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ZEOLITE VITRIFICATION DEMONSTRATION PROGRAM NONRADIOACTIVE-PROCESS OPERATIONS SUMMARY

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SUMMARY

The Submerged Demineralizer System is a process developed to decontaminate high-activity level water at Three Mile Island by sorbing the activity (primarily Cs and Sr) onto beds of zeolite. Pacific Northwest Laboratory's Zeolite Vitrification Demonstration Program has the responsibility of demonstrating the full-scale vitrification of this zeolite material. The first phase of this program has been to develop a glass formulation and demonstrate the vitrification process with the use of nonradioactive materials. During this phase, four full-scale nonradioactive demonstration runs were completed. The same zeolite mixture being used in the SDS system was loaded with nonradioactive isotopes of Cs and Sr, dried, blended with glass-forming chemicals and fed to a canister in an in-can melter furnace. During each run, the gaseous effluents were sampled. After each run, glass samples were removed and analyzed.

Most of the process difficulties were determined and modifications made during the first run. The major problem area was maintaining the temperature in the connecting section between the feed line and canister between 300 and 400°C to prevent feed bridging. Also, the zeolite drying temperature had to be increased to reduce the water content and thus minimize pressure fluctuations from this water flashing to steam.

During each of the four runs, the gaseous effluents and scrub solutions in the offgas system were sampled. When a set of sintered metal filters was installed after the first run, particulate losses were greatly reduced. The total average particulate melter-system DF was 5×10^6 for the last three runs. After passing through the metal filters, the gaseous effluents were drawn through a condenser and two venturi scrubbers. Based on analyses of the condensate and the two scrub solutions, the of Cs and Sr losses were <0.05% during each of the runs. Gaseous effluents were also sampled to determine offgas compositions, particulate compositions, and decontamination factors for the melter system. The average Cs DF from the feed to the effluent system was measured to be 3×10^7.

The glass product from each of the four runs was sampled and subjected to visual examinations, chemical analysis and Soxhlet leach tests. Visually, the glass varied from sample to sample; most samples from the top of the canisters displayed flecks of alumina-enriched material. However, leach test results were very consistent, regardless of where in the canister the sample was taken. Glass from each of the runs displayed excellent durability during Soxhlet leach tests when compared to test results for borosilicate glass formulations being developed for commercial and defense high-level liquid waste solutions. A complete MCC-1 test is being performed on all of the glass samples, and these results will be issued in a later report. Process equipment similar to that described in this document is being fabricated and installed in a radiochemical cell for a radioactive demonstration of the ZVDP process.

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INTRODUCTION

The cleanup of the high-activity-level water at Three Mile Island (TMI) provides an opportunity to further develop waste management technology. Approximately 3.6 x 10^6 L (790,000 gal) of high-activity-level water at TMI's Unit-2 Nuclear Power Station will be decontaminated at the site with the use of the Submerged Demineralizer System (SDS). In the SDS process, the Cs and Sr in the water are sorbed onto a blend of zeolites that are contained within metal liners (Campbell et al. 1980). One disposal option for this zeolite material is to mix it with glass formers and vitrify it to a borosilicate glass product. The U.S. Department of Energy (DOE) authorized the Pacific Northwest Laboratory (PNL) to take a portion of the zeolites from the SDS and demonstrate, on a full scale,(a) that these zeolites can be vitrified with the use of the in-can melting (ICM) process.

The ICM process, which is used to vitrify high-level radioactive waste, was developed at PNL under the sponsorship of the DOE and its predecessors. In the ICM process, the calcined high-level waste and glass-forming chemicals are fed into a canister in a furnace. The waste is heated and vitrified within the canister. The canister serves as the container for the final waste product.

The TMI Zeolite Vitrification Demonstration Program (ZVDP) includes both nonradioactive and radioactive production-scale demonstrations. The specific objectives of the program are to: 1) establish that the vitrification of zeolites is a feasible method for immobilizing high-activity-level special wastes; 2) characterize the process effluents and the vitrified waste form; and 3) provide a radioactive waste form for further analyses and for possible disposal demonstrations.

This document presents the results of the nonradioactive demonstration. The demonstration consisted of four runs. The objectives of each of these runs was to: 1) verify the design of and demonstrate the ZVDP process;

(a) Full scale is defined as an 8-in.-dia canister filled with ~7 ft of glass.

2) fill one 8-in.-dia canister with ~7 ft of glass product (four total); 3) sample and analyze gaseous effluents to determine compositions, process volatilities and particulate losses; and 4) analyze the glass product.

GLASS DEVELOPMENT

When the ZVDP was conceived, a process temperature limit of 1050°C was imposed for glass formulation studies. This limit enabled PNL to use existing nonradioactive and radioactive ICM furnaces. Glass formulation tests were performed to identify which chemicals must be added to the zeolite so that it would dissolve at 1050°C. If the ratio of zeolite to glass-forming chemicals was sufficiently high to make vitrification an attractive option, additional tests would be performed to evaluate the glass durability in comparison to similar glasses developed for high-level liquid wastes. The reference zeolite was Linde Ionsiv IE-96® (which is IE-95 converted to the sodium form). The composition of this zeolite is $Na_2(AlO_2)_2(SiO_2)_4 \cdot H_2O$.

The results of the first glass-formulation tests are shown in Tables 1 and 2. The compositions in Tables 1 and 2 were initial attempts to determine the zeolite loading and alkali requirements. As shown by the following description and these tables, the glass must be ~12% to 20% alkali (Na_2O, Li_2O and/or K_2O) for the zeolite to dissolve in the glass (glasses 80-195 and 80-206).

TABLE 1. Composition of Glasses with Unpulverized Zeolite

	Composition, wt%				
Oxide	Glass No. 80-195	Glass No. 80-196	Glass No. 80-197	Glass No. 80-198	Glass No. 80-199
B_2O_3	5.84	12.93	--	--	--
CaO	2.92	--	--	10.0	2.0
Li_2O	6.50	--	4.39	--	6.0
Na_2O	10.40	5.76	7.69	5.0	2.0
TiO_2	9.14	--	--	--	--
Zeolite (as received)	65.26	81.31	87.91	85.0	90.0

When heated to 1050°C, compositions 80-195 through 80-199 exhibited the following characteristics:

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- 80-195 became a smooth, transparent amber glass with no undissolved zeolite.
- 80-196 only partially melted and most of the zeolite remained free.
- 80-197 only partially melted and much of the zeolite remained undissolved.
- 80-198 did not melt.
- 80-199 only partially melted.

TABLE 2. Composition of Glasses with Pulverized Zeolite

	Composition, wt%					
Oxide	Glass No. 80-202	Glass No. 80-203	Glass No. 80-204	Glass No. 80-205	Glass No. 80-206	Glass No. 80-206A
B_2O_3	24.20	20.75	17.30	3.35	--	--
CaO	--	--	--	1.68	--	--
K_2O	--	--	--	4.00	5.00	5.00
Li_2O	--	--	--	3.72	5.00	5.00
Na_2O	10.80	9.25	7.70	3.72	12.00	12.00
SiO_2	--	--	--	17.52	--	--
TiO_2	--	--	--	6.00	8.00	8.00
Zeolite (as received)	65.0	70.0	75.0	60.0	70.0	70.0

Glasses 80-202 through 80-206A (see Table 2) exhibited the following characteristics at the temperatures indicated:

- 80-202 melted completely at 1150°C and became very viscous; no undissolved zeolite was detected.
- 80-203 melted at 1150°C; much of the zeolite remained undissolved in the glass.
- 80-204 melted at 1150°C; much of the zeolite remained undissolved in the glass.

- 80-205 melted completely at 1100°C and became very viscous. A few large air bubbles and many small air bubbles were trapped in the glass.
- 80-206 melted completly at 1050°C with a viscosity of ~150 poise. The glass was a transparent amber with some white crystalline material; there was no undissolved zeolite.

Glass 80-206A had the same composition as 80-206 but the zeolite was not pulverized. The glass melted at 1050°C, but much of the zeolite remained undissolved in the glass.

With glasses 80-206 and 80-206A, the results indicated that pulverizing the zeolite helped it to dissolve in glass. However, since pulverizing the zeolite would be a costly and difficult process, we decided to continue the glass-formulation tests with unpulverized zeolite. We also decided to load the zeolite with nonradioactive isotopes of cesium and strontium for the remainder of the glass-formulation tests so that leach tests could be performed with the products from the tests.

Table 3 presents the results of the third series of glass-formulation tests. These tests were completed with zeolite that had been loaded with nonradioactive cesium so that leach tests could be conducted. Glasses 80-213

TABLE 3. Composition of Glasses with Cesium-Doped Zeolite

	Composition, wt%					
Oxide	Glass No. 80-213	Glass No. 80-214	Glass No. 80-215	Glass No. 80-216	Glass No. 80-217	Glass No. 80-218
B_2O_3	5.84	5.04	4.20	5.0	--	13.85
CaO	2.92	2.52	2.10	--	--	--
K_2O	--	--	--	--	5.0	--
Li_2O	6.50	5.61	4.68	5.0	5.0	--
Na_2O	10.40	8.98	7.48	8.0	10.0	16.15
TiO_2	9.14	7.89	6.57	7.0	10.0	--
Zeolite with Cesium	65.26	70.0	75.0	75.0	70.0	70.0

and 80-214 were melted at 1050°C; whereas, glasses 80-215 through 80-218 were melted at 1065°C. These glasses exhibited the following characteristics:

- 80-213 became a transparent amber glass with some white crystalline material (probably titanium); no undissolved zeolite was detected.
- 80-214 became a transparent amber glass with very little crystalline material; no undissolved zeolite was detected.
- 80-215 became a transparent amber glass with no crystalline material; no undissolved zeolite was detected.
- 80-216 became a transparent, dark amber glass with many air bubbles trapped in the glass; no undissolved zeolite was detected.
- 80-217 became a transparent amber glass with a great deal of white crystalline material; no undissolved zeolite was detected.
- 80-218 became a greenish-yellow glass; some zeolite could be seen in the glass.

Table 4 shows the results of the leach tests with these glasses that contained the cesium-doped zeolite. Two of these glasses (80-215 and 80-216) had a 75% zeolite loading, a good appearance, and an excellent leach rate when compared to Soxhlet leach tests for reference commercial borosilicate glass 76-68 (6 x 10^{-5} g/cm^2-day) (Mendel et al.) and defense borosilicate glass TDS-211 (8-14 x 10^{-5} g/cm^2-day) (Lukacs et al.). Glass 80-216 was selected as the better glass because of its slightly better leach rate and fewer chemical additives.

TABLE 4. Soxhlet Leach Test Results of Glasses with Cesium-Doped Zeolite

Glass	wt% Lost	g/cm^2-day
80-213	1.80	6.9 x 10^{-5}
80-214	1.39	5.4 x 10^{-5}
80-215	0.99	3.8 x 10^{-5}
80-216	0.94	3.6 x 10^{-5}
80-217	1.18	4.5 x 10^{-5}
80-218	1.14	4.4 x 10^{-5}

The selected glass was produced by melting the zeolite with a chemical mixture, which consisted of $Na_2B_4O_7 \cdot 10\ H_2O$ (Borax, 32 wt%), Na_2CO_3 (23 wt%), Li_2CO_3 (29 wt%), and TiO_2 (16 wt%). For the ZVDP process, these chemicals were agglomerated into particles approximately the same size (-20 to +60 mesh) as the zeolite for feeding to the melter.

By the time the nonradioactive demonstrations were initiated, the TMI SDS process had been modified to use a mixture of IE-96 with a high-alumina zeolite (Linde Ionsiv A-51®). The composition of A-51 is $Na_2(AlO_2)_2(SiO_2)_2 \cdot 4.5H_2O$. The first demonstration test was made with IE-96, but additional glass formulation studies were required for the subsequent runs. Because of the alumina content of the new zeolite, the studies showed that either the process operating temperature would have to be increased, or the waste loading would have to be reduced for the A-51 to dissolve. The exact proportion of IE-96 to A-51 had not been determined; therefore, glass formulations had to be developed for a range of zeolite mixtures. The first phase of these studies was to identify the waste loading in the glass for several different mixtures. There was some concern that a different glass formulation would be required for each zeolite mixture. For 1:1, 2:1 and 3:1 mixtures of IE-96 to A-51, glasses were made with 60, 65 and 70% loadings of zeolite with the same chemical agglomerate (which had already been procured) plus additional silica. Soxhlet leach tests were conducted to evaluate the durability of these glasses. The results are presented in Table 5. Again these results compared favorably with results for the reference commercial and defense waste borosilicate glass compositions.

TABLE 5. ZVDP Glass Soxhlet Leach Test Results (g/cm^2-day)

Ratio IE-96:A-51	Waste Loading 60%	65%	70%
1:1	3.6×10^{-5}	N/A	3.0×10^{-5}
2:1	2.9×10^{-5}	2.9×10^{-5}	2.8×10^{-5}
3:1	3.4×10^{-5}	3.3×10^{-5}	1.2×10^{-5}

Fortunately, the Soxhlet test also indicated that the glass durability as measured by Soxhlet leach tests was not greatly affected by the zeolite combination or the waste loading. However, the glass was extremely viscous at 70% zeolite loading, which may not allow the volatile gases to escape during melting. This would leave voids in the glass. Results also showed that the glass appearance was affected by the loading. There were small amounts of undissolved A-51 in the 65% zeolite-loaded glasses and a larger amount in the glasses with 70% zeolite loading. However, only the visual quality seemed to be affected, not the durability. Since neither the durability nor visual quality was affected at a 60% waste loading for the different zeolite mixtures tested, this waste mixture was tentatively selected as the glass formulation. One last series of tests was completed with different mixtures of IE-96 and A-51 to verify these results. These results are shown in Table 6.

TABLE 6. Soxhlet Leach Tests Results (60% Zeolite Loadings)

IE-96:A-51	wt% Lost	g/cm^2-day
1:1	1.30	5×10^{-5}
3:2	0.84	3.2×10^{-5}
2:1	0.90	3.5×10^{-5}
5:2	0.91	3.5×10^{-5}

Each of the above glasses had a viscosity of <100 poise and no undissolved zeolite at 1050°C. Fortunately, a separate formulation was not required for each combination of IE-96 and A-51. A 60% zeolite loading that had the original chemical agglomerate with additional silica (three parts agglomerate to one part silica) was selected as the glass formulation for the remainder of the process verification tests.

PROCESS DEVELOPMENT

Before designing the ZVDP system equipment, it was necessary to determine whether the process would have a slurry or a solid feed stream. The SDS liners would be shipped wet to PNL. If the zeolite caked and had to be slurried to be removed from the liner, a spray calciner would have to be coupled to the ICM. Fortunately, in tests at PNL, it was determined that when the zeolite was thoroughly dried (bed temperature of 250°C), it became a free-flowing solid that could be easily poured out of the liner.

To make a glass product, it is necessary that glass-forming chemicals be mixed with the zeolite. Since the zeolite could be handled as a dry solid, a decision was made to mix the zeolite and dry, agglomerated glass formers before their introduction into the canister. The major reasons for this were: 1) only one feed stream would need to be metered into the canister; 2) the feed added to the canister would always be mixed in the proper portions; and 3) the resultant glass would be homogeneous. Thus, a vessel was designed in which the zeolites and glass formers could be mixed and fed to the ICM.

To achieve the mixing of glass former and zeolite, a weighed amount of zeolite had to be added to this mixer/feeder vessel. This was accomplished by fabricating a handling fixture designed to pick up and invert either the SDS liner or the mixer/feeder vessel. The SDS liner was inverted over the mixer/feeder vessel, and the two were connected by an adaptor. Then, by using a load cell on the handling fixture, a weighed amount of zeolite was added to the mixer/feeder vessel directly from the SDS liner. A weighed amount of glass formers corresponding to the weight of added zeolite was batched into the same vessel, and the mixer/feeder was tumbled end over end by means of the handling fixture until the mixture was homogeneous. A laboratory test with a plexiglass mixing vessel demonstrated that thorough mixing without any stratification of materials was observed in a few minutes. The mixture remained homogeneous after tumbling was stopped, and the vessel was allowed to sit. The mixer/feeder vessel was then inverted and used as the feed supply for the vitrification system (Figure 1). The feed was metered by means of a star

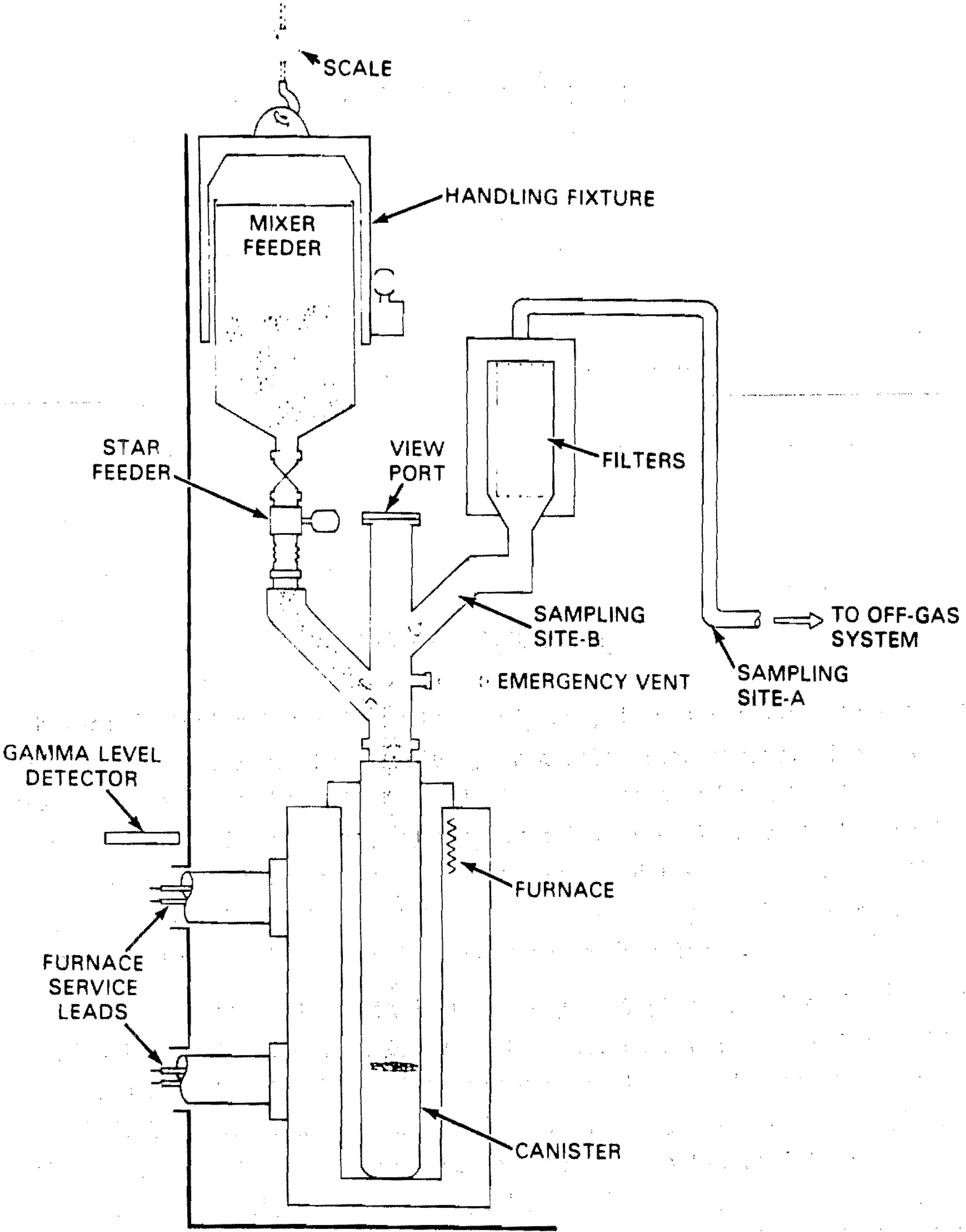


FIGURE 1. Zeolite Vitrification System

valve that had a variable-speed motor. The feed fell through the connecting piping into the canister where the glass was formed. The canisters were fabricated from Sch. 40 8-in. stainless steel pipe.

The equipment interface between the feed piping and the canister (referred to as the canister adaptor) was discovered to be of critical importance. This canister-adaptor must be maintained below 400°C to prevent melting of the glass formers on the walls as they are fed into the canister. Bridging will develop if melting occurs and will eventually block feed from entering the canister. A steam jacket around the canister adaptor prevents this melting. Maintaining the canister adaptor above 100°C was also important because of the offgas water content. Condensation of the water could occur below 100°C and will also cause bridging to occur. The connecting piping and offgas filter system were also electrically heated to prevent condensation problems.

Since the ZVDP process is a solid-feed system, an offgas system was designed with a first-stage particulate removal device. Initially, this was a cyclone separator; however, this was not efficient for this process and was replaced with sintered metal filters.

The filter unit is made up of three 65-μm sintered Inconel® filters that are pulsed about every 20 min to return accumulated dust back to the canister. Two air-driven vibrators were also incorporated in the system to assist in removing any material held up in the connecting piping.

The offgas stream, after passing through the filters, passed through a condenser and two venturi scrubbers before being discharged to the stack. The system, as fabricated, is shown in Figure 2.

The furnace used to heat the canister for the nonradioactive runs was PNL's existing full-scale ICM (see Figure 3). The ICM is a vertical, resistance-heated, 225-kVA, 480-V, 60-cycle, three-phase system. It has six heating zones with four silicon-carbide heating elements in each zone and a maximum temperature of 1200°C. The working cavity is 33 in. x 33 in. x 90 in.

® Tradename of Huntington Alloys Division of the International Nickel Company, Inc., Huntington, West Virginia.

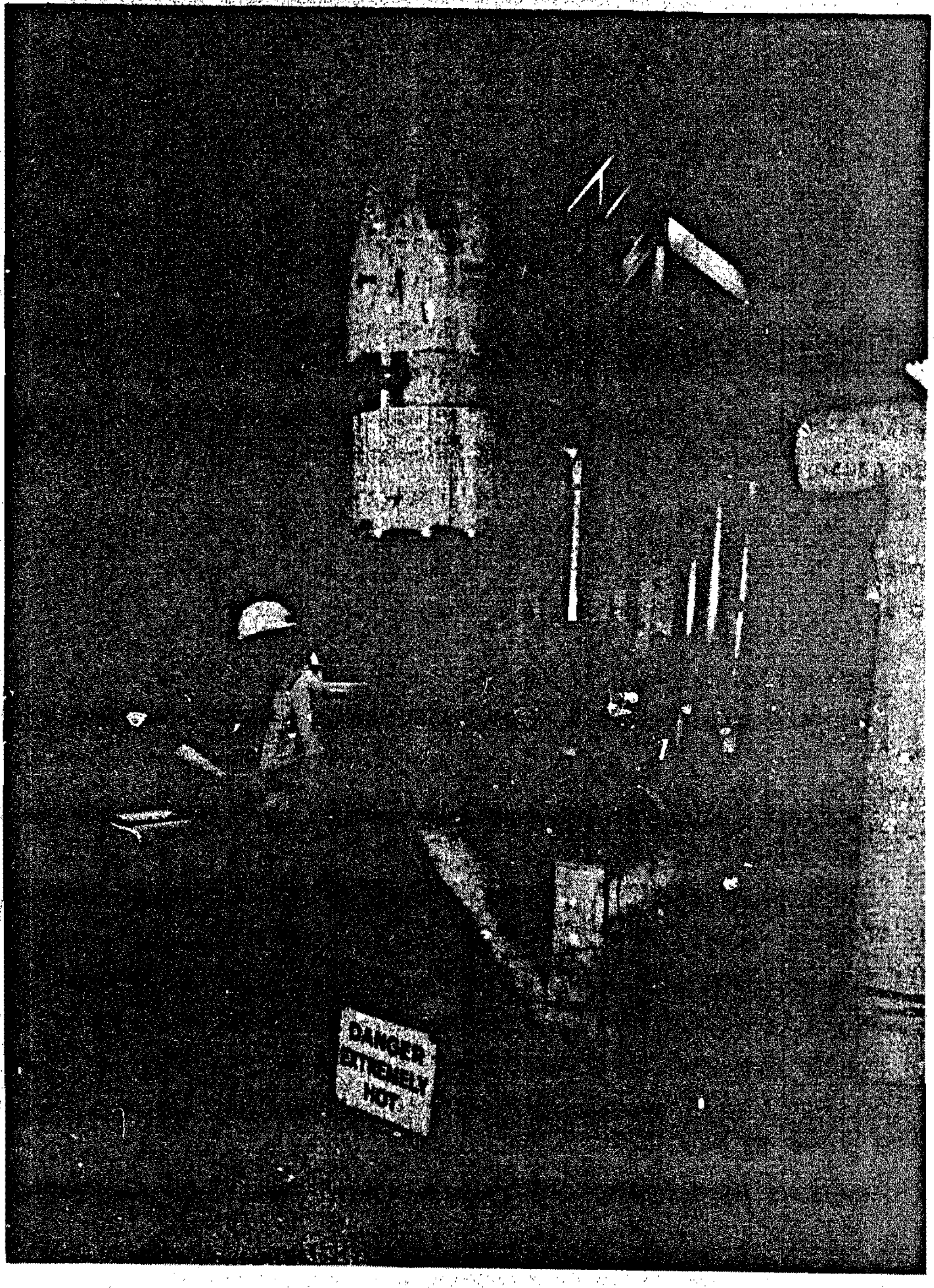


FIGURE 2. Zeolite Vitrification Nonradioactive Process Equipment

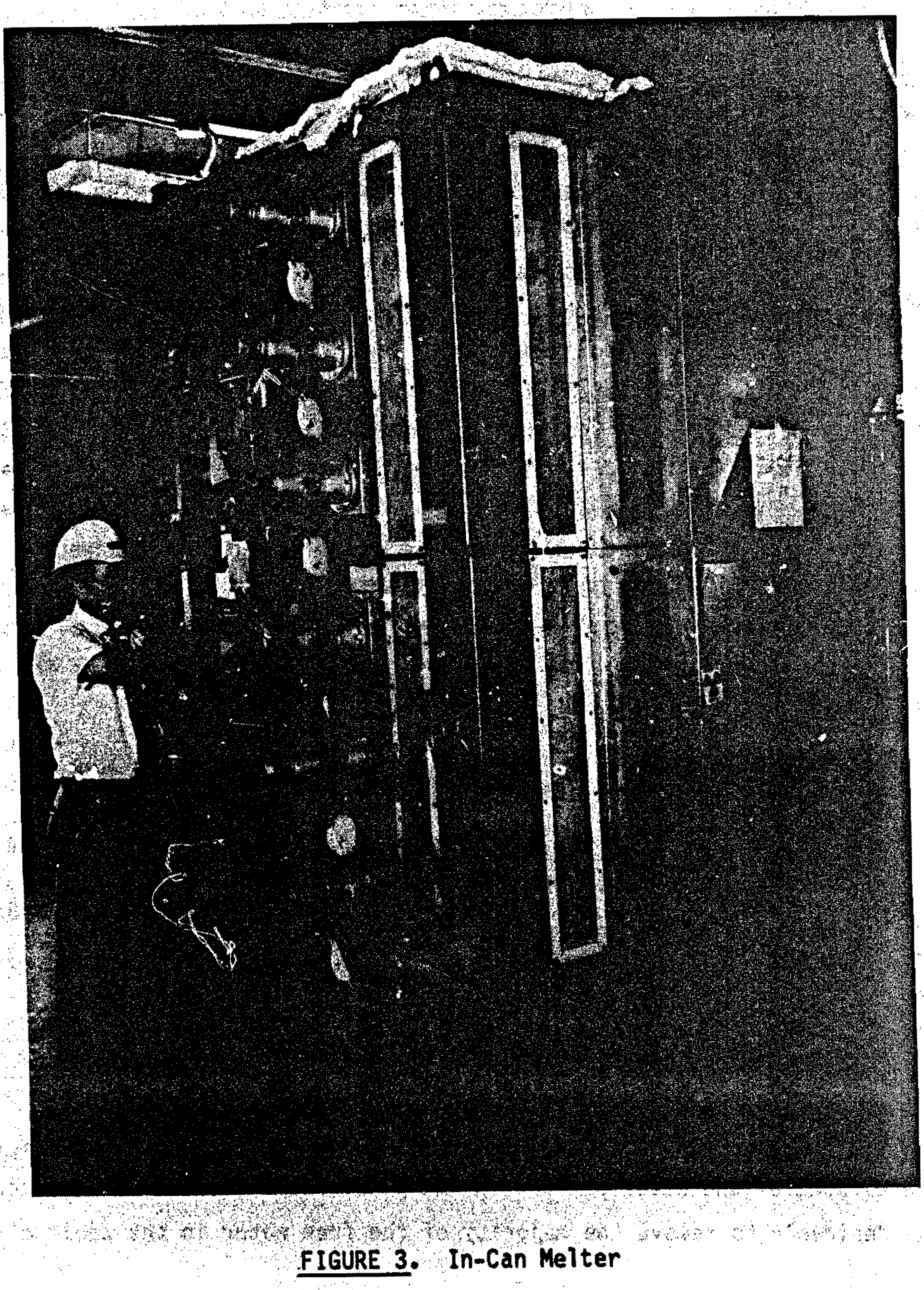


FIGURE 3. In-Can Melter

ZEOLITE PREPARATION

To obtain the maximum benefit from the nonradioactive demonstrations, it was necessary to simulate as closely as possible the zeolite that would be received from TMI. Thus, the zeolites which were being used at TMI for the SDS process were procured. Also, a liner identical to those being used at TMI was fabricated (Figure 4). The liner was filled with 8 ft^3 of zeolite material. Due to the heat released when the zeolite is wetted, the liner was first filled with water, and then the zeolite was slowly added to the liner while the water overflowed to a drain. To simulate the SDS flowsheet, calculated amounts of $CsNO_3$ and $Sr(NO_3)_2$ were dissolved in 50 gal of water. This solution was passed through the liner to load the nonradioactive Cs and Sr onto the zeolite. For the first demonstration, this solution was prepared with the equivalent of about 60,000 Ci of Cs and 2,000 Ci of Sr (SDS flowsheet values). For the subsequent demonstrations, the solution was changed to have the equivalent of about 120,000 Ci of Cs and 2,000 Ci of Sr to account for the nonradioactive isotopes of Cs present in the TMI water, which will also be loaded onto the TMI zeolite. The composition of the loaded zeolites for each run is given in Table 7.

TABLE 7. Loaded Zeolite Description

	Run 1	Run 2	Run 3	Run 4
Composition	100% IE-95	67% IE-96 33% A-51	60% IE-96 40% A-51	60% IE-96 40% A-51
Drying Temperature	~100°C	250°C	350°C	350°C
Water Content	14%	10%	7%	~7%
Cs Content (wt%)	0.15	0.40	0.83	0.64
Sr Content (wt%)	0.02	0.05	0.04	0.03

After the zeolites had been loaded, the damp zeolite was dried. Because of the carbonates and water present in the glass-forming chemical agglomerate, it was desirable to remove the majority of the free water in the zeolite to

FIGURE 4. TMI SDS Liner (Typical)

reduce the volume of gaseous effluents generated when the zeolite/glass formers mixture was vitrified. During the first nonradioactive demonstration, the zeolite was not dried sufficiently. The zeolite dumped in the mixing vessel and evntually plugged the connecting piping, and the gaseous effluents pressurized the process. A Thermal Gas Analysis (TGA) of the IE-96 and A-51 demonstrated that most of the moisture was driven off when the zeolite was heated to 250°C. For the remaining runs, thermocouples were installed in the zeolite, and the liner was placed in the ICM furnace and heated to 250°C for Run 2 and 350°C for Runs 3 and 4.

After the zeolite had been dried and cooled to room temperature, the liner was inverted on the mixer feeder, and the amount of zeolite required to produce 7 ft of glass in one 8-in.-dia canister was emptied into the mixer. Then, the required amounts of glass-forming chemicals were added to the mixer. This mixture was tumbled for 2 hours to provide the feed for the ZVDP process.

OPERATIONS SUMMARY

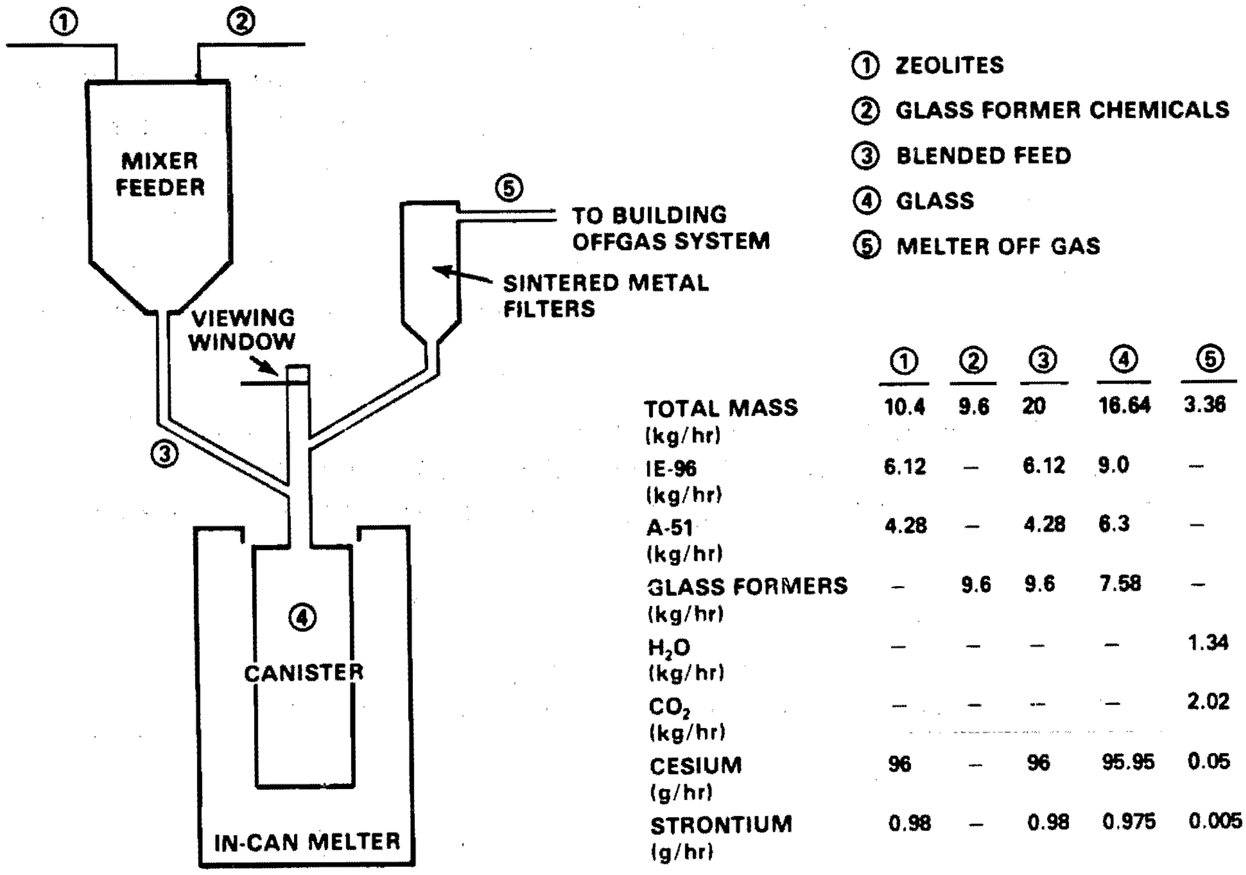
Four runs were completed during the nonradioactive demonstration phase of the ZVDP. For each run, a mixture of zeolites was blended and added to a fabricated liner. The zeolite mixture was loaded with nonradioactive isotopes of Cs and Sr. Then, the loaded zeolite was dried to bed temperatures of up to 300°C, emptied into the mixer/feeder, and blended with the appropriate amounts of glass-forming chemicals. The mixer/feeder was not large enough to hold the entire contents of the liner in addition to the glass formers after the SDS flowsheet was modified to include the A-51 zeolite. Therefore, amounts of zeolite and glass formers were individually weighed and added to the mixer/feeder.

Several process conditions were changed during the course of the nonradioactive demonstrations (see Table 8). Since a process temperature limit of 1050°C was imposed for glass formulations, a stainless steel canister was used for each of the runs. The flowsheet used during Runs 3 and 4 is shown in Figure 5. These runs were based on IE-96 to A-51 ratio of 3:2, which is the probable composition in the SDS liners. The feedrate varied somewhat during each of the runs and was dependent upon the level of glass in the canister. It was possible to maintain a feedrate of 20 kg/h to a canister height of up to ~6 ft of glass while the top-surface temperature of the glass remained

TABLE 8. Process Conditions During Nonradioactive Demonstrations

	Run 1	Run 2	Run 3	Run 4
Furnace and Canister Temperature	1050°C	1050°C	1050°C	1050°C
Average Feedrate	20 kg/h	10 kg/h	10 kg/h	10 kg/h
Maximum Feedrate	29 kg/h	25 kg/h	22 kg/h	20 kg/h
Annealing Time(a)	1 h	1 h	4 h	6 h
Canister Length	8 ft	9 ft	9 ft	9 ft

(a) Annealing times were increased for the purpose of glass homogeneity.



	①	②	③	④	⑤
TOTAL MASS (kg/hr)	10.4	9.6	20	16.64	3.36
IE-96 (kg/hr)	6.12	–	6.12	9.0	–
A-51 (kg/hr)	4.28	–	4.28	6.3	–
GLASS FORMERS (kg/hr)	–	9.6	9.6	7.58	–
H_2O (kg/hr)	–	–	–	–	1.34
CO_2 (kg/hr)	–	–	–	–	2.02
CESIUM (g/hr)	96	–	96	95.95	0.05
STRONTIUM (g/hr)	0.98	–	0.98	0.975	0.005

FIGURE 5. ZVDP Process Flowsheet

above 900°C. At a canister fill height greater than 6 ft, slower feedrates were required due to greater heat losses at the opening of the furnace.

The first run was terminated after 3 hours because feed was bridging across the canister adaptor. When the adaptor was examined, feed had actually vitrified in the adaptor. The temperature in this section was too hot, so a cooling jacket was fabricated. When the run was restarted, it was again terminated after 3 hours because feed was bridging across the adaptor. This time, the bridge consisted of a clump of damp feed. Cooling water in the jacket was keeping the adaptor temperature too cold; and moisture was collecting on the walls, causing the feed to clump to the adaptor walls. The run was restarted with steam as the canister adaptor coolant. A vibrator was also installed on the feed line to eliminate the bridging. This was successful, and bridging has not been a problem since.

Another problem discovered during the first run was that the star feeder (used to meter feed to the canister) fed in batches, which pressurized the offgas system when steam and CO_2 was released as the feed hit the melt surfaces. The steam condensed in the feed lines and the feed clumped. The star feeder was modified to reduce the volume of the feed batches. The feed and offgas lines were insulated and heated with electric heaters to eliminate condensation problems.

During the first run, the process offgases were drawn by vacuum through a cyclone for particulate removal, then through a condenser and two venturi scrubbers. After the run, it was discovered that 5% of the feed processed had been lost to the offgas system. As a result, the unit was replaced with a bank of three sintered metal filters. This greatly reduced the particulate losses during the subsequent runs. Sample filters were installed at two points in the process offgas system to measure the particulate loss, and the particulates were analyzed to determine their composition.

The condensate and scrub solutions were sampled hourly during each of the runs and analyzed for Cs and Sr. Less than 1 g of Cs and 1 g of Sr were found in the offgas system during each of these runs. This is less than 0.5% volatility or entrainment for these elements. A side stream of the process effluents was drawn through a sampling apparatus to determine the composition of the offgas.

During the second run, the feedrate was increased from 20 kg/h to 25 to 30 kg/h to establish an upper limit on feeding. The higher rates caused the melt to begin to "boil" and foam. A maximum feedrate of 20 kg/h was set for the last two runs and foaming was never again observed. During the four runs, the feedrate was reduced as the canister was filled, due to dropping canister temperatures. The rate was reduced to 1 to 2 kg/h at the end of the runs. After the feed was shut off, the glass was annealed by maintaining the furnace at 1050°C for a period of time. During Run 2, a 1-hour annealing time was found to be insufficient, as there was unmolten material at the top of the canister. A 4- to 6-hour annealing time proved to be sufficient. The surface of the melt was glassy. Although some undissolved particles were detected at the top of the melt, this was attributed to: 1) formation of slag in the ICM process, and 2) the increased alumina from the A-51 zeolite. The glass durability was not affected; if anything it was slightly improved. (These results are discussed in more detail in the next section.)

GLASS CHARACTERIZATION

After each of the demonstrations, core samples of the glass product were taken from the top, middle and bottom of the canisters. These glass samples were subjected to visual inspections, chemical analyses, and Soxhlet leach tests. In addition, one glass sample from each canister will be subjected to an MCC-1(a) leach test. The chemical analyses for Run 1 are given in Table 9. This run was performed with all IE-96. Visually, these samples were of good quality and no undissolved material was detected.

The second run was completed with a 2:1 mixture of IE-96 and A-51. The bottom and middle samples were of good quality, and no undissolved material was detected. The top sample was lighter in color, and undissolved material was observed. Unmolten material was seen at the top of the melt. The canister was heat-soaked for 1 hour at the end of this run. This heating was obviously insufficient, and longer soaking times were used for subsequent runs. This helped but did not eliminate the presence of this undissolved material. The chemical analyses of the glass from Run 2 are presented in Table 10.

TABLE 9. ZVDP-1 Glass Product Analysis

	wt%		
Component	Top	Middle	Bottom
Al_2O_3	10.4	13.4	10.2
B_2O_3	7.1	4.4	7.0
Fe_2O_3	3.3	1.9	3.0
Li_2O	5.7	4.2	5.7
Na_2O	12.3	13.0	12.0
SiO_2	42.0	46.0	41.0
TiO_2	9.9	7.0	9.2
Cs_2O	0.24	0.41	0.22

(a) A test developed by the PNL Materials Characterization Center.

TABLE 10. ZVDP-2 Glass Product Analysis

Component	wt% Top	wt% Middle	wt% Bottom
Al_2O_3	10.4	13.4	10.2
B_2O_3	7.1	4.4	7.0
Fe_2O_3	3.3	1.9	3.0
Li_2O_3	5.7	4.2	5.7
Na_2O	12.3	13.0	12.0
SiO_2	42.0	46.0	41.0
TiO_2	9.9	7.0	9.7
Cs_2O	0.24	0.41	0.22

Runs 3 and 4 were completed with a 3:2 mixture of IE-96 and A-51. Flecks of unmolten material were detected in the top samples. The chemical analyses (Table 11) show a higher alumina content in these samples, which would account for these flecks.

TABLE 11. ZVDP-3 and -4 Glass Product Analysis

Component	wt% Run 3 Top	Run 4 Top	Run 3 Middle	Run 4 Middle	Run 3 Bottom	Run 4 Bottom
Al_2O_3	14.0	14.60	12.9	14.00	12.9	14.30
B_2O_3	3.7	4.90	4.4	5.30	4.3	4.88
$CaO^{(a)}$	---	0.85	---	0.96	---	0.94
Fe_2O_3	1.8	1.60	2.1	1.86	2.1	1.82
Li_2O	4.4	4.89	4.7	4.57	4.6	4.64
Na_2O	15.3	16.30	15.5	15.20	15.3	15.90
SiO_2	46.6	46.90	42.6	44.80	42.8	45.40
TiO_2	6.5	6.95	7.6	7.26	7.4	7.04
Cs_2O	0.7	0.46	0.64	0.44	0.64	0.46
SrO	0.03	0.03	0.03	0.03	0.03	0.03

(a) Impurity not detected in Run 3.

The undissolved material detected in the top samples from Runs 2 and 3 and 4 were partly attributed to the presence of alumina in the A-51. However, one feature of the ICM process is the formation of a durable layer of "slag" at the top of the melt. This slag layer can be reduced by the addition of extra glass-forming chemicals at the end of the run. However, this addition would reduce the glass durability, and thus was not attempted. The glass durability was evaluated by completing Soxhlet leach tests on the glass product samples. These results are shown in Table 12 (the numbers 1 through 4 indicate the particular runs).

As can be seen, the test results were very consistent. The glass showed good durability regardless of the zeolite mixture used or the location at which the sample was taken. The top samples from Runs 3 and 4 show the best test results. This was expected due to the slight enrichment in Al_2O_3. As

TABLE 12. ZVDP Soxhlet Leach Test Results

Sample	wt% Lost		g/cm^2-day	
ZVDP-1--Top	1.29		4.97×10^{-5}	
ZVDP-1--Middle	1.31		5.04×10^{-5}	
ZVDP-1--Bottom	1.09		4.20×10^{-5}	
ZVDP-2--Top	1.02		3.93×10^{-5}	
ZVDP-2--Middle	1.15		4.43×10^{-5}	
ZVDP-2--Bottom	0.96		3.70×10^{-5}	
ZVDP-3--Top(a)	0.82	0.73	3.16×10^{-5}	2.81×10^{-5}
ZVDP-3--Middle	1.15	0.99	4.43×10^{-5}	3.81×10^{-5}
ZVDP-3--Bottom	1.29	0.70	4.97×10^{-5}	2.70×10^{-5}
ZVDP-4--Top	0.78	0.79	3.00×10^{-5}	3.04×10^{-5}
ZVDP-4--Middle	0.90	1.12	3.47×10^{-5}	4.31×10^{-5}
ZVDP-4--Bottom	0.82	1.03	3.16×10^{-5}	3.97×10^{-5}

(a) Duplicate tests were completed for the samples from Runs 3 and 4.

previously mentioned, samples from all of the runs will be subjected to MCC tests for quality evaluation and comparison with other waste forms. This data will be issued as a separate publication at a later date.

OFFGAS STUDIES

Offgas and effluent characterization studies were established to support the ZVDP. The purpose of these studies was to provide basic offgas engineering data around which an effective offgas processing system could be designed for any future solidification facility that would utilize ZVDP technology. The scope of these studies includes: 1) establishing the gaseous composition of the process exhaust; 2) identifying the pathways for effluent escape; and 3) quantifying melter effluent losses.

The effluent characterization studies conducted during nonradioactive testing were primarily concerned with the stable elemental substitutes for the radiologically important isotopes of ^{137}Cs, ^{134}Cs, ^{90}Sr, ^{14}C, and ^{3}H, which will be present in TMI-generated waste zeolite. The results of these studies would be generic to other ICM systems in that all classes of effluents, including volatile, semivolatile and nonvolatile matter, were investigated.

SAMPLING SYSTEM

Sampling site selection was based upon the need to obtain representative samples and the desire to locate the sampling site as close to the process source (melter) as was physically possible. These conditions were most closely satisfied by establishing the primary sampling site at a process line elbow located ~6 ft from the in-can melter feeding and exhaust line lid, or "tree." In terms of the offgas line schematic illustrated in Figure 1, this sampling site, designated by "A," is situated at the end of a 5-ft straight run of melter exhaust line downstream from the particulate removal device, which was a cyclone for the first run and a set of sintered metal filters for the subsequent runs.

An auxiliary sampling site ("B") was also established in the tree assembly (Figure 1). This site, upstream of the particulate removal device, allowed effluents to be sampled directly above the melter.

Sampling of the process exhaust was accomplished with the system illustrated in Figure 6. A tapered 1/4-in.-dia stainless-steel sampling nozzle,

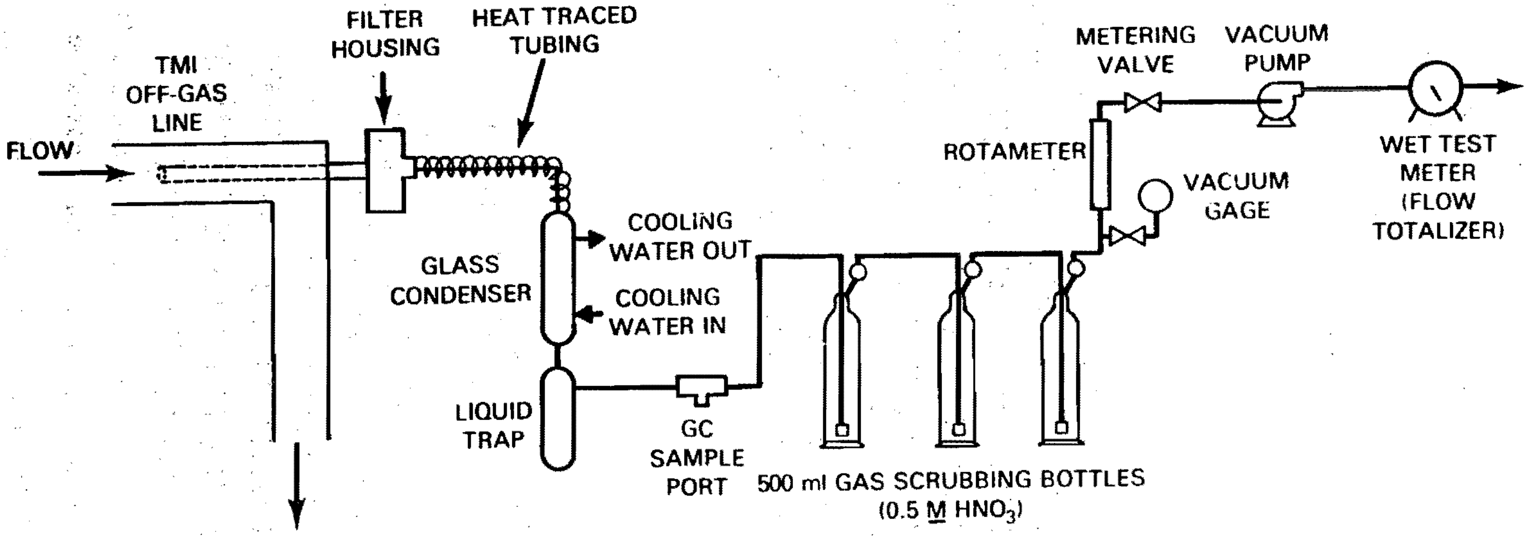


FIGURE 6. Offgas Effluent Sampling System

located along the axis of the 2-in.-dia process line, allowed samples to be extracted upstream from the turbulence created by elbows (A) or bends (B) in the offgas line. The sampled gas and all entrained particles moved along this uniform-diameter sampling nozzle directly to a commercially available filter. This filter was located as close as physically possible to the process line and along a common central axis defined by the collection tube and the process line itself, thereby ensuring a straight, short trajectory to the filter. The filtered gas was then transferred via heat-traced tubing to a condenser and three gas-washing bottles in series. Gas samples required for offgas compositional analysis were extracted after the condenser at the port labeled GC in Figure 6. The volumetric sampling rate of this system was always adjusted to match the sample nozzle inlet velocity to that of the average velocity of the offgas stream.

LABORATORY ANALYSIS

Analytical results generated by this study were of two general types: 1) those pertaining to sample composition, and 2) those relating to particle-size distributions. Compositional analyses of particulate matter, condensate and scrub solutions were conducted using emission spectrometry, atomic adsorption, neutron activation, and x-ray fluorescent analytical techniques. The noncondensable process exhaust gas composition was routinely established with the use of a gas chromatograph. The data generated with this instrument provided quantitative information with regard to CO, CO_2, N_2, O_2 and H_2. In addition, the average water loading of the process exhaust was also established through use of condensate sample data.

Particle size analysis was conducted by scanning electron microscopy (SEM). The central portion of particulate filters was examined under 1000X magnification with the SEM instrument. Various magnified regions of individual filters were then photographed. The particles appearing in these magnified photographs were subsequently sized by an automated particle size analysis system.

RESULTS

Gross process entrainment was measured with glass depth filters at sampling site B during the first two runs. The results obtained from these studies are summarized in Table 13. If it is assumed that all entrained particulate matter was carried over into the offgas system (which certainly was not the case during the second cold run), then melter decontamination factors (DFs) can be estimated from the measured data. These estimated DFs appear in Table 13. During the second cold run, particulate sampling was conducted at both the primary and auxiliary sampling sites, which allowed filter assembly DFs to be estimated from the combined data. These values are also included in Table 13.

TABLE 13. Results of Melter Entrainment Measurements

			Average Rates		Particle Loading, g/L		DF	
Time	Date	Run No.	Feeding, kg/h	Flow, scfm	A	B	Melter	Filter
10:20 12:15	7/23/81	1	17.8	4	---	0.015	170	---
08:10 09:00	8/06/81	2	14.5	4	6×10^{-7}	0.017	130	3×10^{4}
09:31 10:05	8/06/81	2	20.5	4	6×10^{-7}	0.024(a)	130	4×10^{4}

(a) Entrained matter falling back from the sintered metal filter housing contributed to this value in an undetermined way.

The composition of the entrained matter collected at sampling point B was analyzed and found to be compositionally enriched in agglomerate, but was otherwise quite comparable to the mixed feed. Table 14 compares the composition of representative particulate samples to that of the feed. These data further suggest low process-induced Cs volatility rates, which is of particular importance with regard to this demonstration program.

Particulate size analysis of process-generated aerosols were conducted on samples collected at sampling site A during the last three cold runs. The basic empirical parameters extracted from these size distributions are

TABLE 14. Compositional Comparison of Melter-Entrained Matter and Feed

Element	wt% Aerosol-1	 Aerosol-2	 Feed	Agglomerate Component
Al	2.1	1.9	6.7	
B	4.4	5.3	0.98	Yes
Ba	0.021	0.016	0.039	
Ca	0.22	0.18	0.26	
Fe	0.54	0.39	1.1	
Li	5.7	5.7	1.8	Yes
Mg	0.04	---	0.17	
Na	8.7	9.7	8.7	
Si	5.8	5.2	17.4	
Sr	0.038	0.026	0.029	
Ti	8.0	8.3	3.3	Yes
Zn	0.23	0.09	0.04	
Cs	0.17	0.14	0.31	

summarized in Columns 4 through 9 of Table 15. The major assumption used in deriving these parameters is that of particle sphericity. In addition, the calculated particle loading data, also included in this table, assume a uniform particle distribution across the filter as well as an average density of particulate matter of 0.66 g/cm^3. The bias in these loading calculations, if any, should be high, providing for an overestimate of aerosol concentrations. Total system (process and filter) particulate DFs, based upon process feeding data and on an average offgas flowrate of 4 scfm, were also derived from the above offgas loading figures and appear in Column 12 of Table 15. It should be kept in mind that the loading and DF values listed in Table 15 are semi-empirical in nature and were not directly measured. However, the assumptions used in their derivation are all quite reasonable and, above all, conservative.

The actual Cs content of these "massless" filter samples had to be analyzed with neutron activation analysis techniques. Table 14 presents the results obtained from these analyses. The curie loading of the filter and the offgas stream was calculated on the basis of a 2:1 radioactive-to-stable Cs

TABLE 15. Melter System Particulate Emission Characteristics

Experiment	Date	Sampling Period	Mean Dia, µm		Median Dia, µm		Maximum Dia, µm	% <1 µm	Loading		System DF
			Dia	Vol.	Dia	Vol.			#/L	µg/L	
Run 2	8/06/81	08:36 to 10:35	3.20	5.24	2.5	12.0	19.5	11.6	1×10^4	0.60	4×10^6
Run 3	9/02/81	10:33 to 14:52	1.95	5.00	1.0	14.5	24.5	51.1	3×10^4	1.4	2×10^6
Run 3	9/02/81	15:46 to 23:50	2.73	4.87	2.0	10.0	14.0	28.1	0.9×10^4	0.38	3×10^6
Run 4	9/23/81	12:37 to 18:58	1.5	3.22	1.1	1.0	12.5	51.0	1×10^4	0.13	1×10^7

ratio and a $^{134}Cs:^{137}Cs$ isotopic ratio of 1:150. Using basic process feed and flowrate data, particulate Cs DFs were determined for the total system (melter and sintered filters). These derived DFs also appear in Table 16. The loading and DF values listed in Table 16, unlike those in Table 15, are based entirely upon measured parameters that require no basic assumptions. The limiting parameter used in these calculations is that of flowrate. Because of the fluctuating nature of this quantity, an average value had to be utilized.

TABLE 16. Cesium Aerosol Emissions (Total System)

Experiment	Date	Sampling Period	Average Rates Feeding, kg/h	Flow, scfm	Filter Loading μg	μCi	Offgas Loading ng/L	nCi/L	Total DF
Run 2	8/06/81	08:36 to 10:35	16.3	4	2.0	63	4.3	140	2.2×10^6
Run 3	9/02/81	10:33 to 14:52	19.7	4	1.0	32	0.91	29	2.6×10^7
Run 3	9/02/81	15:46 to 23:50	7.9	4	1.4	44	0.60	19	1.6×10^7
Run 4	9/24/81	10:00 to 11:35	22.2	4	0.11	3.5	0.33	11	6.4×10^7
Run 4	9/24/81	12:37 to 18:58	11.8	4	0.94	30	0.46	15	2.4×10^7

The degree to which Cs existed as a volatile gas at sampling site A was assessed with gas-scrubbing techniques (see Figure 6). Analysis of condensate and scrub solutions by using atomic absorption was totally inadequate for the levels of Cs existing in these solutions. As a result, samples were analyzed by neutron activation techniques. This analytical approach also proved to be too insensitive for the detection of Cs in these samples. An upper limit for volatilized Cs emissions was extracted from the analytical results obtained from Run 4 samples. This result appears in Table 17 along with a lower limit value of the melter system DF for volatilized Cs. These data clearly show that vapor-state Cs does not significantly contribute to process system losses. This is not to say that volatilization has no effect upon process losses. However, it appears that most volatilized Cs has condensed upon

TABLE 17. Volatilized Cesium Emissions (Total System)

Experiment	Sampling Period	Cs Content, ng	Total Vapor DF
Run 4	10:00 to 18:58	<90	>3 x 10^8

entrained particulates before ever reaching the sintered metal filter housing (i.e., the heavy process-generated entrainment acts to scrub out vapor-phase Cs before it gets to the offgas system).

The Sr content of the filters and solutions previously described for Cs were not detectable. Conventional analytical techniques provided only upper compositional limits for this element (i.e., it could not be detected). Even neutron-activation techniques provided too little sensitivity for adequate Sr quantitation. However, Sr is unequivocally a nonvolatile under all existing process operating conditions. Consequently, high, pessimistic estimates of the Sr content of particulate samples can be derived from the previously discussed Cs data and the Cs:Sr ratio of the feed. Using this approach, Sr loading and DF values were calculated and are presented in Table 18. The

TABLE 18. Strontium Aerosol Emissions (Total System)

Experiment	Date	Sampling Period	Feed Composition, wt%		Filter Loading		Offgas Loading		Total Sr DF(a)
			Sr	Sr/Cs	ng	μCi	pg/L	nCi/L	
Run 2	8/06/81	08:36 to 10:35	0.05	0.13	250	21	540	46	2 x 10^6
Run 3	9/02/81	10:33 to 14:52	0.04	0.048	48	4.1	44	3.7	3 x 10^7
Run 3	9/02/81	15:46 to 23:50	0.04	0.048	67	5.7	29	2.4	2 x 10^7
Run 4	9/24/81	10:00 to 11:35	0.03	0.047	5.1	0.43	16	1.3	6 x 10^7
Run 4	9/24/81	12:37 to 18:58	0.03	0.047	44	3.7	22	1.8	2 x 10^7

(a) Same as those of Cs by definition.

curie-loading values presented in this table were based upon a ratio of ^{90}Sr to a total Sr of 0.6. Again, the results appearing in Table 18 are semi-empirical, but they are based upon realistic estimates that should provide overestimates of the offgas loadings and underestimates of melter DFs for particulate Sr.

The process exhaust gas composition was routinely analyzed with a gas chromatograph. The results generated by this instrument appear in Table 19. The average water content of the offgas stream was calculated from condensate samples collected with the sampling system illustrated in Figure 6. These data can be quickly used to estimate average inleakage rates, but more importantly, they identify the chemical channels through which isotopes of carbon and hydrogen escape the system. Furthermore, the data establish the relative importance of each of these channels and suggest that the ^{3}H and ^{14}C present in TMI-generated waste will be released to the offgas system primarily as water vapor and carbon dioxide, respectively.

TABLE 19. Process Offgas Composition

		% Molar Composition (Dry)					Average Molar %,
Date	Time	CO_2	CO	O_2	N_2	H_2	H_2O
7/08/81	09:29	0.039	$<10^{-3}$	20.4	79.6	$<10^{-1}$	
	13:44	1.8	$<10^{-3}$	19.0	79.1	$<10^{-1}$	
	14:22	0.75	$<10^{-3}$	19.1	80.1	$<10^{-1}$	
	Avg.	0.85	---	19.5	79.6	---	24
8/06/81	08:26	7.61	0.14	17.9	74.4	$<10^{-1}$	
	09:40	11.4	$<10^{-3}$	18.1	70.5	$<10^{-1}$	
	12:08	31.7	$<10^{-3}$	13.4	54.9	$<10^{-1}$	
	13:18	24.2	$<10^{-3}$	14.9	60.9	$<10^{-1}$	
	13:57	27.2	0.003	14.3	58.5	$<10^{-1}$	
	Avg.	20.4	0.003	15.7	63.8	---	12

TABLE 19. (contd)

Date	Time	% Molar Composition (Dry)					Average Molar %, H_2O
		CO_2	CO	O_2	N_2	H_2	
9/02/81	11:59	50.6	$\sim10^{-3}$	9.4	40.0	$<10^{-1}$	
	12:41	38.6	0.001	12.0	49.4	$<10^{-1}$	
	13:36	46.4	0.003	10.3	43.3	$<10^{-1}$	
	14:15	42.9	0.001	11.0	46.0	$<10^{-1}$	
	14:49	35.8	0.001	12.6	51.6	$<10^{-1}$	
	16:03	35.0	$\sim10^{-3}$	12.6	52.4	$<10^{-1}$	
	16:48	8.8	$<10^{-3}$	18.6	72.5	$<10^{-1}$	
	Avg.	36.9	0.001	12.4	50.7	---	07
9/24/81	10:20	12.0	$<10^{-3}$	18.6	69.5	$<10^{-1}$	
	11:25	13.7	$<10^{-3}$	18.2	68.1	$<10^{-1}$	
	12:52	17.4	$<10^{-3}$	17.2	65.4	$<10^{-1}$	
	13:52	13.0	$<10^{-3}$	18.2	68.8	$<10^{-1}$	
	15:25	6.1	$<10^{-3}$	19.6	74.2	$<10^{-1}$	
	18:58	6.8	$<10^{-3}$	19.4	73.8	$<10^{-1}$	
	Avg.	11.5	---	18.5	70.0	---	04

CONCLUSIONS

For the Zeolite Vitrification Demonstration Program, a borosilicate glass formulation was developed for the Linde Ionsiv IE-96 zeolite. When the A-51 zeolite was added to the SDS flowsheets, glass formulation studies were conducted to identify a glass composition for mixtures of A-51 and IE-96. As long as the ratio of IE-96 to A-51 is 3:2 or less, a good-quality glass (based on Soxhlet leach tests and compared to commercial glass 76-68 and defense glass TDS-211) can be obtained with a 60% loading of zeolite when using 36 wt% of agglomerated glass-forming chemicals and 12% silica sand.

The ZVDP process coupled a solids mixing/feeding vessel to a canister in an in-can melting furnace to complete the vitrification of zeolite during four nonradioactive runs. The main operational problems encountered were maintaining the temperatures of the feed and offgas lines below 400°C to prevent melting and above 100°C to prevent condensation. The process was designed and developed for the use of IE-96 zeolite.

Effluent characterization studies were conducted during the TMI-ZVDP cold tests in order to establish the emission characteristics of the radiologically important isotopes of Cs, Sr, C and H. These studies have shown that the semivolatile element Cs, as well as the nonvolatile element Sr, are transported to the offgas system primarily as particulate matter. The gross particulate escaping into the offgas system exhibited a size distribution characterized by a mean diameter of 2.3 µm and a 35% integral probability below 1 µm. A total average particulate, melter system DF of 5×10^{-6}, was estimated from the data collected during the last three cold tests. The total Cs particulate DF associated with these same cold tests was measured to be 3×10^7. A Sr DF could not be determined directly from the experiments conducted; however, being a totally nonvolatile element under melter operating conditions, Sr would be expected to exhibit a DF value greater than that of Cs. The elements H and C, present in the simulated TMI feed, escaped the melter system primarily as the volatile chemical compounds of H_2O and CO_2, respectively. Partial melter system DFs for these elements are assumed to be ~1.

Glass samples from each of the four runs were analyzed for chemical constituents and subjected to Soxhlet leach tests. These test results were very consistent. These samples will also be subjected to MCC-1 tests to evaluate their quality.

The ZVDP nonradioactive runs demonstrated that the designed process was a simple, successful method for solidifying TMI's liners of zeolite material. With a few modifications, identical equipment will be installed in a radiochemical cell and demonstrated with radioactive liners of zeolite shipped to PNL from TMI.

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