fe2O3	0.73	2.47	0.42	1.92	
K2O	1.31	0.56	0.95	0.55	
Li2O	0.00	0.00	0.00	0.00	
MgO	2.28	0.34	0.01	0.02	
MnO2	0.00	0.00	0.00	0.01	
MoO3	0.03	0.02	0.03	0.03	
Na2O	43.80	23.06	39.69	23.42	14.84
Nb2O5	0.00	0.00	0.00	0.00	
NiO	0.00	0.03	0.00	0.06	
P2O5	0.02	0.01	0.01	0.01	
PbO	0.00	0.00	0.01	0.00	
SiO2	0.50	0.60	0.35	0.89	2.91
SrO	0.00	0.00	0.00	0.00	
TiO2	0.03	0.05	0.01	0.02	0.061
ZnO	0.03	0.02	0.14	0.03	
ZrO2	0.01	0.01	0.00	0.00	
Cl					
S	59000	124000	96000	101000	30660
C	54000	233000	19000	95000	38770
SUM	53.84	28.68	41.72	27.34	18.24

Table 5: Glass compositions in Resin Test #R03

Oxides	Bottom	Middle	Top
Al2O3	16.46	15.55	15.49
B2O3	8.45	8.45	8.55
BaO	0.17	0.15	0.16
BeO			
CaO	0.13	0.08	0.08
CoO			
Cr2O3	0.03	0	0.01
Cs2O		0	
CuO	0.01		
Fe2O3	1.04	0.86	0.95
K2O	0.09	0.16	0.16
Li2O			
MgO	0.03	0.03	0.03
MnO2	0	0	
MoO3	0.01	0.02	0
Na2O	22.73	23.02	22.7
Nb2O5			
NiO	0	0	0
P2O5	0	0	0
PbO			
SiO2	49.99	47.87	47.78
SrO			
TiO2	0.4	0.36	0.36
ZnO	0	0	
ZrO2	0.18	0.16	0.16
Cl			
S			
C			
SUM	99.72	96.71	96.43

Table 6: Compositions of Dust or Glassy Material deposited in Resin Test #R03

Oxides	CCM-P1	CCM-P2	CCM-P3	HTF-B1	PCR-D1	PCR-D2
Al2O3	0.41	0.41	0.05	0.043	0.14	0.2
B2O3	0.00	0.00	0.00			
BaO	0.00	0.00	0.00			
BeO	0.00	0.00	0.00			
CaO	0.03	0.06	0.02			
CoO	0.00	0.00	0.00			
Cr2O3	0.00	0.08	0.05			
Cs2O	0.00	0.00	0.00			
CuO	0.01	0.00	0.00			
Fe2O3	0.22	1.22	0.26			
K2O	0.93	0.38	0.87			
Li2O	0.00	0.00	0.00			
MgO	0.00	0.00	0.00			
MnO2	0.00	0.02	0.00			
MoO3	0.01	0.00	0.01			
Na2O	35.37	14.84	31.53	39.25	28.3	16.83
Nb2O5	0.00	0.00	0.00			
NiO	0.00	0.06	0.02			
P2O5	0.02	0.01	0.02			
PbO	0.00	0.00	0.00			
SiO2	0.15	1.53	0.29	0.17	0.52	0.58
SrO	0.00	0.00	0.00			
TiO2	0.02	0.06	0.01	0.003	0.009	0.029
ZnO	0.05	0.01	0.03			
ZrO2	0.00	0.00	0.00			
Cl						
S	66100	11480	19620	25830	46090	6420
C	131100	484900	120800	16500	49540	79550
SUM	37.25	18.70	33.15	39.47	28.97	17.64