PNCT 841—82—26

DEVELOPMENT OF HIGH LEVEL LIQUID WASTE SOLIDIFICATION IN PNC

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April 1982

To be presented at the American Nuclear Society Topical Meeting on the Treatment and Handling of Radioactive Wastes held in Richland, Washington, USA, on April 19-22, 1982.

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ABSTRACT

R & D activities on the solidification of HLLW and related technologies are being performed with the aim of designing and constructing the HLLW Solidification Pilot Plant at Tokai which is planned to start operations in 1987.

Solidified waste forms and compositions have been studied with the aid of characterizing solidified products and evaluating solidification technologies, and two typical series of borosilicate glass products have been found to be feasible for the solidification of HLLW generated by the Tokai Reprocessing Plant.

The HLLW Engineering Test Facility (ETF) with denitration and concentration equipment, two different types of Joule-heated ceramic melters, off-gas treatment equipment and a canister handling system, has been in operation since February 1980 in order to obtain various kinds of engineering data and perspectives. Air-cooling tests are also in progress to characterize natural or forced convection heat transfer in the storage of the HLLW solidified waste.

INTRODUCTION

Following the preliminary calcination experiment with a fluidized-bed calciner[1], various kinds of basic and engineering cold tests have been performed on pretreatment and vitrification of HLLW such as spray calcination, denitration with formic acid, direct induction melting with high frequency, and Joule-heated melting with a ceramic furnace to determine key requirements and to develop the techniques of solidification of HLLW under the decision of the Japan Atomic Energy Commission issued on October 8, 1976[2,3]. Canister behavior and handling techniques in pouring in molten glass, welding to seal the container, annealing the glass product, and cooling in air have also been studied as well as the development and characterization of the waste form.

This presentation shows the developmental results of waste forms, especially, two series of borosilicate glass products, development of HLLW vitrification process composed of denitration and concentration, glass melting, and canister handling. The development of storage techniques with a one-module air-cooling test apparatus is also summerzied.

DEVELOPMENT OF WASTE FORM

Since HLLW contains highly radioactive fission products and long-life actinides, it is desirable in solidifying HLLW into a stable form in order to ease and to make reliable of its management. Borosilicate glass, glass ceramics of diopsides, ceramics, and metal matrix were studied, and borosilicate glass was selected as the most promising waste form from the viewpoint of good chemical durability, low melting point, homogeneity in dispersing many kinds of HLLW elements, and engineering practicality[4,5].

A number of types of borosilicate glass prepared from non-radioactive simulated HLLW have been tested. Typical compositions and properties of borosilicate glass are shown in Tables 1 and 2. The effect of pH on the leaching rate has been studied at 100°C. Though the leaching rate of the glass at pH 3 was about ten times higher than that in the pH range of 5 to 10, the borosilicate glass P0545 of the G-2 series showed good chemical durability.

TABLE 1. Glass Compositions

	Glass code	P0545 of G-2 series	P0577 of GB series
Glass Additives	SiO_2	43.4	47.5
	B_2O_3	14.2	13.6
	Li_2O	3.0	1.9
	Na_2O	1.0	1.9
	K_2O	2.0	1.0
	CaO	2.0	1.0
	BaO	—	1.0
	ZnO	2.0	1.0
	Al_2O_3	3.5	2.4
Wastes	F.P. Oxides	12.9	12.9
	Na_2O	7.4	7.4
	Fe, Cr, Ni Oxides	8.4	8.4

TABLE 2. Glass Properties

Glass code		P0545 of G-2 series	P0577 of GB series
Leaching Rate at 100°C ($\times 10^{-5}$ g/cm².day)	pH 5.7	1.9	1.8
	pH 7	2.6	2.5
	pH 9.5	2.2	2.1
Density (g/cm³)		2.79	2.76
Viscosity 10^2 poise (°C)		1054	1129
Softening Point Ts (°C)		597	624
Contraction Point Tc (°C)		490	500
Thermal Expantion (10^{-7} /°C)		87	78

The effect of the melting temperature and time on the homogeneity of the glass was examined by density distribution measurements. The total density range of glass P0545 of the G-2 series (d = 2.79 g/cm^3) are plotted in Figure 1, which shows that melting at higher temperature produces glass products of best homogeneity during a short time. This figure and the values of viscosity and the softening point in Table 2 have an important role in determining the operational conditions and the structure of the melter.

Table 2 also shows other thermal and physical properties which are related with the interaction of the glass product and its container.

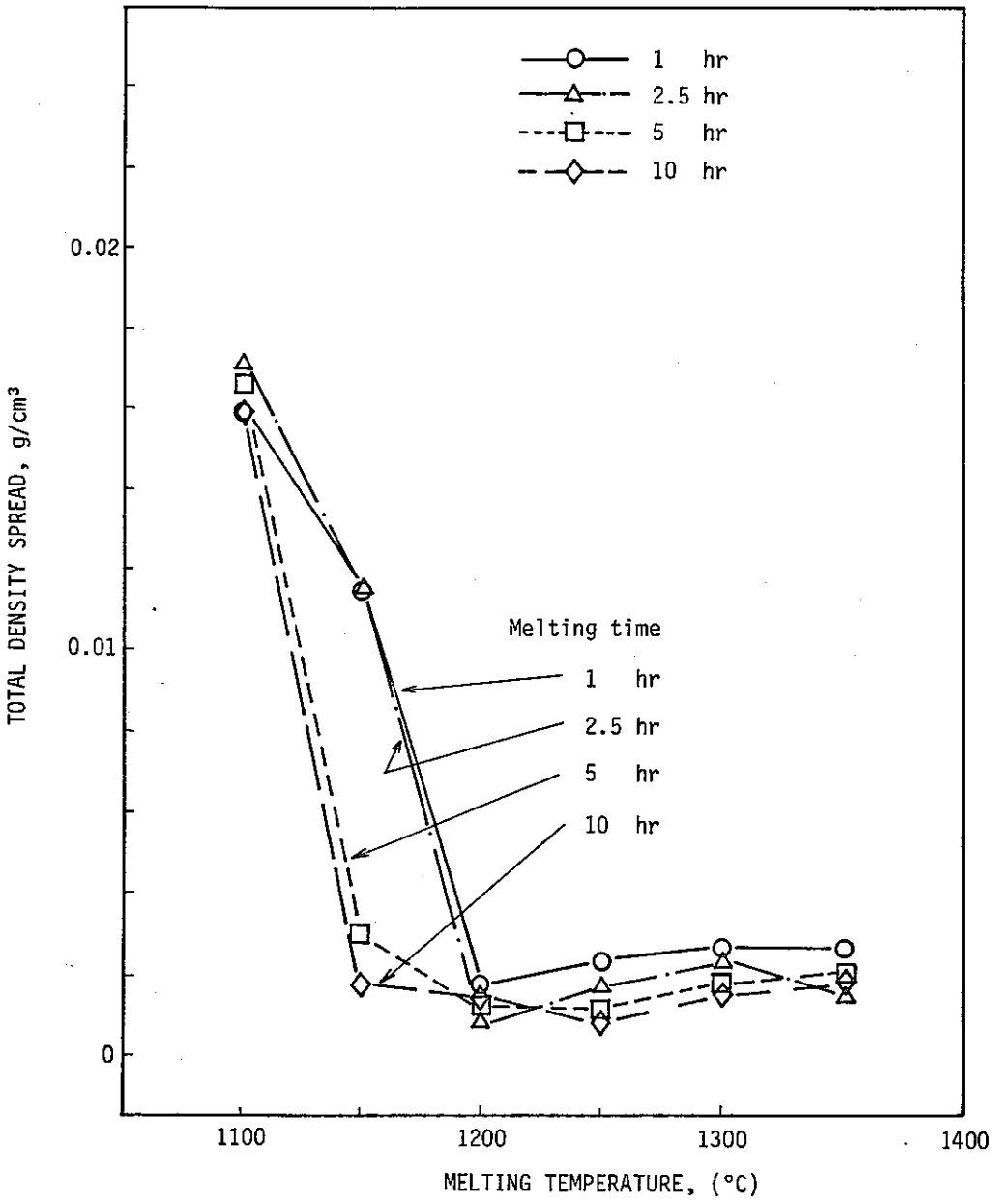


FIGURE 1 Effect of Melting Temperature and Time on Homogeneity of P0545

DEVELOPMENT OF THE HLLW VITRIFICATION PROCESS

The process flow and specification of the HLLW Engineering Test Facility (ETF) are shown in Figure 2 and Table 3, respectively. In the denitration-concentration vessel, simulated HLLW is denitrated with formic acid and then concentrated. The main purpose of the denitration step is to prevent the volatilization of ruthenium during melting in the furnace.

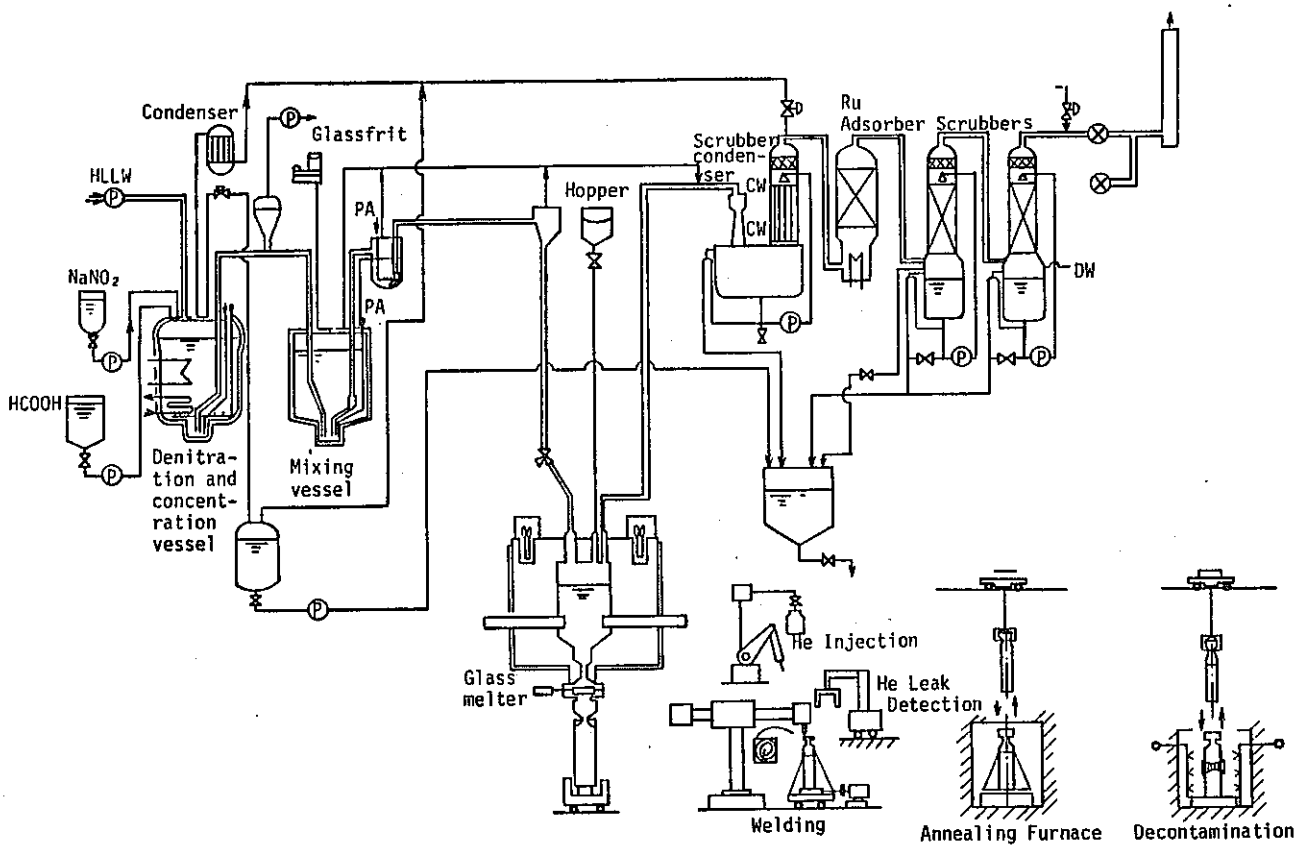


FIGURE 2. HLLW Vitrification Process (ETF)

Denitration could be initiated mildly by the addition of 0.014 mol of sodium nitrate per liter of the waste solution at the temperature just prior to the introduction of formic acid as shown in Figure 3.

TABLE 3. Specification of ETF Vitrification Process

(Pretreatment)			
1) Capacity	:	945 ℓ/day	
2) Denitration	:	continuous supply of Formic acid (80%)	
3) Concentration	:	2	
4) Grass materials	:	glass frit, glass bead	
(Glass melting)			
		(Melter B)	(Melter C)
1) Capacity	:	80 ℓ/day	: 80 ℓ/day
2) Melting temperature	:	1200°C (1250°C Max)	: 1200°C (1250°C Max)
3) Type, structure	:	Joule-heating oun vessel, overflow	: Joule-heating one vessel, bottom drain
4) Dimension (outside)	:	1245W×2000L×1245H	: 1426W×1526L×2081H
5) Heating up system	:	indirect heating, SiC	: indirect heating, $MoSi_2$
6) Electrode	:	Molybdenum (100φ)	: Molybdenum (50φ) or Inconel 690 (50φ)
7) Discharge system	:	resistance heating nozzle(Inconel 600,Pt)	: high-frequency heating nozzle (Inconel 601)
8) Melting volume	:	Max 260ℓ (0.59 m²)	: Max 145ℓ (0.3 m²)
(Off-gas treatment)			
1) Capacity	:	50 Nm³/hr	
2) Substances	:	Ru, NOx, particulates, vapor	
(Canister handling)			
1) Canister	:	318.5φ × 1655, SUS304L, 80ℓ glass	
2) Weighing	:	load-cell	
3) Handling	:	rail carrier (motor), crane	
4) Sealing	:	TIG welder (arc control)	
5) Inspection	:	He leak detector (bell jar chamber)	
6) Heat treatment	:	annealing furnace, max 700°C	
7) Decontamination	:	wire brush and water spray	

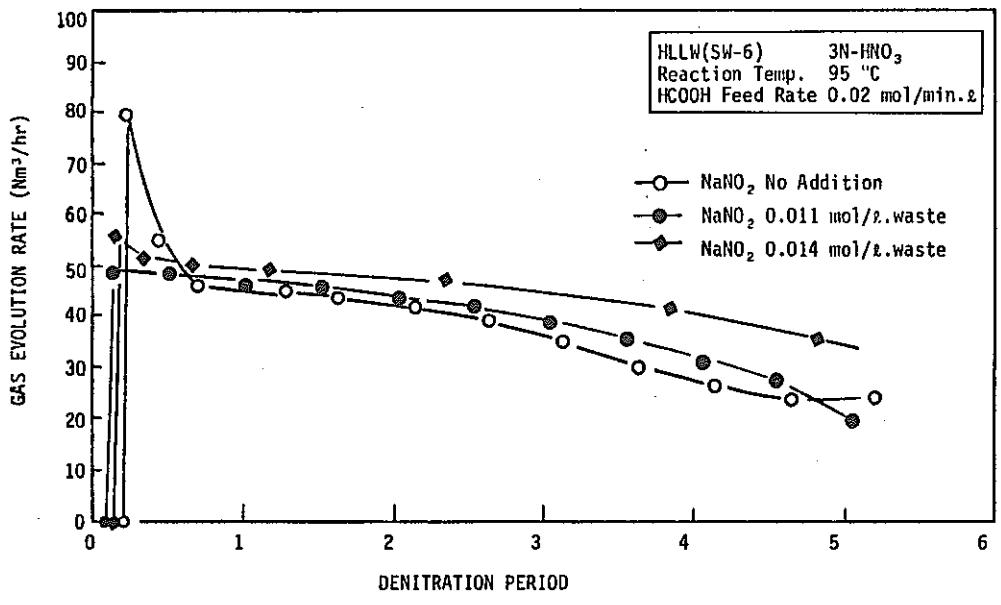


FIGURE 3. Effect of $NaNO_2$ Addition on the Gas Evolution Rate

The analysis of gas evolved during denitration showed that the reaction of equation (1) occurred initially to produce NO gas and the second reaction of equation (2) followed to produce N_2O gas at the lower concentration of HNO_3.

$$2HNO_3 + 3HCOOH \rightarrow 3CO_2 + 2NO + 4H_2O \quad \text{—— (1)}$$

$$2HNO_3 + 4HCOOH \rightarrow 4CO_2 + N_2O + 5H_2O \quad \text{—— (2)}$$

Denitration efficiency was found to be over 85% of the total nitrate ions at a 1.35 mol ration between [HCOOH] and [NO_3] as shown in Figure 4. This result shows that over 95% of the free nitrate ions is decomposed and the nitrate ions of alkali and alkali-earth metals still remain in the solution.

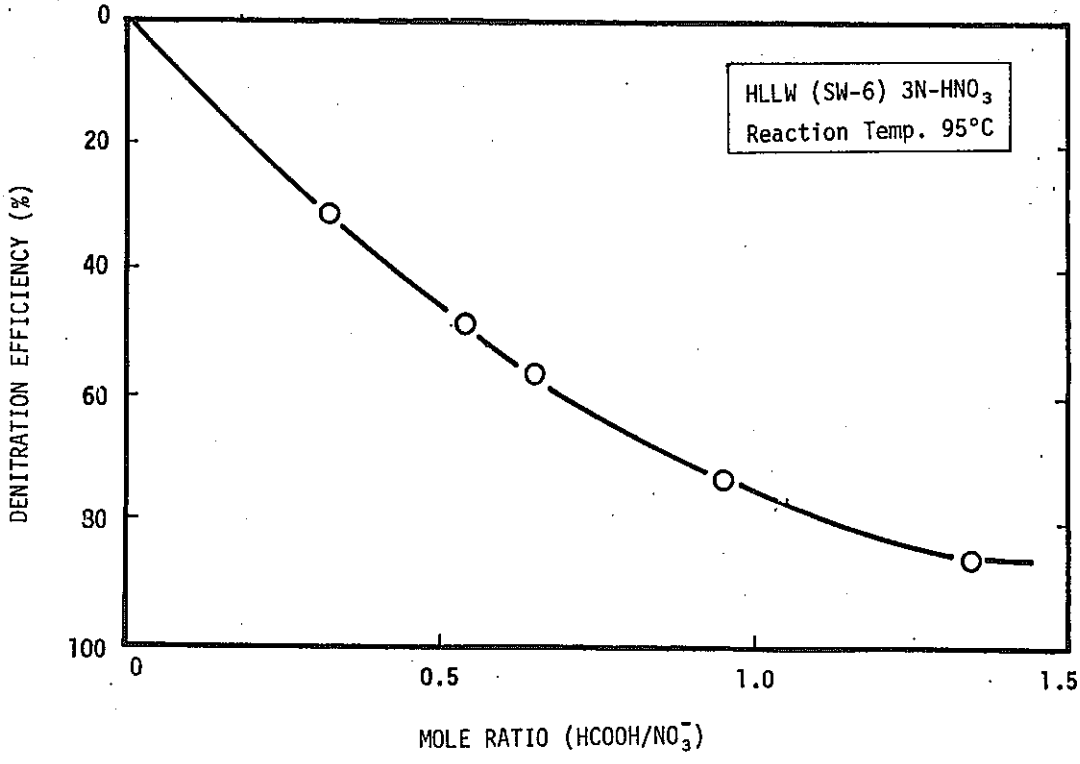


FIGURE 4. Effect of the Mole Ratio of HCOOH/NO_3^- on the Denitration Efficiency

The operation mode of denitration and concentration was compared with the reflux and non-reflux modes as shown in Figure 5. Since denitration and concentration procedures were conducted simultaneously in the case of the non-reflux mode, the processing time is shorter than in the case of the reflux mode. And the total acid concentration of the condensate in the non-reflux method was higher than that in the reflux method.

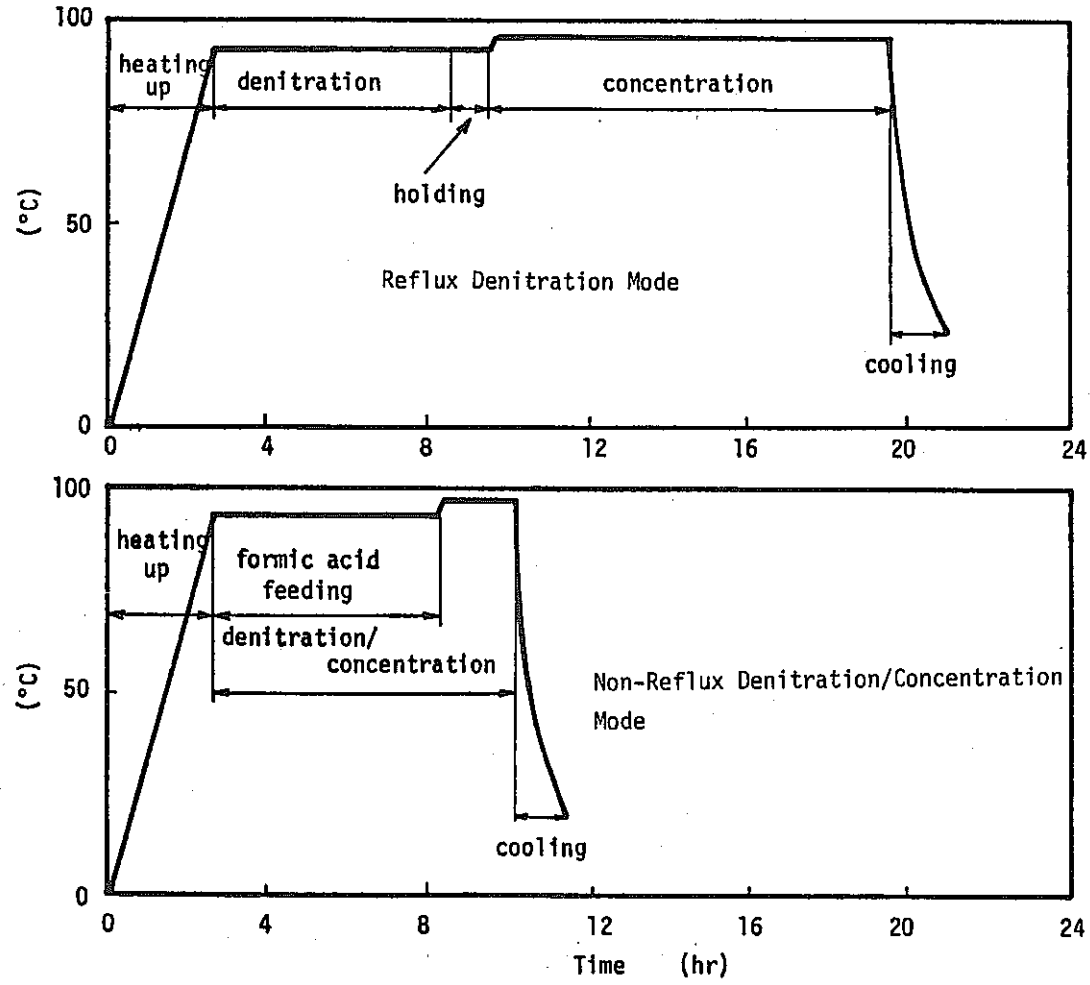


FIGURE 5. Operation Mode of Denitration and Concentration

Table 4 shows operational results of the three Joule-heated ceramic melters. Through operation until the end of 1981, the total in-service period reached 1406 days, and 51.3 tons of glass products were produced. Also, about 17 tons were filled into 79 canisters.

Corrosion of electrodes and refractories were measured during every operation as shown in Table 5. Average corrosion rates of the molybdenum electrodes in the B and C melters were observed to be 0.81 g/hr and 1.06 g/hr, respectively. This corrosion rate depends on the melter structure and operation conditions as well as HLLW compositions. In the B melter, the molybdenum corrosion rate decreased during the 4th and 5th campaigns. This may be induced from the fact that water-cooling support of the electrodes maintains a lower temperature and that current density of the electrodes decreases as the distance of the pair electrodes increases.

On the other hand, the obtained result indicates superiority in corrosion-resistance of Inconel 690 against corrosive molten glass of HLLW, and this tendency is very consistent with the preliminary lab-scale comparison test on Inconels 690 and 601, and molybdenum.

TABLE 4 Operational Results of Joule-heated Ceramic Melters

(up to 1981.12.31)

Item \ Melter		A Melter (Prototype)	B Melter	C Melter	Total
Operation period (Campaigns)	Date	1978.1.2 ∿ 1980.12.9 (8)	1980.2.1 ∿ 1981.12.12 (5)	1980.2.9 ∿ 1981.12.17 (4)	
In service	hr	12,840	12,144	8760	33,744
	day	535	506	365	1406
heating up	hr	684	530	753	1,967
Joule-heating	hr	12,156	11,614	8,007	31,777
Glass produced	ton	24.7	18.0	8.6	51.3
Slurry *1	ton	7.4	10.6	4.4	22.4
Glass beads *2	ton	—	2.0	—	2.0
Raw batch material	ton	8.1	—	—	8.1
Glass cullet	ton	9.2	5.4	4.2	18.8
Glass discharge		313	234	86	633
Canisters glass fileed		28	34	17	79

*1 Slurry (ton) refers to the weight of Glass Frit and Waste Oxides included in Denitrated/Concentrated HLLW.

*2 Glass Beads refers to the weight of Glass Beads and Waste Oxides included in Denitrated/Concentrated HLLW.

TABLE 5 Corrosion Rate of the Electrodes

Campaign	B Melter		C Melter		
	Running Days (day)	Melybdenum Corrosion Rate (g/hr)	Running Days (day)	Corrosion Rate (g/hr) Molybdenum	Inconel 690
1	165	1.17	155		
2	111	1.09	56	1.06	
3	16	1.34	87		
4	96	0.37	67	—	0.052
5	118	0.34			
Total	506	0.81	365		

GLASS BEAD FEEDING

During the slurry feeding operation, certain problems such as clogging of the slurry feed line were observed. Efforts to resolve these problems have been performed, and the glass bead feeding concept was tested 9 times up to the end of 1981.

In the glass bead feeding test, glass beads of sizes 1ϕ, 3ϕ, or 5ϕ and denitrated/concentrated HLLW were separately supplied to the melter. With a fixed power of 60 KW, the feeding rate and feeding period were controlled to be almost the same values as the slurry feeding operation.

The generating amount of particles which adhered to the melter off-gas piping or which were trapped in the scrubber-condenser, were measured. Additionally, the molten glass was sampled during draining and its properties such as density, leaching rate and softening point were measured.

Obtained results in Table 6 show that the glass properties by bead feeding are similar to those by slurry feeding.

TABLE 6 Test Results of Slurry Feeding and Glass Bead Feeding

	Slurry Feeding	Glass Bead Feeding		
		1$^{\phi}$	3$^{\phi}$	5$^{\phi}$
Power Fixed (kW)	60	60	60	60
Feed Rate (ℓ/hr)	24	Beads 6.9 kg/hr	7.1 kg/hr	7.0 kg/hr
		liquid 24.7 ℓ/hr	24.9 ℓ/hr	24.5 ℓ/hr
Total Fed (ℓ)	516	Beads 134 kg	135 kg	135 kg
		479 ℓ	471 ℓ	472 ℓ
Melting Temp. (°C)	1150-1250	1150-1230	1150-1200	1150-1200
particles (%)	0.53	0.52	0.49	0.40
Glass Properties				
Density (g/cm^3)	2.79	2.81	2.81	2.80
Leaching Rate at 100°C PHM(10^{-5} g/cm^2·day)	2.73	2.84	2.76	2.88
Softening Point (°C)	592	594	593	593

* particles (%) show the weight ratio of the particles to the glass frits/beads and waste oxides.

Canister behaviors such as temperature distribution, residual stress, deformation, and cracking during and after glass filling were observed. Figure 6 shows one example of the drange in temperature distribution of simulated HLLW glass products without any heat generation. These curves have been useful in analyzing the interaction of glass-canister materials and determining the operation mode of canister handling in the storage area.

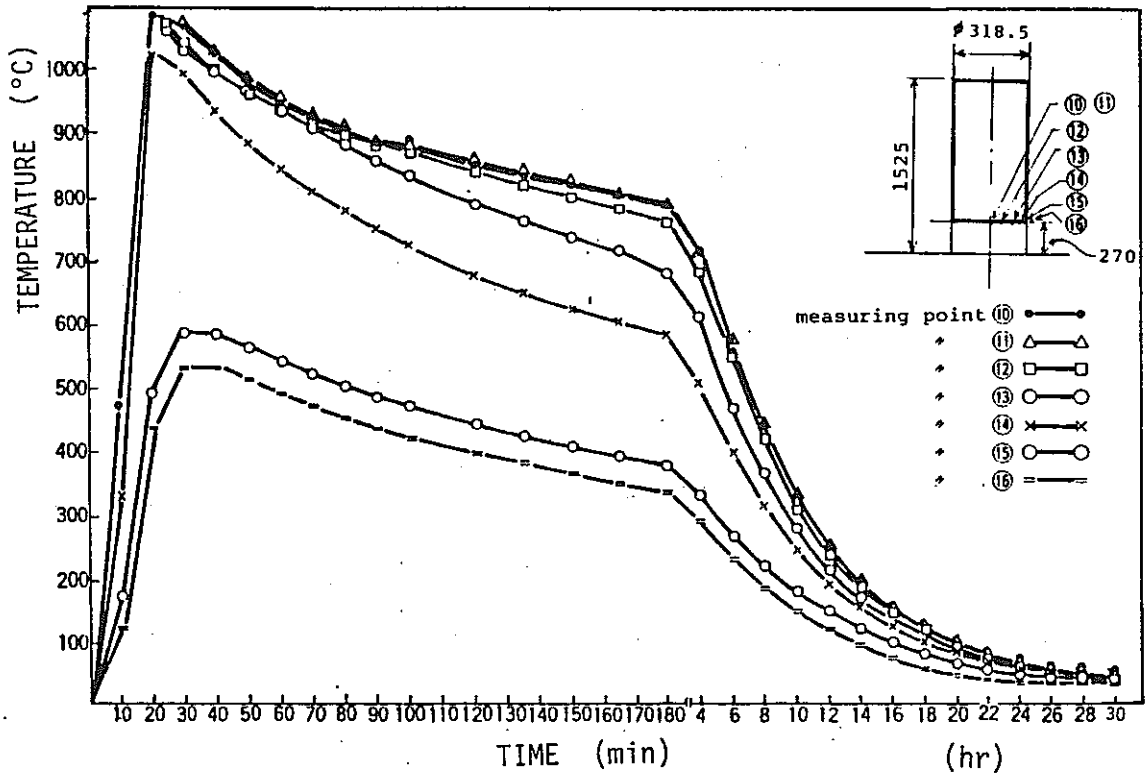
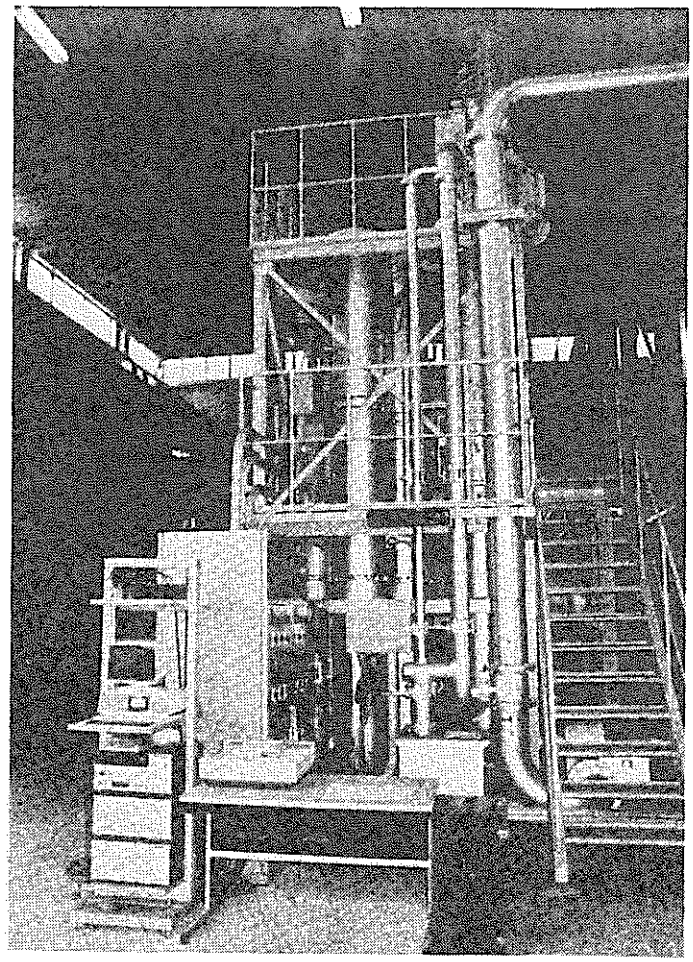


FIGURE 6 Transition of Temperature of Canister and Glass during and after Glass-filling

DEVELOPMENT OF STORAGE TECHNIQUE

Since the canister contains solidified high level radioactive waste which generates decay heat, it should be cooled effectively by which the integrity of canister will be assured in a storage environment. Development of a storage technique has been advanced mainly regarding the air-cooling concept due to cost economy and effect on the canister.

Engineering-scale cold tests have been carried out using one-module test apparatus and a 1/5 scale air-cooling system model. Along with the experimental study, development of a computer code for heat transfer in cooling is now under way.



The photo shows the one-module cooling test apparatus. Three full-scale canisters in which electric heaters are installed are installed in one pit. The different pit sizes are equipped, namely, with a clearance between the pit and canister of 12 mm, 38 mm and 60 mm, respectively.

A series of tests on the steady state of natural or forced convection and transient states in case of blower stop or pit blockade have been conducted. The obtained results are summarized as follows.

1) Forced convection has a higher cooling capacity than natural convection although air flow velocity in the gap is of a similar degree.
2) Natural convection is found to be applicable if suitable clearance is selected.
3) Suitable clearance is 30 ∿ 60 mm in air-cooling, however, it should be selected taking into consideration canister handling problems.
4) Blower stop test shows that the time to reach a critical canister temperature (450°C at the center) is approximately 10 ∿ 20 hours in case of a 1.5 KW/canister.

CONCLUSION

Typical compositions of borosilicate glass have been developed in the form of solidified waste from HLLW generation from the PNC Reprocessing Plant, and they will be characterized by hot laboratory-scale tests at the Chemical Processing Facility (CPF) from the present.

Engineering-scale cold tests until now have shown that the PNC vitrification process — denitration of HLLW with formic acid, vitrification with the Joule-heated ceramic melter and air-cooling storage concept — is feasible. The HLLW Mock-up Test Facility (MTF) based on former R & D activities with ETF and others has just started operation to establish process performance in the total system and remote handling technology, and also to obtain further design data for the HLLW Solidification Pilot Plant.

REFERENCES

1. Techniques for the Solidification of High Level Wastes, Technical Report Series No. 176, IAEA, VIENNA (1977).

2. H. Nagaki, N. Oguino, N. Tsunoda and T. Segawa, Development of Engineering Scale Vitrification Technique at PNC, Proc. Int. Symp. on Ceramics in Nuclear Waste Management held in Cincinnati, Ohio, April 30 - May 2, 1979.

3. T. Zaitsu, E. Inada, N. Sasaki, H. Nagaki and N. Tsunoda, Development of Vitrification Process of the High Level Liquid Waste by the Engineering Test Facility, PNCT-831-81-01 (1981).

4. S. Torata, H. Igarashi, N. Kawanishi, H. Nagaki and N. Tsunoda, Vitrification of High Level Liquid Waste (III) - Research on Glass Composition and Characterization of High Level Waste Glass, PNCT - 81 - 01 (1981).

5. M. Ninomiya, et al., Diopside Glass-Ceramics Material for the Immobilization of Radioactive Wastes, Int. Seminar on Chemistry and Process Engineering for High Level Liquid Waste Solidification held in Jülich, June 1 - 5, 1981 (to be published).