PILOT-SCALE TESTS TO VITRIFY KOREAN LOW-LEVEL WASTES

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ABSTRACT

Korea is under preparation of its first commercial vitrification plant to handle LLW from her Nuclear Power Plants (NPPs). The waste streams include three categories: combustible Dry Active Wastes (DAW), borate concentrates, and spent resin. The combustible DAW in this research contains vinyl bag, paper, and protective cloth and rubber shoe. The loaded resin was used to simulate spent resin from NPPs.
As a part of this project, Nuclear Environment Technology Institute (NETEC) has tested an operation mode utilizing its pilot-scale plant and the mixed waste surrogates of resin and DAW. It has also proved, with continuous operation for more than 100 hours, the consistency and operability of the plant including cold crucible melter and its off-gas treatment equipment. Resin and combustible DAW were simultaneously fed into the glass bath with periodic addition of various glass frits as additives, so that it achieved a volume reduction factor larger than 70. By adding various glass frits, this paper discusses about maintaining the viscosity and electrical conductivity of glass bath within their operable ranges, but not about obtaining a durable glass product. The operating mode starts with a batch of glass where a titanium ring is buried. When the induced power ignites the ring, the joule heat melts the surrounding glass frit along with the oxidation heat of titanium. As soon as the molten bath is prepared, in the first stage of the mode, the wastes consisting of loaded resin and combustible DAW are fed with no or minimum addition of glass frits. Then, in the second stage, the bath composition is kept as constant as possible. This operation was successful in terms of maintaining the glass bath under operable condition and produced homogeneous glass. This operation mode could be adapted in commercial stage.

INTRODUCTION

Pilot scale vitrification facility was established by KHNP (Korea Hydro & Nuclear Power Company, Ltd.) /NETEC (Nuclear Environment Technology Institute) to treat the low- and intermediate-level radioactive wastes (LLWs) from nuclear power plants. A series of pilot tests has been conducted with simulated wastes to produce the design data for the construction of a commercial plant. In our vitrification process, organic wastes including ion exchange resin and combustible dry active wastes (DAW) are combusted and vitrified in a cold crucible melter (CCM) and the non-combustible wastes are treated by a plasma torch. Through the vitrfication, organic bulk wastes are converted to an inorganic stable glass form suitable for safe disposal.
In the environmental and economical aspects as well as safety, optimizing the vitrification conditions in the melter will be very important because it affects the generation of secondary wastes, hazardous gases and a waste glass.
With best operation parameters selected after previous short-term tests, additional parameters have been tested in this long-term test, such as a mixing ratio of resin and DAW. It was to reduce the formation of

metallic phase in the glass melt by improving the oxygen permeability at the interface between the glass surface and accumulated waste. It was also to test the consistency and operability of the plant in an operating mode of long duration. However, this paper discusses mainly about the property change and control of glass bath during the each phase of operation mode. The effect on the reduction of metal formation, by the simultaneous feed of DAW along with resin, is not discussed in this paper.

EXPERIMENTAL

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 buried in the raw glass and then melts the glass in the CCM. The top of the melter is equipped with a waste feeding pipe and several oxygen injectors.
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.

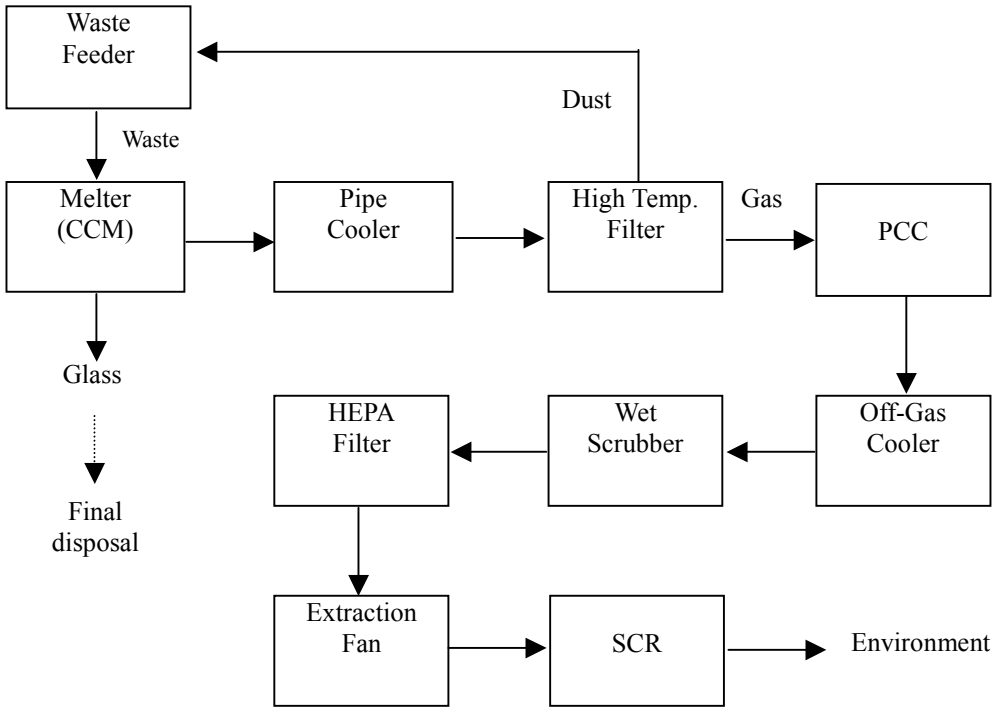

Fig. 1. A schematic diagram of the pilot scale vitrification process

At first, particles contained in the gas flow are removed in the High Temperature Filters (HTF). Its main function is to prevent 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 pressure of 4 bar. The dust is 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 lease 2 seconds. Off-gas from the PCC are cooled below 500°C in the Off-Gas

Cooler (OGC). The following Wet Scrubber cools the gas temperature and absorbs the acid gases such as HCl and SOx 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 HETA filter. Then NOx gases produced by the oxidation of waste nitrogen (fuel NOx) and in-leaked air (thermal NOx) are removed in the Selective Catalytic Reactor (SCR) where NOx is converted to nitrogen gas by the ammonia injection. Finally, gas is monitored by the on-line Continuous Emission Monitoring System when it is released to stack. Important process parameters such as flowrate, temperature, pressure, etc are measured and recorded by on-line.

Waste

Low-Level Radioactive Waste (LLW) from Korean nuclear power plant is characterized elsewhere.[1] Among them, DAW represents around 41 % of the total waste volume and is composed of various materials such as paper, clothes, plastics, and so on. Its vitrification characteristics depend on the physical and chemical properties of each waste. Cellulose is the major constituent (47.7 %) of DAW and the others are PE (33.3 %), Rubber (10.8%), Polyester (8.2%) etc. DAW used in this test excluded Polyvinyl chloride (PVC) since it could burden the off-gas system by corrosion and its use would diminish in the nuclear power plants. The characteristics of main constituents of DAW are summarized in Table I.
The composition of mixed waste in Table V was determined on the basis of average material composition data.

Table I. Physical and chemical characteristics of DAW

Waste	Ash content (wt%)	Heat of combustion (kcal/kg)	Major elements
Cellulose	0.3 ~ 0.5	3700 ~ 4300	C, H, O
PVC	6.8	6300	C, H, Cl
PE	0.4	10900	C, H
Rubber	2.4	10100	C, H
Average composition	1.8		

To simulate resin used in nuclear power plants, a tank solution is prepared by adding compounds of cations and anions. An ion loading system was used to load the ions onto the mixed resin of anions and cations. The ionic concentrations loaded in the simulated resin are shown in Table II.

Table II. Estimated concentration of Ions loaded in the resin surrogates. (g ions/kg resin)

	Fe	Ni	Li	B	Co	Cs
Batch A	3.70	5.00	3.60	3.90	0.9	0.9
Compounds dissolved in solution	$Fe(NO_3)_3 \cdot 9H2O$	$Ni(NO3)_2 \cdot 6H2O$	-	H_3BO_3	$CoCl_2 \cdot 6H_2O$	CsCl

Test Overview

Long-term pilot plant tests were performed by simultaneously feeding resin and DAW with no or minimum addition of glass frits. Operation lasted 130 hours including about 30 hours of idling operation. The waste of resin and DAW was simultaneously fed with the mixing ratio of 1:2 in this test.
In order to optimize the vitrification process of the mixed waste, some operation parameters were selected in previous tests such as melt temperature, feeding ratio of DAW and resin, and excessive oxygen amount including bubbler flowrate. This test is to provide oxygen-rich environment in the glass pool as well as in the combustion chamber so that the metal formation can be minimized in the glass pool.
However, in this test, the control of some glass properties is focused in relation to the melter operation such as viscosity and electric conductivity.

Ignition
In order to provide melt glass, 60 kg of the mixture of glass frits A1 and A2 is loaded into CCM with a titanium ring positioned in it. To achieve its proper ignition, it was important to let oxygen pass through the glass frit and oxidize the titanium to supply the heat for its ignition. Therefore, until the heat accumulated in titanium ring reaches a critical point for its ignition, the ambient glass should be kept as porous material through which oxygen penetrates into the titanium ring.

Preparation of glass bath with additives
Particularly for this long duration test, about 47 kg of A3 glass was added into the melt glass to reduce its viscosity and to increase the electrical conductivity. As the result, the estimated viscosity and electrical conductivity were changed from 140 to 50 poise and from 0.55 to 0.7 S/cm at 1100°C, respectively.

Feed of mixed waste
Resin has been loaded with high concentration of Fe, Ni etc., which simulates the real ion exchange resin in the nuclear power plant. (refer to Table II). In order to reduce the formation of metal, some ways had been tested to increase the oxygen pressure near the interface between the accumulated resin and the glass surface. Due to the water content in resin, the resin in the accumulation has a limited contact with the oxygen supplied by upper oxygen feeders. To overcome this limitation, shredded DAW was simultaneously fed with the resin to provide the pores or channels through the accumulated resins.

Complete Combustion
With oxygen supplied, the accumulated waste was digested out while the flowrate of bubblers was increased for the mixing of the bath. Then, additive glasses were fed into the melter. After the glass pool is prepared, a part of the melted glass was poured out to meet an operating level of glass.

RESULTS AND DISCUSSIONS

A scenario of feeding some glass additives was designed by estimating compositions of final glasses and the investigation of their glass properties such as leach resistance, viscosity and electrical conductivity using GlassForm [2]. A candidate of final glass formula is also selected when the composition is predicted to have acceptable properties by GlassForm. In order to judge this acceptance, major constraints described in Table III was used.

Table III. Glass property constraints used to develop candidate glass formulas

Glass Property	Constraint	Remark
Viscosity	Between 10 and 100 Poise	Melter Operation
Electrical conductivity	Between 0.2 and 0.6 S/cm	
Processing Temperature	About 1,150°C	
Density	>2.5g/cm^3	Product quality
Chemical durability	Lower than EA glass* and pass TCLP	
Compressive strength	>500 psi	
Phase stability	No secondary phase	
Waste loading	Reasonable volume reduction factor >30	Economics

* EA glass is Environment Assessment glass used as a standard of high-level radioactive glass

Glass Properties for Melter Operation

The operation mode consisted of 1) ignition, 2) 10 feeding cycles, 3) complete combustion, 4) addition of glass frits, and 5) pouring of produced glass between cycles. The composition of waste ashes was referred for the prediction of some important parameters for melter operation such as viscosity and electrical conductivity. Based on the melter operation mode, glass frits are added after the complete combustion of the accumulated waste.
While 368 kg resin and 751 kg DAW were fed into the melter, the four different type of glass were added to the melter as necessary: A1 through A4. The estimated compositions of mixed waste ash and final glass were presented in Table V.
As shown in Table IV, the glass frit A2 increases the viscosity of the melt by its addition, while the glass frit A3 decreases it. However, the glass frit A2 decreases the electrical conductivity of the melt by its addition, while the glass frit A3 increases it.

Table IV. Estimated Properties of Some Glass Additives Used in Long Duration Test.

Additives	A1	A2	A3	A4
Electrical conductivity(S/m)*	0.67	0.49	1.59	0.64
Viscosity (poise)*	52	453	12	79

* Using GlassForm, the major properties were estimated at 1150°C

The base glass G1 was prepared by adding A3 as much as 47 kg into the ignition glass. After the feeding of 160 kg resin and 320 kg DAW along with 12 kg of glass frit A4, the glass pool G2 was prepared in the first stage of this mode. Also, 68 kg resin and 145 kg DAW is fed into CCM and then the bath G3 was homogenized with addition of 2 kg A3 and 8 kg A4.

Table V. Compositions of Waste Ash and Produced Glass

	Resin+DAW	Produced Glass
Al_2O_3	0.83	9.65
B_2O_3	23.37	14.73
CaO	8.36	1.44
CoO	2.21	0.32
Cs_2O	1.84	0.26
Fe_2O_3	10.11	1.46
K_2O	2.76	0.48
Li_2O	14.34	3.73
MgO	4.70	0.81
MnO_2	0.12	0.02
NaO	1.33	19.58
NiO	11.76	1.69
P_2O_5	0.98	0.17
SiO_2	14.87	45.25
TiO_2	2.43	0.42
SUM	100	100

For the glass G3~G6 in the second stage, the glass additives A1~A4 was added to control the viscosity, electrical conductivity of glass pool as well as the quality of the produced glass.

The estimated viscosity and electrical conductivity of glass pool during the operation was 13~41 poise and 0.60~0.72 S/cm, respectively, at 1150°C. While the viscosity was around the lower limit of the glass property constraints, the electrical conductivity was just above the upper limit.

Table VI. Estimated Compositions and Properties of Glass Pool in Long Duration Test

	G1	G2	G3	G4	G5	G6 (final)
Al_2O_3	12.10	10.84	10.02	10.33	11.75	9.65
B_2O_3	10.73	13.29	14.66	14.89	11.97	14.73
CaO	0.00	0.75	1.44	1.39	1.30	1.44
CoO	0.00	0.20	0.33	0.31	0.29	0.32
Cs_2O	0.00	0.16	0.28	0.26	0.24	0.26
Fe_2O_3	0.00	0.90	1.54	1.45	1.34	1.46
K_2O	0.00	0.25	0.47	0.46	0.43	0.48
Li_2O	3.42	3.84	4.30	4.33	3.96	3.73
MgO	0.00	0.42	0.81	0.78	0.73	0.81
MnO_2	0.00	0.01	0.02	0.02	0.02	0.02
NaO	23.80	21.34	19.60	19.72	20.99	19.58
NiO	0.00	1.05	1.78	1.67	1.55	1.69
P_2O_5	0.00	0.09	0.17	0.16	0.15	0.17
SiO_2	49.95	46.65	44.17	43.83	44.90	45.25
TiO_2	0.00	0.22	0.42	0.40	0.38	0.42
SUM	100.00	100.00	100.00	100.00	100.00	100.00
Resin Accumulated (kg)	0	160	228	284	326	368
DAW Accumulated (kg)	0	320	284	580	666	751
Electrical conductivity(S/m)*	0.72	0.68	0.68	0.7	0.7	0.6
Viscosity (poise)*	41	22	13	13	20	17

* Using GlassForm, the major properties were estimated at 1150°C

Glass Properties for Product Quality

With respect to the chemical durability, glass samples will be tested on basis of TCLP and PCT. Also, the compressive strength will be confirmed whether it exceeds 500 psi for a typical specimen of the samples collected from CCM. Other property constraints will apply to the samples for this test. (Table III)

CONCLUSIONS

In an operation mode, the wastes can be fed along with balanced amount of glass frits to keep the target composition of final glass even after one or more feeding cycles. A scenario of feeding some glass additives was designed by estimating compositions of final glasses and investigating their glass properties such as leach resistance, viscosity and electrical conductivity using GlassForm. By adding glass frits, the glass pool was controllable during this long-term test in terms of glass properties such as viscosity and electrical conductivity. The parameters of the bath such as temperature, impedance, current and voltage were observed to be consistent during the operation. In addition, the estimated values of viscosity and electrical conductivity were within the constrained ranges during this long duration test. This operation was successful and produced homogeneous glass. This operation mode could be adapted in commercial stage. The leach resistance of poured samples will be tested on basis of TCLP and PCT as well as its compressive strength. The quality of final glass can be reviewed on basis of the test results of final glass samples and new additives will be proposed to improve the product quality, if necessary.

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