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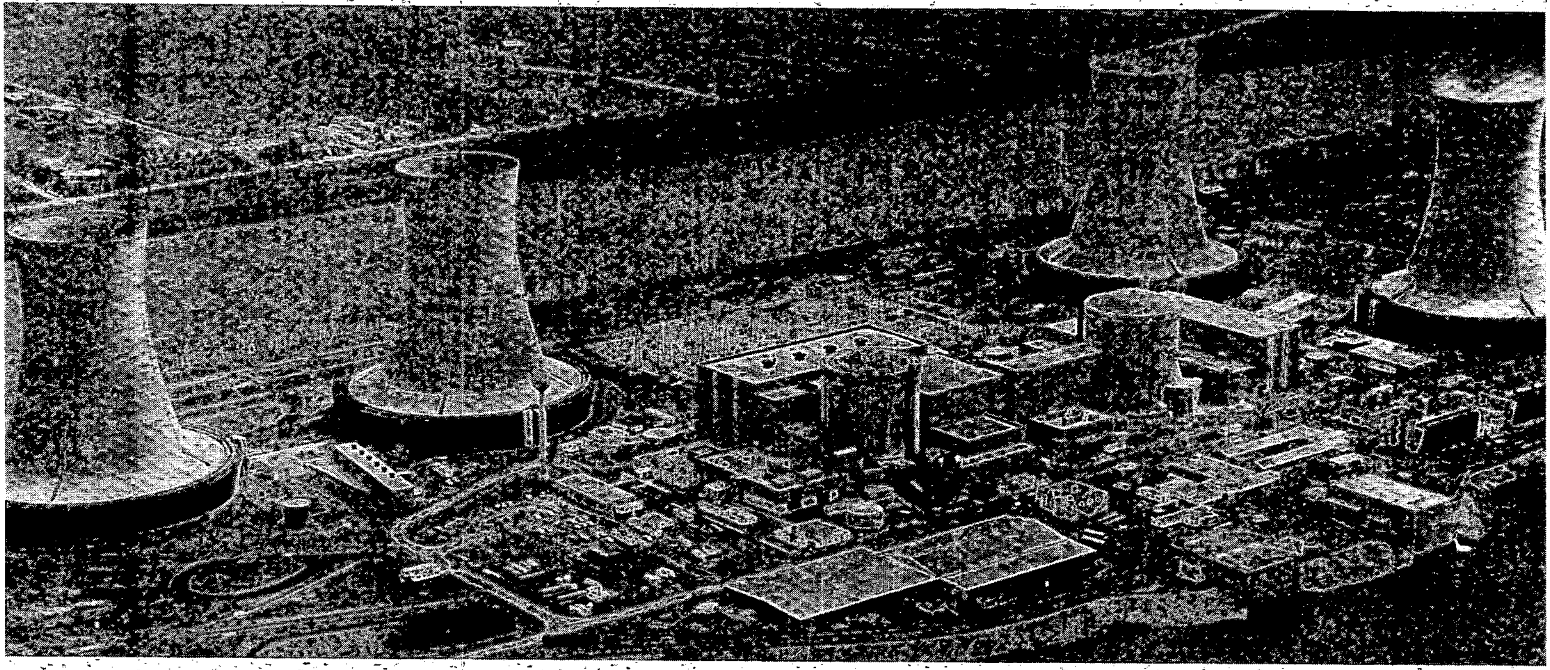

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Summary of Radioactive Operations for Zeolite Vitrification Demonstration Program

G. H. Bryan
R. W. Goles
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ABSTRACT

The Zeolite Vitrification Demonstration Program (ZVDP) has successfully vitrified the zeolite used in the Submerged Demineralizer System (SDS) at Three Mile Island (TMI) Unit 2 to a borosilicate glass product. Under the ZVDP, the U.S. Department of Energy authorized the Pacific Northwest Laboratory (PNL) to demonstrate the vitrification process on a full scale by use of the in-can melter process.

This program was accomplished in two phases. The first phase developed a glass formulation and demonstrated the vitrification process with nonradioactive materials. The second phase received three radioactive liners from the SDS and vitrified the zeolite contained in each.

The first of the three radioactive liners contained a total of ~13,000 Ci (^{137}Cs, ^{90}Sr, and associated daughter products), and was received from TMI during May of 1982. The second and third SDS liners were received in January of 1983 and contained a total of ~113,000 Ci each.

The radioactive zeolite from each of the three liners was vitrified in four canisters. Each canister was filled to a height of about 2 m with vitrified product and weighed about 170 kg. The process effluents were also characterized to provide basic off-gas engineering data around which an effective off-gas processing system could be designed.

These studies concluded that emission of melter-generated aerosols is responsible for most radioactive, process-related losses to the off-gas system. Tritium, in the form of water vapor, is the only significant gaseous radioactive effluent generated by the vitrification of TMI zeolite waste.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the efforts of G. N. Buck, E. L. Doan, S. D. Halstead, S. J. Kostorowski, and C. M. Andersen. Without the sincere dedication and initiative demonstrated by these individuals, the successful completion of this project would not have been possible.

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SUMMARY OF RADIOACTIVE OPERATIONS FOR ZEOLITE VITRIFICATION DEMONSTRATION PROGRAM

SUMMARY

The Zeolite Vitrification Demonstration Program (ZVDP) was successfully completed when three radioactive liners of TMI zeolite were vitrified to a borosilicate glass product. The zeolite has been used to decontaminate high-activity water at Three Mile Island Unit 2 (TMI-2). The first phase of this program developed a glass formulation and demonstrated the vitrification process with nonradioactive materials. During this phase, four full-scale nonradioactive demonstration runs were completed. The second phase received three radioactive Submerged Demineralizer System (SDS) containers or liners, and vitrified the zeolite ion-exchange media from the liners. This report is an operations summary of the second phase.

The process equipment placed in the hot cell for vitrification of radioactive SDS zeolites was basically of the same design as that used during the nonradioactive process, though some minor modifications were necessary to make the equipment compatible with requirements for hot-cell remote operation.

The first of the three liners, containing about 12,900 Ci of activity, was received from the TMI SDS in May 1982. In January 1983 PNL received the second and third liners, which contained 112,635 and 112,622 Ci of activity, respectively.

The radioactive SDS zeolite from the three liners was vitrified in four canisters. Each canister was filled to a height of about 2 m with vitrified product that weighed about 170 kg. Gamma scans of the canisters indicated a uniform cesium distribution in the glass.

During each vitrification run, the process effluents were characterized through use of off-gas sampling equipment and process-related scrub solution. An apparent filter malfunction did result in somewhat lower particulate decontamination factors than was noted during the cold runs with the same filters.

The study demonstrated that radionuclide-loaded inorganic ion-exchange media can be vitrified into cylindrical logs prior to storage and/or disposal.

INTRODUCTION

The cleanup of the high-activity water at TMI-2 provided an opportunity to further develop radioactive waste management technology. Approximately 3.6×10^6 L of high-activity water was decontaminated using the SDS. In this process, the cesium and strontium in the water are sorbed onto a blend of zeolites contained within metal liners. One disposal option for this zeolite is to mix it with glass formers and vitrify it to a borosilicate glass product. Under the ZVDP, 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 melter (ICM) process.

Both nonradioactive and radioactive production-scale demonstrations have been conducted under the ZVDP. A summary of the nonradioactive operations can be found in Reference 1, while this document presents the results of the radioactive demonstration. This demonstration consisted of the vitrification of the zeolite from one low-activity and two high-activity SDS liners. The objectives of the demonstration were to: a) demonstrate the ZVDP process using actual SDS zeolites, b) sample and analyze airborne effluents to determine their concentration and composition, and c) analyze the glass product.

PROCESS DEVELOPMENT FOR HOT-CELL OPERATIONS

The process equipment designed to be placed in the hot cell for vitrification of radioactive SDS zeolites was basically of the same design as that used for the nonradioactive process.[1] The equipment had to be modified slightly to make it compatible with hot-cell remote operational requirements.

After receipt of the SDS liner via cask from TMI, the liner was unloaded, vented, and placed in a hot cell for further processing. Drying of the zeolite, the first step in the processing sequence, was accomplished by placing the entire liner in a resistance-heated dryer (Figure 1). Connected to the existing cell off-gas system, the dryer removes water vapor and confines particulate matter that might be expelled from the liner.

(a) Full scale is defined as an 0.2-m-dia canister filled with 2 m of glass.

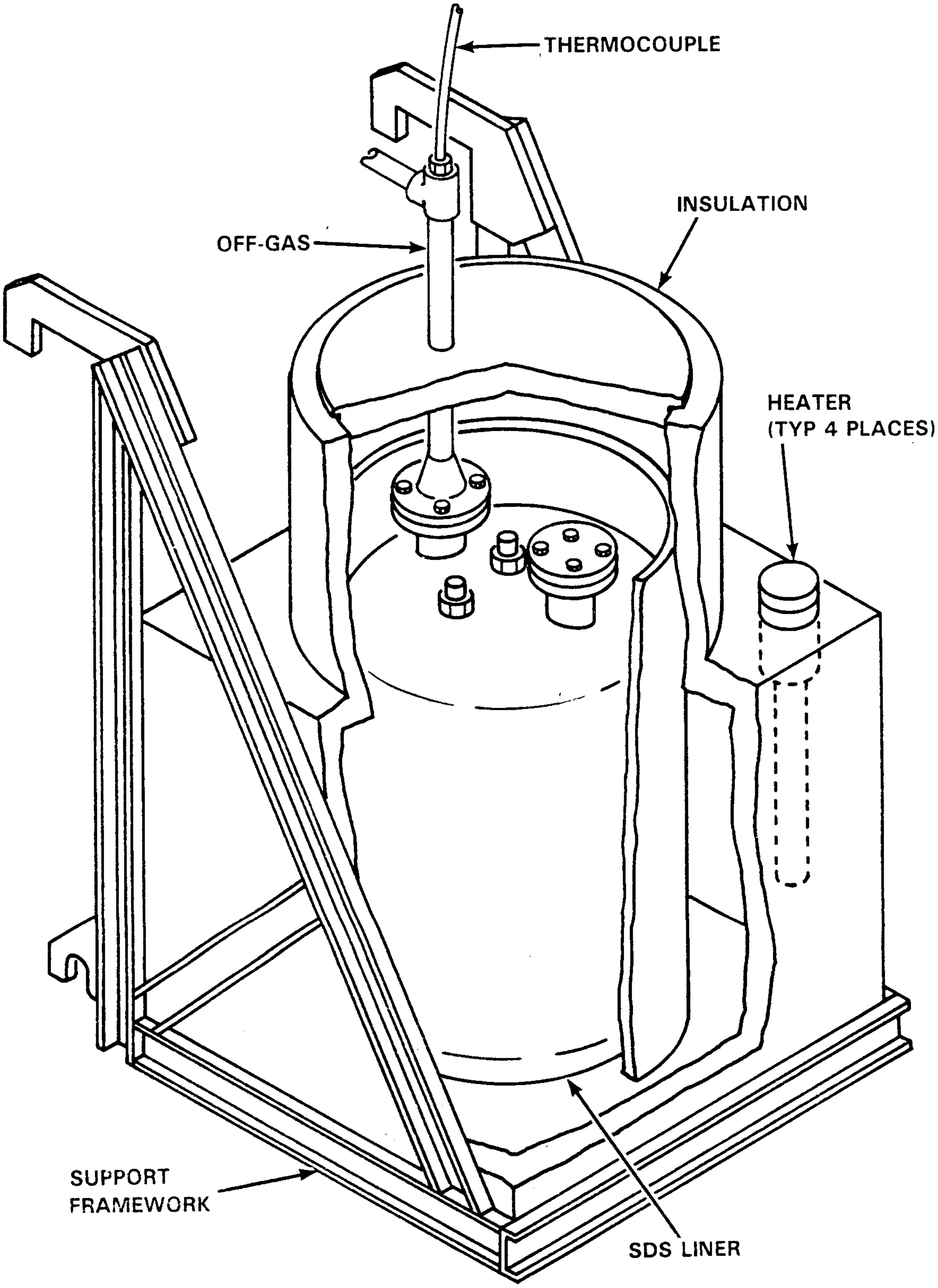

FIGURE 1. Zeolite liner dryer.

The B-Cell off-gas system was originally installed for a project requiring a much larger capacity system than the ZVDP; therefore, much of it was oversized and not fully utilized. The off-gas system (Figure 2) is capable of maintaining the ZVDP vitrification system at up to -0.5 m of water relative to the cell pressure.

The mixer/feeder vessel (Figure 3) is large enough (0.5 m^3) to hold the entire contents of the SDS liner and glass formers with enough free space to allow homogenizing of the mixture while tumbling the vessel. The handling fixture (see Figure 3) is designed to tumble the mixer/feeder vessel and support it and the star feeder when connected to the vitrification system as shown in Figure 4. The fixture is basically the same as the one designed for the nonradioactive process; however, a larger gearbox and motor are used for increased reliability.

The interface between the mixer/feeder vessel and the canister adapter, referred to as the "tree," is shown in Figure 5. This portion of the system is simply piping to contain and guide the feed as it falls into the canister. Because condensation can cause feed to clump and adhere to the piping walls, the piping is heated by means of a steam jacket to prevent condensation of the steam produced when the zeolite and glass formers are subjected to the 1050°C heat necessary to make the borosilicate glass. The canister adapter, which connects the vitrification system to the canister, is also provided with a steam jacket to keep it cool. If the temperature of the canister adapter walls is allowed to exceed 400°C, the glass formers could melt as they pass through the adapter, resulting in bridging that could eventually block feed from entering the canister.

The canisters (Figure 6) are fabricated from Sch 40 0.20-m-dia 304L stainless steel pipe. They are 2.58-m long and are connected to the vitrification system by a flange machined into the head of the canister that mates with the canister adapter. The canister is held in place by two "J" bolts connected to the system piping.

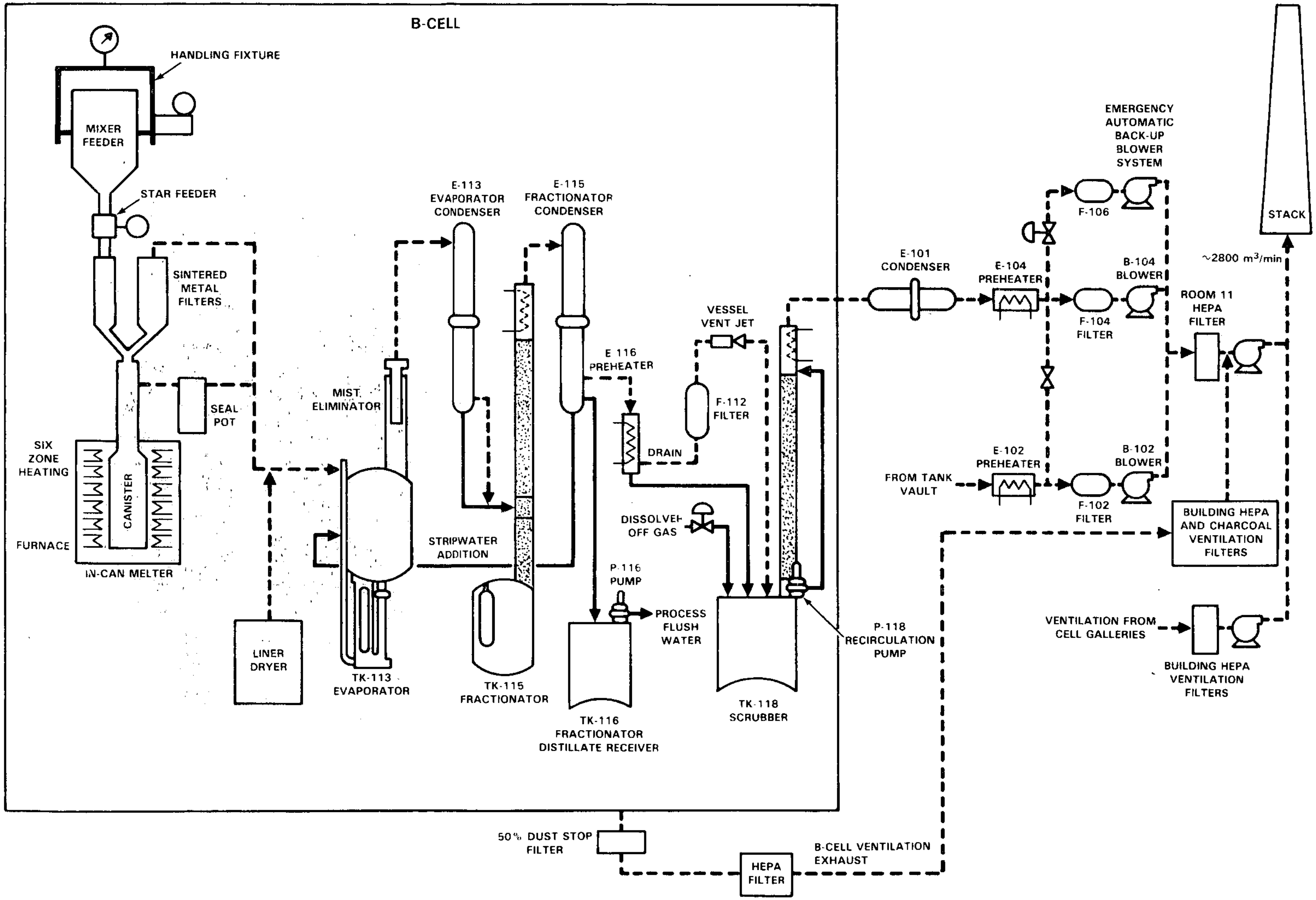

FIGURE 2. 324 Building effluent control system.

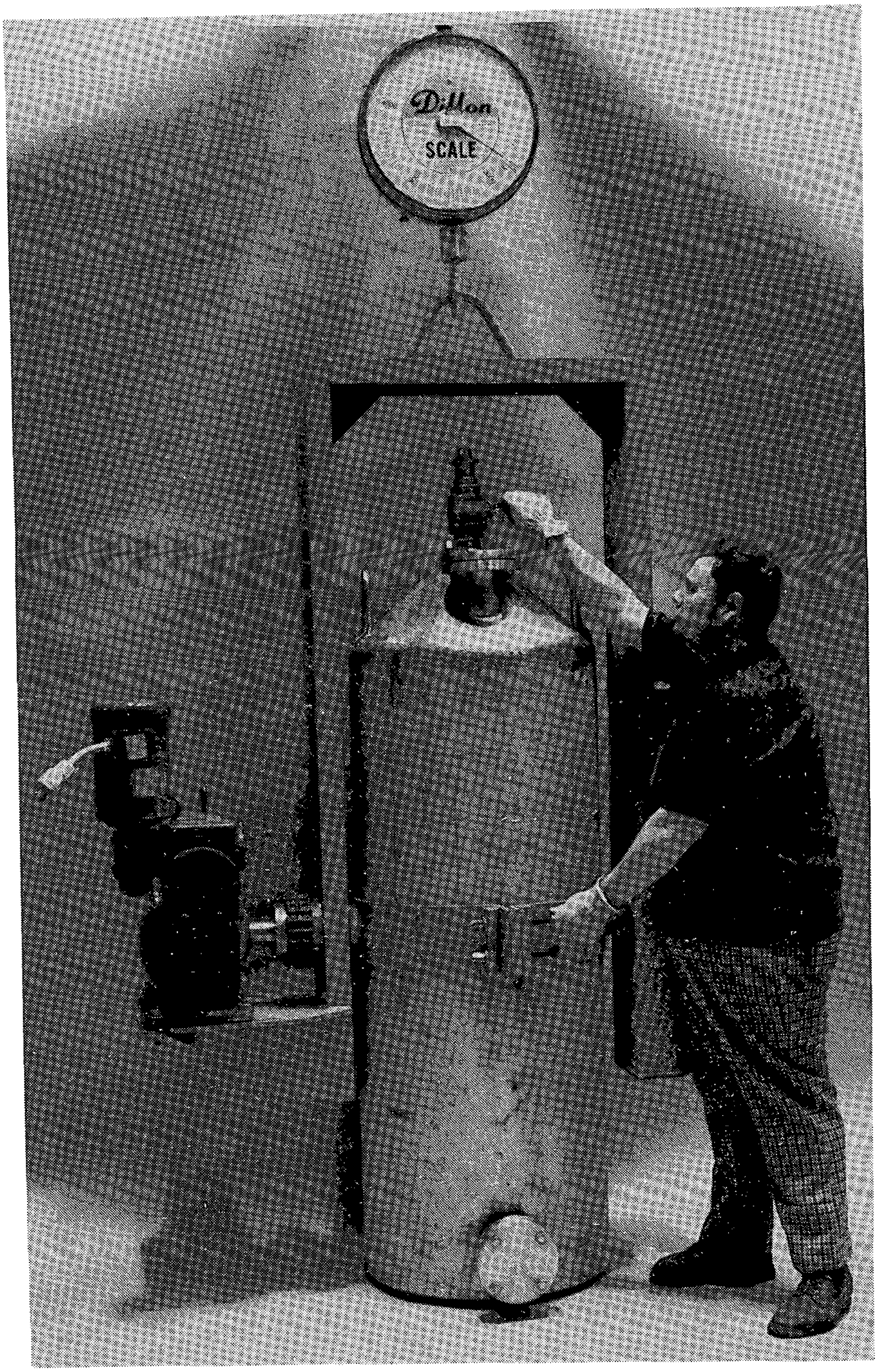

FIGURE 3. Mixer/feeder vessel and handling fixture.

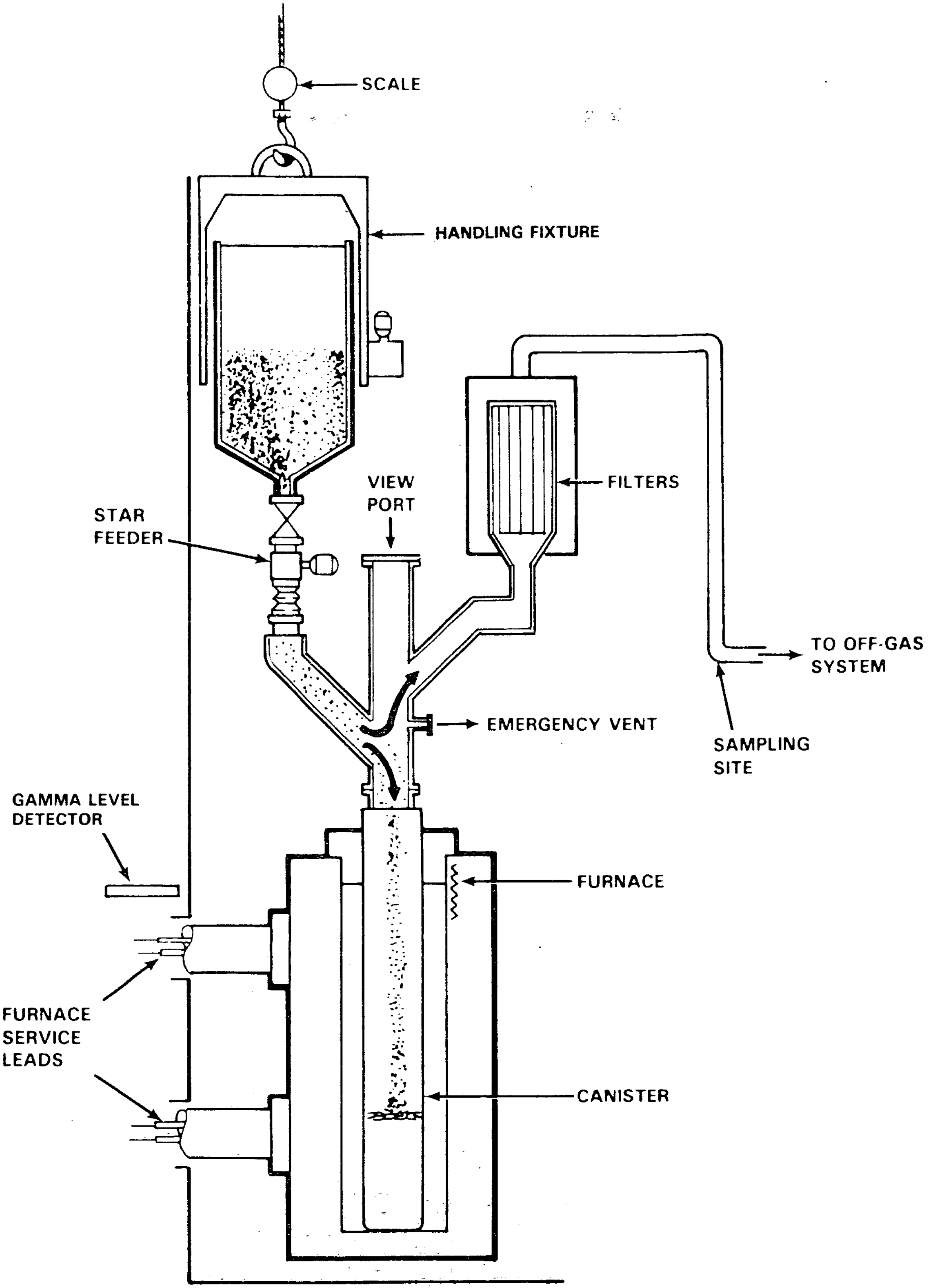

FIGURE 4. Zeolite vitrification system and off-gas sampling site location.

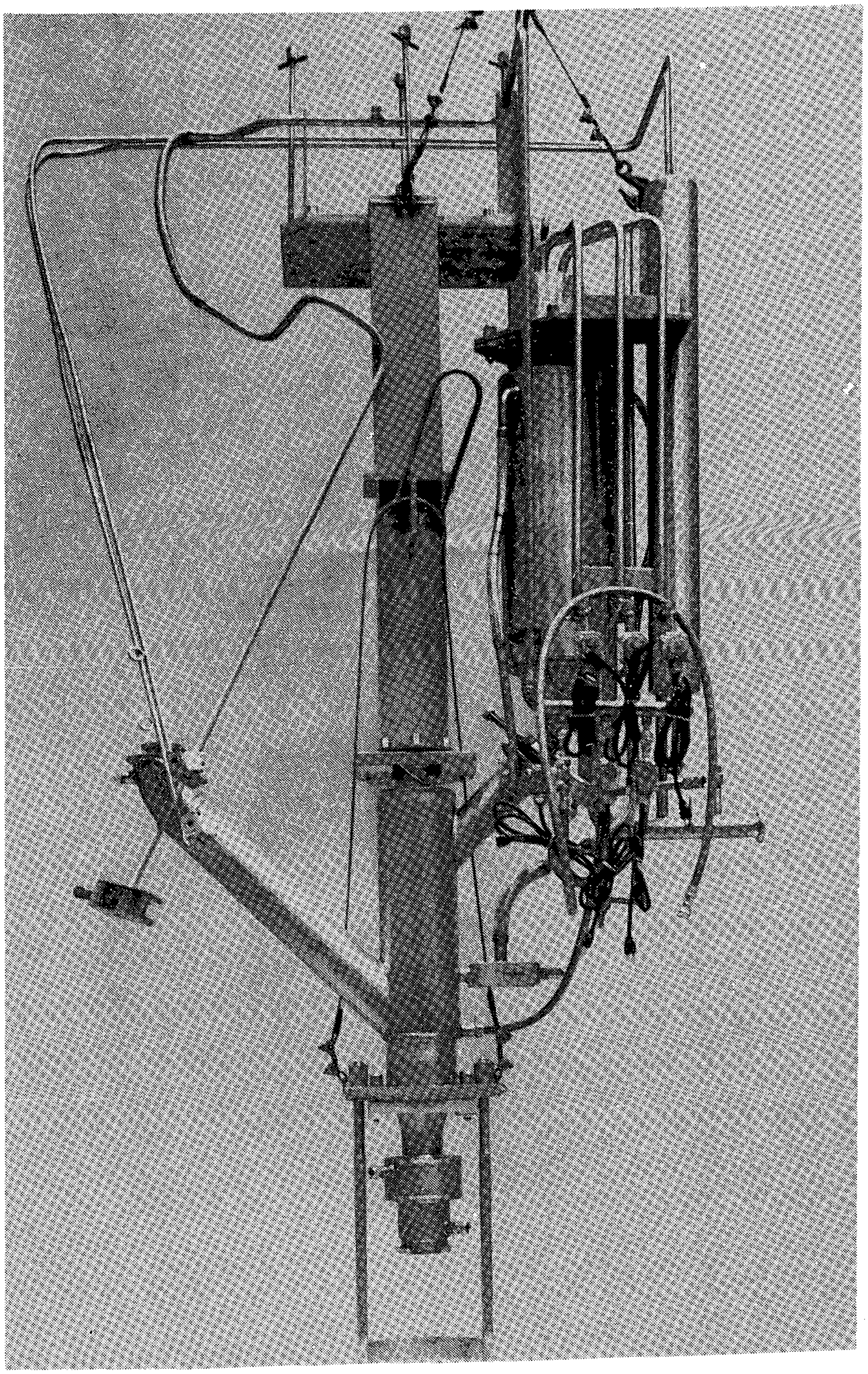

FIGURE 5. Zeolite vitrification system "tree."

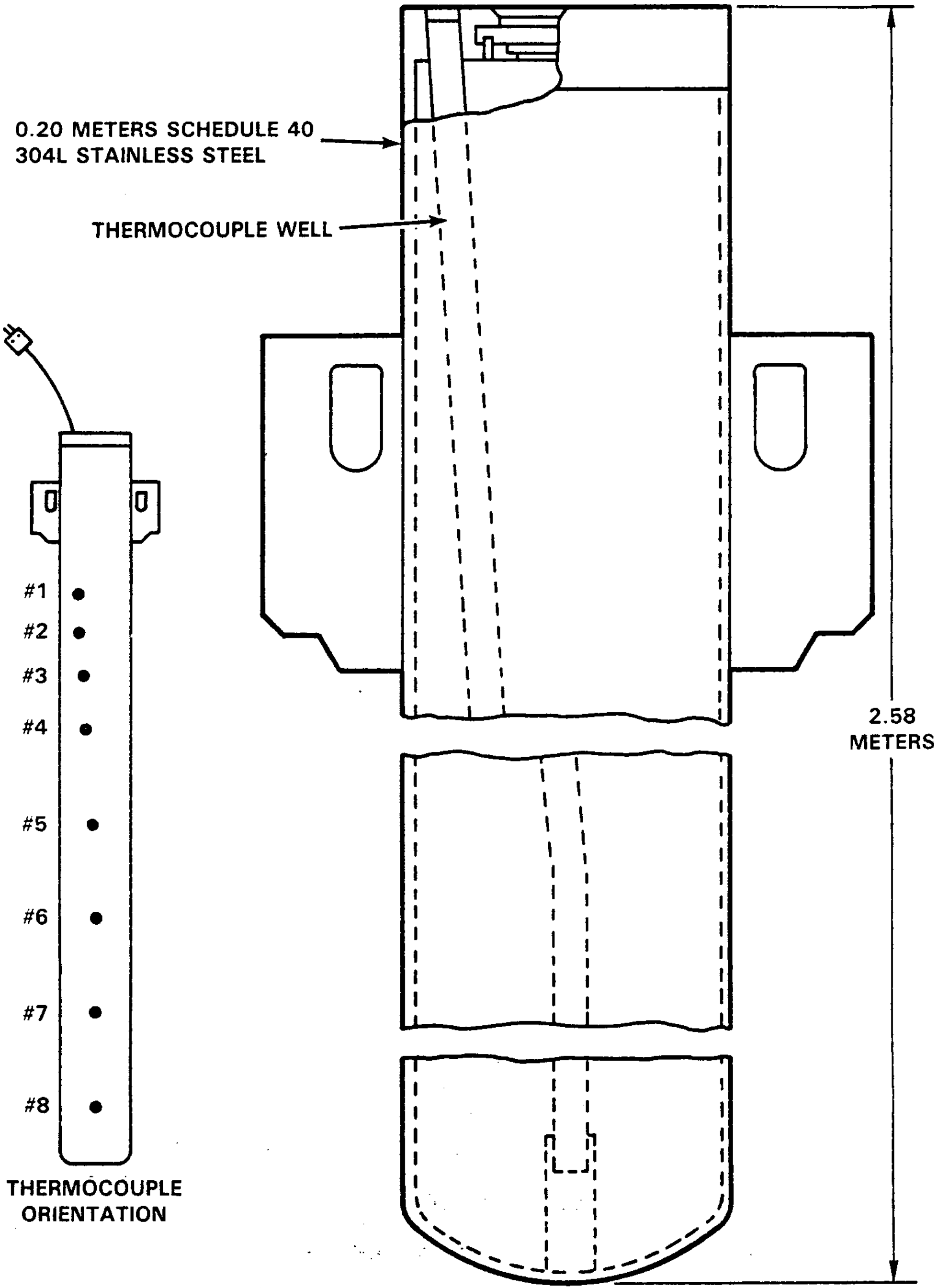

FIGURE 6. TMI canister.

The furnace used to heat the canisters is a full-scale ICM previously used during the vitrification of high-level waste (HLW) from reprocessing power reactor spent fuel.[2] The ICM is a six-zone resistance type, with each zone 0.36-m high and capable of 15 kW of power.

The filter unit (Figure 4) is made up of three 65-μm sintered Inconel® filters that are pulsed every 20 minutes to return accumulated dust to the canister. Two air-driven vibrators are also incorporated into the system to assist in removing any material held up in the connecting piping. An emergency vent line with a seal pot prevents pressurization of the vitrification system in case the filters plug.

ZEOLITE PREPARATION

Three liners of zeolite were received from the Three Mile Island SDS system for vitrification. The first liner (D-10015) was received at PNL in May 1982, and contained about 12,900 Ci of activity of which 5,767 Ci were cesium and 1,012 Ci were strontium (the balance was various daughter products). The two high-activity liners were received in January 1983. Liner D-10012 contained about 112,635 Ci of activity (53,046 Ci of cesium and 2,003 Ci of strontium) and liner D-10016 contained about 112,622 Ci of activity (52,358 Ci of cesium and 1,869 Ci of strontium).

After removing the liners from their shipping cask and placing them in the hot cell, the liners were sampled for gas content and then purged with nitrogen as a safety measure because of the possibility that hydrogen had built up from the radiolysis of water. The results of these analyses will be discussed in the Off-Gas Studies section of this document.

As received, these liners had a water content ranging from about 8 to 19 wt%. It was necessary to lower the water content to the point where the zeolite was dry and pourable to prevent plugging in the connecting piping and reduce the volume of gaseous effluents generated when the zeolite/glass former mixture was vitrified.

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The zeolite was dried by a resistance-heated furnace. Two thermocouples were inserted into the zeolite through one of the flanges of the liners (Figure 7) to a depth of about 6 in. and 24 in., respectively. An insulated lid was then placed on the dryer (Figure 1), which was connected to an off-gas system to aid in the removal of the water as it was driven from the zeolite. The liner was then heated until both thermocouples reached a minimum temperature of 250°C.

After the zeolite in the two high-activity canisters cooled, it was sampled to determine the water content. This analysis was performed in the hot cell by heating a weighed zeolite sample to 1000°C and assuming the entire weight loss was due to water. The water content of the zeolite both before and after drying is shown in Table 1.

The weight of the dried zeolite was determined by pouring the entire contents of the liner into a mixer/feeder vessel and reweighing. From this weight and the water content, the correct amount of glass formers and silica to be added to the zeolite was determined. To be sure the formulation was correct, the calculated portions of glass formers and silica were added to a weighed sample of zeolite, homogenized, and placed in a furnace at 1050°C for 2 hours to determine if glass was formed. The glass formers and silica to be added to the bulk of the zeolite were placed in a hopper in the airlock of the hot-cell complex and then transferred to the hot cell where they were added to the mixer/feeder vessel containing the zeolite.

The mixture was homogenized by tumbling the mixer/feeder vessel end-over-end for 1 hour, using the handling fixture. Following this procedure, a sample of the mixture was removed and heated in a furnace to 1050°C to be sure that the glass had formed and the proportions of zeolite, glass formers, and silica were correct. At this point, the preparation of zeolite for vitrification was complete.

TABLE 1. WATER CONTENT OF ZEOLITE LINERS

Liner	As Received, wt%	After Drying, wt%
D-10015 (low activity)	~19	~10*
D-10012 (high activity)	16	10
D-10016 (high activity)	8	7

* Estimated value.

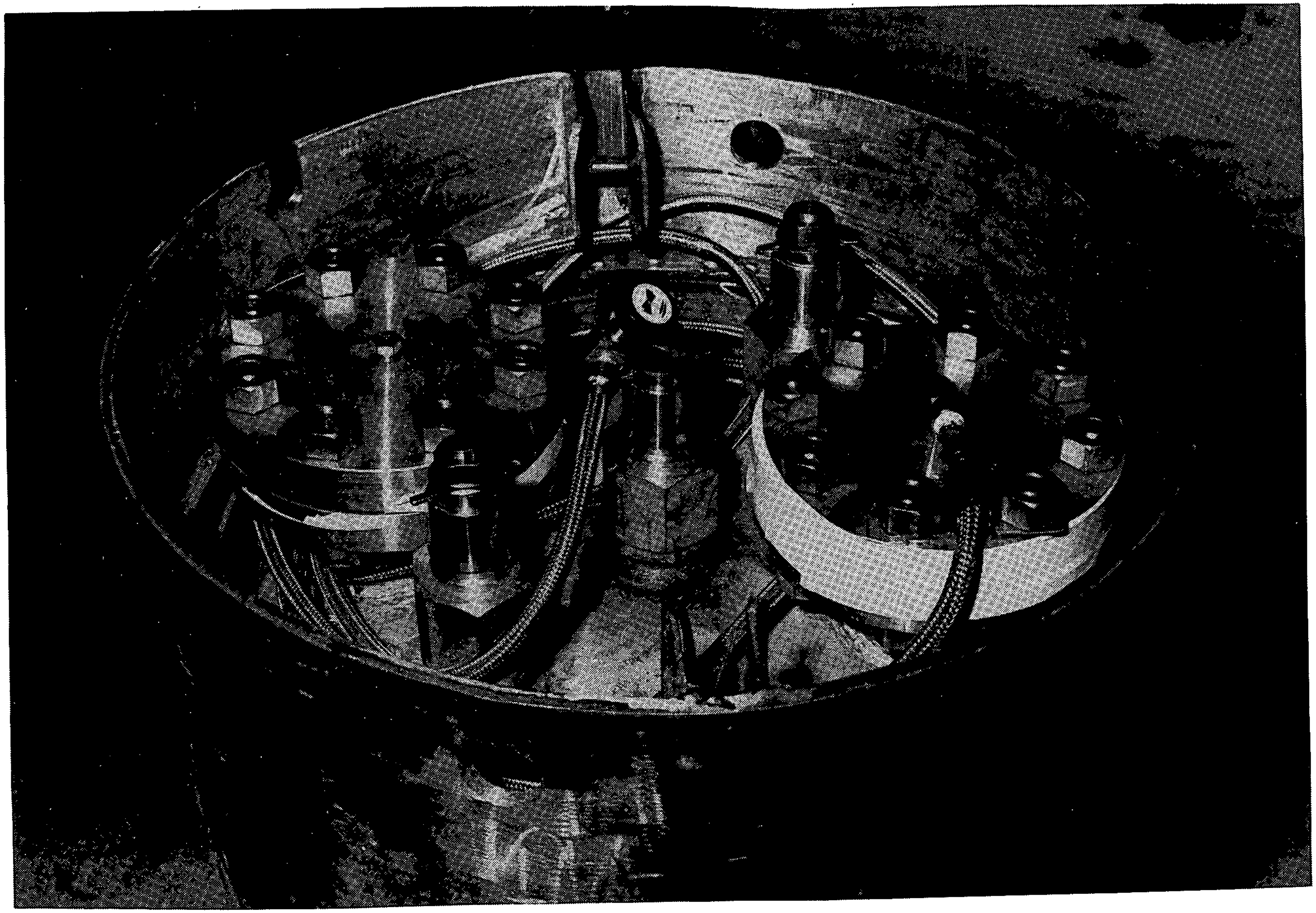

FIGURE 7. SDS liner.

OPERATIONS SUMMARY

After the zeolite was dried and blended with glass-forming chemicals, the mixer/feeder was inverted and connected to the feed and off-gas piping (tree) as shown in Figure 4. A 0.2-m-diameter x 2.58-m stainless steel canister was inserted in the ICM furnace and connected to the bottom of the tree. Connections were tightened until there was a 0.13- to 0.25-m Hg vacuum at the tree provided by the building's radiochemical ventilation system blower. Process effluents were drawn from the ZVDP system sintered metal filters through two condensers, a HEPA filter, a packed scrubber, another condenser, and two more HEPA filters before being vented to the building stack (Figure 2).

The objective of each vitrification run was to fill the canister with 2.0 m of glass product. Before, during, and after each run the packed scrubber solution was sampled. Off-gas samples were also taken during each run (see section on Effluent and Analytical Studies).

The feed rate was to be controlled at ~0 kg/h or a minimum temperature of 900°C in the zone where melting was occurring. The canister had six zones, with thermocouples installed in each zone to monitor the temperature. As a zone was filled with feed, additional power was required to melt this material. As a result, the canister zone temperature would start to fall. Increasing or decreasing the feed rate would increase or decrease this temperature drop. Because of heat losses, the feed rate would be reduced to only 1 to 2 kg/h to maintain the 900°C temperatures near the top of the container.

This method was also used to determine how full the canister was. The level was verified by the total amount of feed fed (~30 kg feed/1 m glass) and by the use of the gamma level detector. A gamma detector probe was inserted in a plug in the cell wall and aimed at the canister in the furnace. Plugs were located at the 0.9-m, 1.8-m, 1.9-m, and 2.0-m levels referenced to the canister. The probe monitored the radiation background. When the glass level in the canister reached the height of the probe, the radiation reading increased several orders of magnitude due to the concentrated activity of the feed. The probe was moved to the next higher plug location.

Prior to the start of radioactive operations, the in-cell equipment was tested with nonradioactive zeolite. The system was started up, operated, and shut down several times to complete training of personnel. In addition, the off-gas sampling system was checked out during these short runs.

Next, the low-activity liner was vitrified. This was the first continuous run in the hot cell to fill a canister. It had been calculated that it would take 190 to 200 kg of feed to fill a canister. However, the gamma level detector observed the glass level at 1.9 m after only 135 kg of feed had been processed. Feed was then shut off for several hours, and the radiation readings returned to background levels.

Apparently, either a bridge of unmolten material had developed in the canister, or the glass had foamed, giving the faulty detector reading. Feed rates up to 23 kg/h had been used during the first hours of operation. This was probably too high for the in-cell furnace. For subsequent operations, a limit of 15 kg/h was imposed. The desired feed rate was 10 kg/h. The faulty detector reading was the only operational difficulty experienced. A total of 209 kg of feed was processed to produce 177 kg of glass in canister Z-3. The balance of the feed material left in the mixer was vitrified in the canister designated Z-1, which was used earlier for the nonradioactive test runs.

The first high-activity liner (D10012) was dried and blended with glass-forming chemicals. Vitrification operations were started with 315 kg of feed to be processed. The feed rate was initially ~10 kg/h, was slowed to ~5 kg/h when the can (Z-2) was two-thirds full, and was reduced to 1 to 2 kg/h to fill the can. A total of 191 kg of feed was vitrified. A new canister (Z-4) was installed and the remaining 124 kg of feed left in the mixer were vitrified. After the second high-activity liner (D10016) was dried and blended with glass-forming chemicals, Z-4 was filled with 70 kg of this feed material. One more empty canister (Z-5) was installed, and 180.5 kg of feed were processed. The ~30 kg of feed remaining was vitrified in canister Z-1. An Operations Summary for these radioactive runs is presented in Table 2. All of the filled ZVDP canisters were heat soaked at 1050°C after the feed was terminated to improve glass quality.

Canisters Z-2, Z-3, Z-4, and Z-5 were core drilled to obtain samples of the glass product. Samples from canisters Z-2, Z-4, and Z-5 will be characterized by the Materials Characterization Center. These data will be published later.

TABLE 2. OPERATIONS SUMMARY

Canister	Feed, kg	Maximum Feed Rate, kg/h	Annealing Time, h	Canister Fill Height, m	Glass, kg	Description
Z-1*	NA	NA	NA	NA	NA	Nonradioactive Zeolite Remainder Low-Level Liner Remainder Second High-Level Liner
Z-2	191	12.3	6	2.0	167	First High-Level Liner
Z-3	209	23	6	1.9	177	Low-Level Liner
Z-4	194	13.6	4	2.0	164	Remainder First High-Level Liner Start of Second High-Level Liner
Z-5	180.5	10	8	1.9	161	Second High-Level Liner

---

* Used to train personnel and to vitrify small quantities of zeolite left from the various liners. Product will not be characterized.

As was mentioned earlier, the packed scrub solution was sampled before, during, and after each run. These samples were analyzed for cesium to determine what losses, if any, were observed at this stage of the effluent treatment system. No significant changes in the cesium content were detected during any of the runs.

EFFLUENT AND ANALYTICAL STUDIES

Effluent characterization studies have been established to support the TMI ZVDP. The purpose of these studies is to provide basic off-gas engineering data around which an effective off-gas processing system can be designed for these studies include: a) establishing the gaseous composition of melter-generated exhaust, b) identifying the pathways for effluent escape, c) quantifying the degree to which melter effluent losses occur, d) characterizing the cesium distribution in zeolite liners and resultant canisters, and e) establishing the influence of radiolysis upon liner cover gas composition and pressure.

The effluent characterization studies that were conducted during the vitrification of TMI zeolite waste were primarily concerned with the radiologically important isotopes ^{137}Cs, ^{134}Cs, ^{90}Sr, ^{129}I, ^{14}C, and ^{3}H. The results of these studies are, however, generic to other ICM systems in that all classes of effluents, including volatile, semivolatile, and nonvolatile matter, are dealt with in these investigations. The following sections discuss the off-gas characterization studies conducted in support of ZVDP, including a description of the sampling system used, the laboratory techniques employed, and the analytical results obtained.

SAMPLING SYSTEM

Off-Gas

Selection of a sampling site was based upon the need to obtain representative samples and the desire to locate 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 ~1.8 m from the ICM feeding and exhaust line lid or "tree." In the off-gas-line schematic illustrated in Figure 4, this sampling site is at the end of a 1.5-m straight run of melter exhaust line, downstream from the sintered metal filter housing.

The melter exhaust was sampled by the system illustrated in Figure 8. A tapered 0.01-m stainless-steel sampling nozzle, located along the central axis of the 0.05-m process line, allowed samples to be extracted upstream from the turbulence created by elbows or bends in the off-gas 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 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

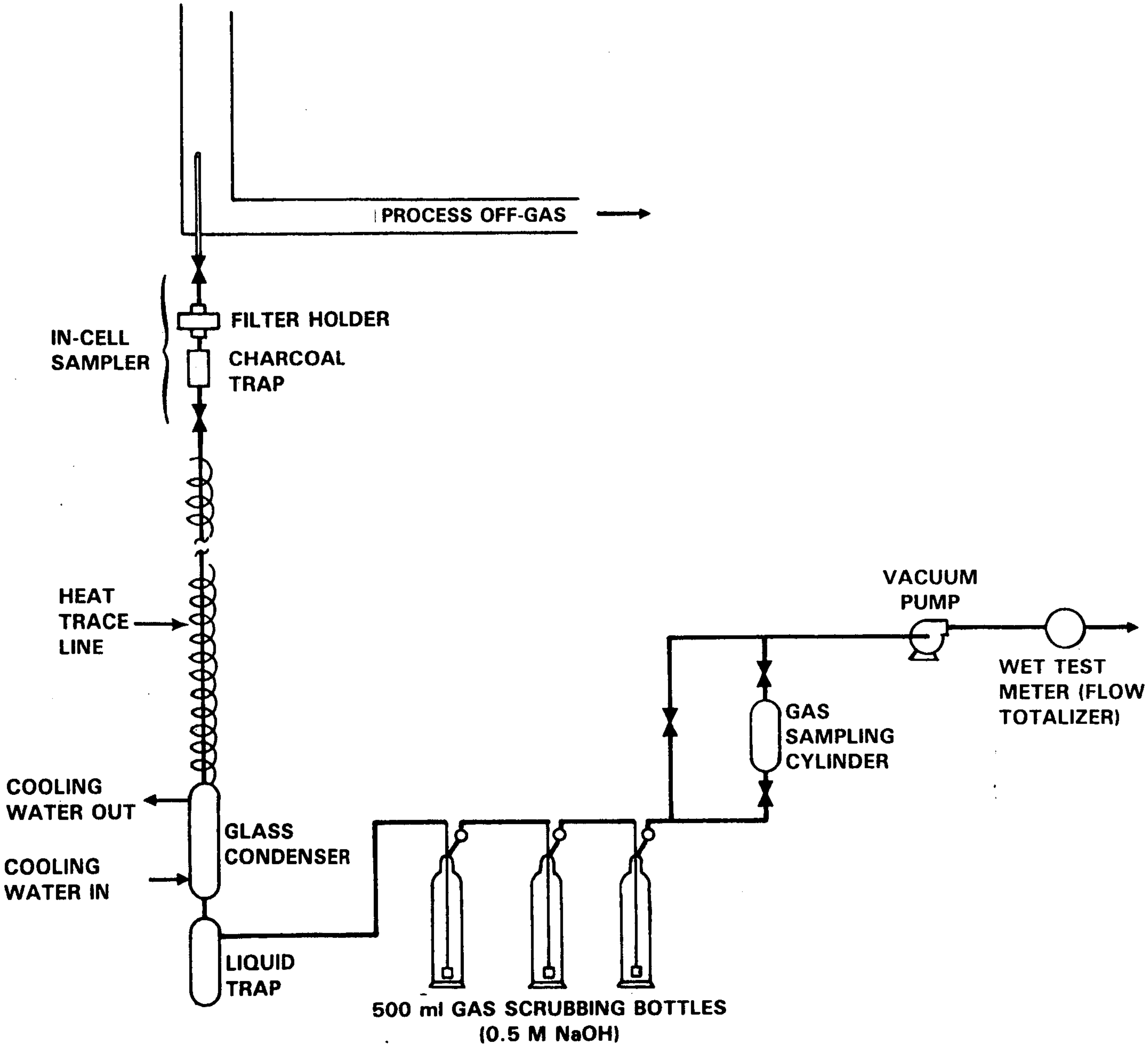

FIGURE 8. Off-Gas effluent sampling system.

trajectory to the filter. The filtered gas was subsequently passed through a charcoal trap and transferred via heat-traced tubing to a condenser and a series of three gas-washing bottles.

Gas samples required for off-gas compositional analysis were extracted after the gas scrub trains, as is detailed in Figure 8. The volumetric sampling rate, as well as the integrated sampling volume, were established through use of a wet test meter. True isokinetic sampling was not achievable during these tests due to the pulsating nature of the off-gas flow rate produced by the batch feeding process.

Liner/Cask/Canister

Due to the radiolytic generation of gases within the loaded zeolite beds, the sealed TMI shipping casks and liners were sampled in order to collect data on vessel pressures and gas compositions. The sampling systems used for this purpose are detailed in Figure 9. In order to reduce the significance of atmospheric gases upon the analytical results obtained from the gaseous samples collected, inert neon was used to displace these components from the sampling system. The partial pressures of the neon remaining in samples were subsequently excluded from gas-composition calculations.

The distribution of cesium across the TMI zeolite ion exchange beds was also established for each of the liners processed at PNL. This was accomplished by mapping the ^{137}Cs γ-ray activity as a function of bed depth. The γ-ray scanning system used in the studies is detailed in Figure 10. This system was also used to examine the uniformity of ^{137}Cs in the product glass canisters. Strontium-90 profiles could not be established using this remote γ-scanning system, since the decay of this isotope is not accompanied by γ-emission.

LABORATORY ANALYSIS

Laboratory analysis of samples collected in support of the TMI Zeolite Vitrification Program included both radiological and compositional determinations. The radioactive isotopes of cesium were directly quantified by γ-ray spectrometry. The quantity of ^{90}Sr present was determined through β^- counting techniques after ion-exchange separation from cesium isotopes. Analysis of ^{129}I, which was differentially collected on the charcoal absorber, required the

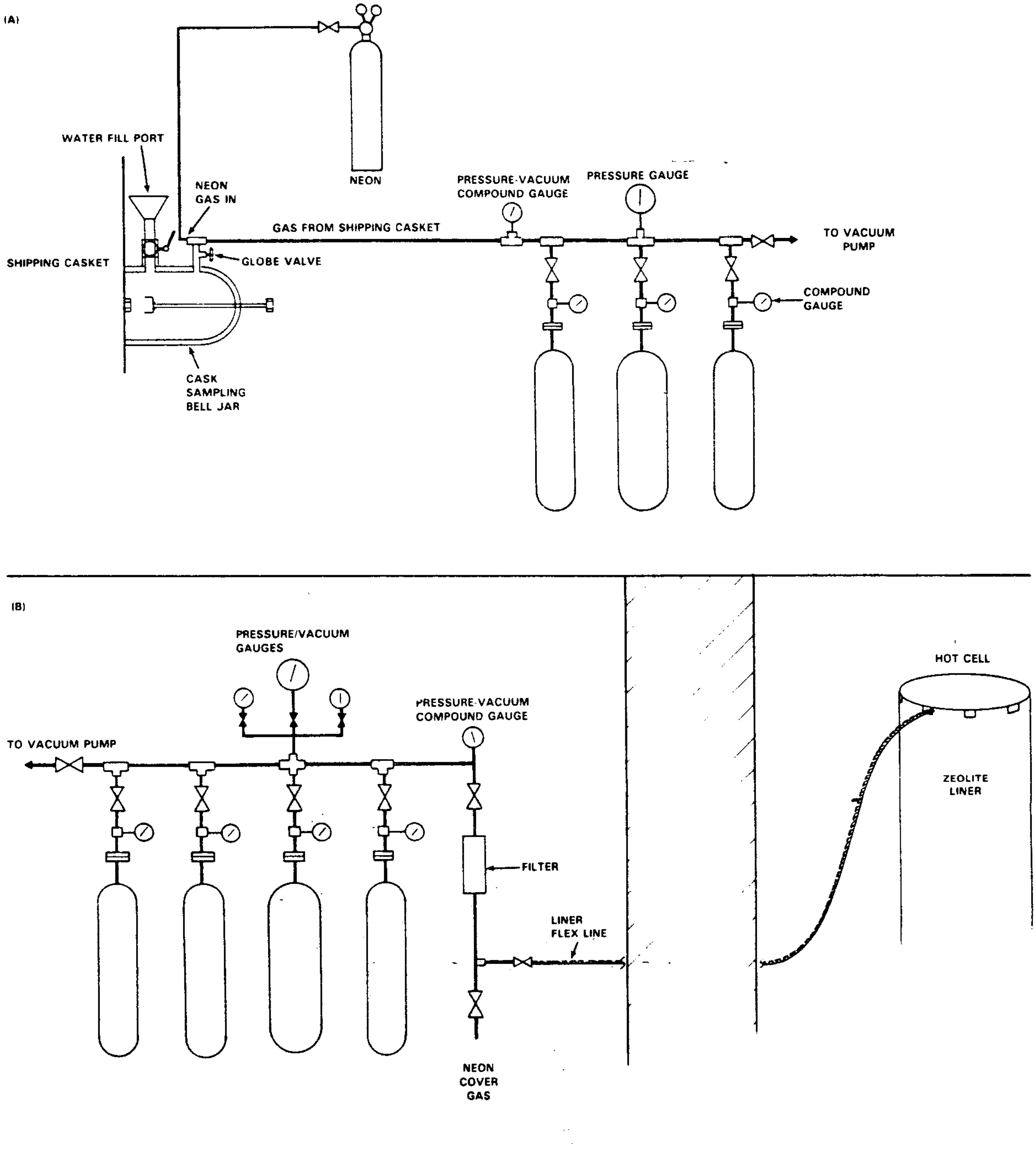

FIGURE 9. Gas sampling system for cask.

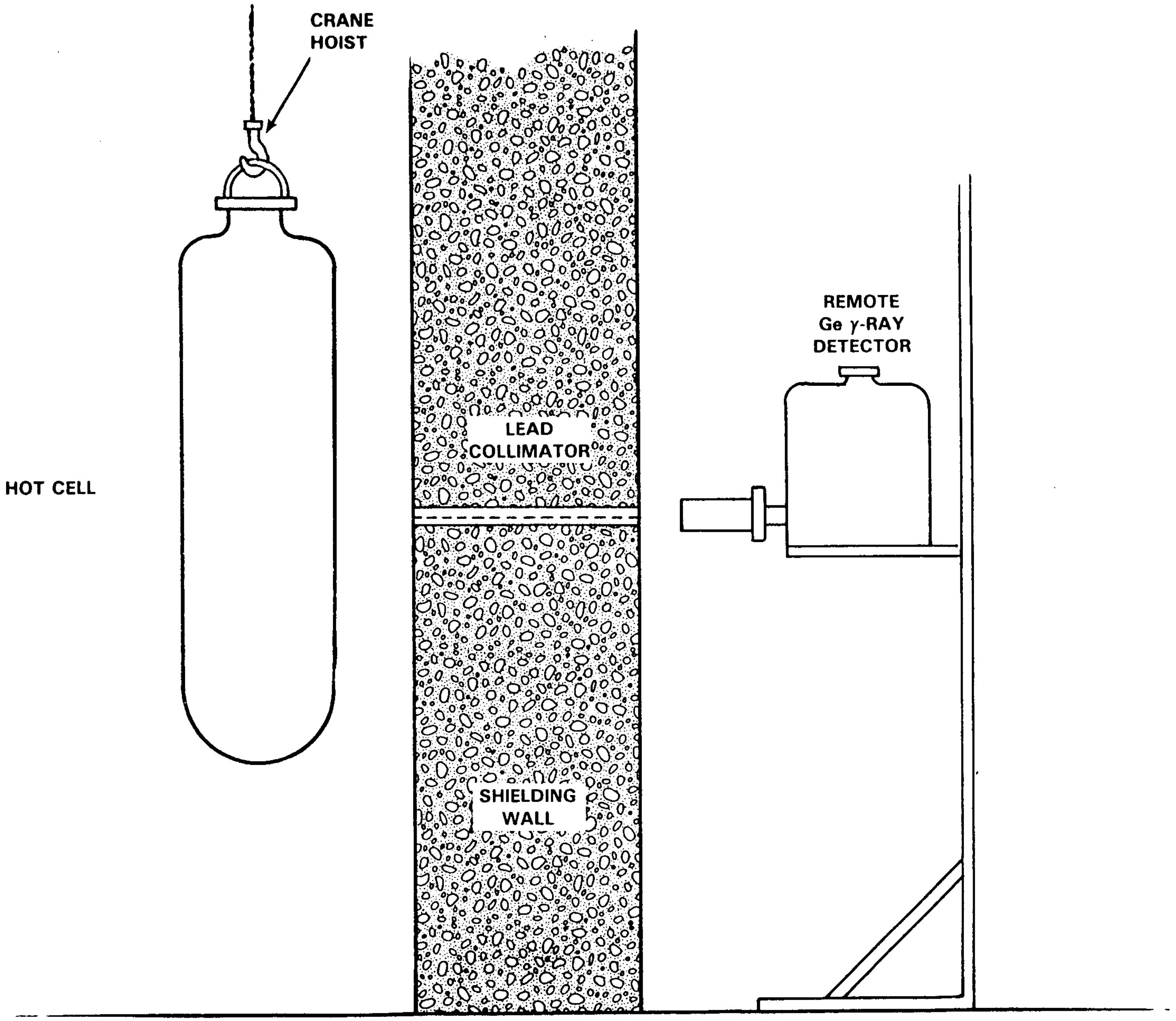

FIGURE 10. Remote γ-ray scanning system.

use of neutron activation analysis. Finally, the ^{3}H and ^{14}C content of melter-generated condensible and/or scrubber gases was established through liquid scintillation counting techniques.

The gross elemental composition of condensed-phase samples was established by an inductively-coupled plasma spectrometer and atomic absorption spectroscopy.

The composition of the noncondensible melter exhaust stream was routinely determined using a mass spectrometer, which yielded on the amounts of CO, CO_2, N_2, O_2, and H_2 present. In addition, the average water loading of the melter exhaust was also established through use of condensate sample data.

Results of Off-Gas Characterization

Effluent generated by the solidification of TMI zeolite waste was sampled by five discrete collection devices: a) a filter, b) a charcoal trap, c) a condenser, d) gas scrubbers, and e) gas cylinders. The nature of the samples collected by these devices will now be discussed.

- Filter Samples

Aerosol generation was found to be the predominant mechanism responsible for the solidification process losses of ^{134}Cs, ^{137}Cs, and ^{90}Sr. Table 3 summarizes melter system decontamination factors (DFs) for ^{134}Cs, ^{137}Cs, ^{90}Sr, and total gross melter entrainment. These measurements are quite different from those obtained during cold testing of the vitrification equipment.[1] This strongly suggests a breached or malfunctioning filter housing (see Figure 4). The sample collected from the D-10015 liner most strongly supports this notion. Calculated emission parameters associated with this liner were deliberately excluded from Table 3 due to the unrealistically high filter loading that was observed for this sample. Apparently, the sample nozzle had accumulated particulate matter during the processing of the D-10015 liner. When sampling was initiated toward the end of this processing campaign, the integrated sample was collected by the sampling filter. This was evidenced by a sharp decrease in the sample stream pressure drop that occurred soon after sampling was initiated. Such an accumulation of matter could not have occurred had the process filter housing been functioning according to design. The accumulation affect mentioned above did not influence the data obtained from the two high-level liners, since the sampling nozzle was cleaned prior to liner sampling.

TABLE 3. CHARACTERISTICS OF MELTER SYSTEM PARTICULATE EMISSIONS

				Quenched Off-Gas Loading,*			Melter System DF		
Zeolite Liner	Processing Date	Sampling Period	Feeding, kg/h	^{134}Cs & ^{137}Cs, μCi/L	^{90}Sr, μCi/L	Particulate mg/L	^{134}Cs & ^{137}Cs	^{90}Sr	Particulate
D-10015	09/22/83	105 min	5.0	--	--	10.0	--	--	--
D-10012	01/18/83	79 min	7.0	19.0	0.99	0.26	23,000	31,000	9,400
D-10016	03/06/83	60 min	7.7	9.8	0.95	0.36	69,000	49,000	12,000

* Temperature/Dew Point: 20°C.

The chemical composition of the aerosol samples are compared with the melter zeolite feed in Table 4. The entrained matter is compositionally enriched with agglomerating elements B, Li, and Ti, as well as Na, but is otherwise quite similar to the waste zeolite feed. This is precisely what was found in aerosol samples collected <u>before</u> the sintered metal filter housing during the cold testing phase of the ZVDP.

TABLE 4. COMPARISON OF MELTER-ENTRAINED MATTER AND FEED COMPOSITIONS

	Melter Generated Aerosol, wt%			
Element	Liner 1	Liner 2	Liner 3	Zeolite
Al	1.76	2.76	1.99	10.9
B	2.21	1.75	1.47	0.12
Ba	0.13	0.24	0.16	0.20
Ca	0.67	0.95	0.87	1.72
Fe	0.76	0.65	0.37	1.60
Li	7.68	6.56	7.63	0.0
Mg	0.18	0.26	0.24	0.69
Mn	0.04	0.20	0.08	0.09
Na	10.9	13.5	11.8	6.25
Si	2.86	4.42	4.11	22.00
Sr	0.03	0.03	0.02	0.10
Ti	7.64	7.0	7.0	0.12
Zn	0.09	0.14	0.08	0.03

Due to the high loading of particulate matter on the aerosol filter, the particle size distribution of melter-generated aerosols could not be determined. However, even if this data could have been extracted, it would not have been representative of the overall system (in-can melter/sintered metal filter) performance in light of the apparent filter housing failure.

- Charcoal Trap

Although there is no reason to believe that ^{129}I would be present on cation exchangers, the potential for physical adsorption always exists. Consequently, charcoal sampling for the ^{129}I isotope was conducted. Direct γ-ray counting of the charcoal proved too insensitive to even establish the presence of this isotope. As a result, chemical separation of iodine was conducted, followed by very sensitive high-efficiency γ-ray analysis. The results of this study, which are summarized in Table 5, suggest that ^{129}I is not a significant process-related effluent and thus would not require off-gas emission control. This conclusion is, however, highly specific to the particular waste form being processed in this study.

TABLE 5. GASEOUS IODINE-129 EMISSION ASSOCIATED WITH TMI ZEOLITE VITRIFICATION

Zeolite Liner	Feed, kg/L	Iodine-129 Loading: Off-Gas, fCi/L	Iodine-129 Loading: Zeolite, pCi/kg
D-10015	5.0	67	34
D-10012	7.0	57	46
D-10016	7.7	140	64

- Condensate

SDS liners were predried before shipment to PNL to reduce production rates of radiolytic gases. However, significant quantities of water remained in the zeolite liners after this drying process, thus presenting a radiological ^{3}H burden to the off-gas system. In order to measure the impact of this isotope upon melter processing equipment, water vapor generated by the solidification process was sampled, condensed, collected, and analyzed for its ^{3}H content. The results of these analyses appear in Table 6. Since the vitrification process has no capacity for water (DF = 1), the radiological impact of this isotope upon the off-gas system of any future solidification process will be dependent upon both the water loading of the melter feed and the specific activity of this water. Another important volatile isotope, which if present in melter feed would be totally converted to an off-gas effluent, is ^{14}C. Thus, the condensate samples were also analyzed for this isotope; no activity was detected. Carbon-14, as will be discussed below, does not appear to be a significant radiological effluent.

TABLE 6. TRITIUM EMISSION ASSOCIATED WITH TMI ZEOLITE VITRIFICATION

Zeolite Liner	Tritium Loading (μCi/kg) Feed	Tritium Loading (μCi/kg) Zeolite	Condensate Specific Activity, ηCi/g
D-10015	0.075	0.14	1.3
D-10012	0.99	1.9	17.0
D-10016	0.011	0.20	2.5

- Gas Scrubbers

Since conversion of ^{14}C to CO_2 is most probable, gas scrubbing techniques were used to sample for this acidic gas. Analysis of these scrubbers failed to detect any significant quantities of this isotope in the off-gas stream. This was expected, since ^{14}C is not a direct fission product and, in any case, would be tremendously diluted by the carbonate present in glass formers that are added to the melter feed.

- Gas Samples

The composition of the noncondensible melter exhaust gas composition was routinely analyzed with a mass spectrometer. The results generated by the instrument appear in Table 7 along with the water content of the off-gas stream, which was calculated from the collected condensate samples. This table clearly characterizes the process exhaust gas composition as being little more than wet, CO_2-enriched inleakage, which presents no significant demands upon the design of a process-related off-gas system.

TABLE 7. COMPOSITION OF MELTER EXHAUST GAS

Zeolite Liner	Average Molar Composition (Dry), %					
	CO_2	CO	O_2	N_2	H_2	Ar
D-10015	20.4	<0.5	15.3	63.3	0.16	0.8
D-10012	12.7	<0.1	17.6	68.6	0.3	0.8
D-10016	18.3	<0.1	16.9	64.0	<0.01	0.8

Results of Cask/Liner/Canister Analysis

- Gas Pressure/Composition

Vessel pressure and gas composition were measured on both shipping casks and zeolite liners upon arrival at PNL. These results are compared with initial vessel conditions established at TMI prior to shipment (see Table 8). Significant differences in initial shipping conditions of the low-activity and the two high-activity liners are responsible for the differences in the final gas compositions of these liners. The high-activity liners were dried and shipped with a platinum-palladium recombiner (H_2-O_2) and a rarified (28 in. Hg vacuum) argon atmosphere. However, the initial shipping conditions represented a gas composition which was not in equilibrium with the zeolite which possessed significant quantities of adsorbed gases. As a result, the final gas composition measured at PNL represented a reestablished equilibrium condition which had been modified by radiolysis, recombination, and inleakage. The results of these studies have shown that dried high-activity liners can be sealed and transported over significant periods of time without risking overpressurization and/or the production of flammable mixtures of combustibles.

TABLE 8. MEASUREMENTS OF CASK/LINER PRESSURE COMPOSITION

Shipment	Vessel	Condition	Absolute Pressure Hg*, m	Avg Molar % Gas Composition (Dry)					
				CO_2	CO	O_2	N_2	H_2	Ar
D-10015	Liner	Initial	(0.86)	--	--	--	100.0	--	--
	Liner	Final	0.93	0.55	<0.1	0.05	92.8	5.60	--
D-10012	Cask	Initial	(0.76)	--	--	--	100.0	--	--
	Cask	Final	0.76	0.03	<0.1	1.6	98.3	<0.01	0.08
	Liner	Initial	(0.10)	--	--	3.2	15.4	0.4	81.0
	Liner	Final	0.09	1.3	<0.1	12.3	83.2	2.1	1.1
D-10016	Cask	Initial	(0.76)	--	--	--	100.0	--	--
	Cask	Final	0.67	0.02	<0.1	1.4	98.4	<0.01	0.07
	Liner	Initial	(0.05)	--	--	0.6	3.7	0.1	95.6
	Liner	Final	0.17	3.3	<0.1	4.3	90.8	1.5	0.05

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* Values in parentheses were calculated from gauge pressures assuming 0.76 m Hg ambient conditions.

- Cesium-137 Profiles

The distribution of cesium in TMI zeolite liners and product glass canisters was established using remote γ-ray scanning equipment. In this approach, the 662 keV γ-ray activity of ^{137}Cs emanating from a small volume element of the canister was used as a direct measure of the cesium concentration in that element. By mapping the γ-ray activity along the central axis of the liners and/or canisters, the distribution of cesium within these vessels was established. Figures 11 and 12 illustrated the type of distribution which was obtained by this technique for liners and canisters, respectively. All three liners processed possessed well defined cesium band structures totally confined to the top two-thirds of the bed. On the other hand, the product glass canisters exhibited uniform cesium concentrations throughout the entire glass volume as is clearly shown in Figure 12. The last point in this profile was influenced by the rounded geometrical shape of the canister bottom and, consequently, is not indicative of an heterogeneity.

CONCLUSIONS

A nonradioactive solids feeding ICM process was developed and demonstrated for the immobilization of TMI zeolites. Similar equipment was fabricated and installed in a PNL radiochemical cell. Three SDS liners were shipped to PNL for vitrification by this process equipment. The only operational problem experienced was foaming or bridging at high feed rates. The ZVD program successfully demonstrated vitrification as an option for permanent disposal of this material.

ZVDP effluent characterization studies have shown that emission of melter-generated aerosols is responsible for most radioactive, process-related losses to the off-gas system. Average melter system DFs for cesium and strontium were 17,000 and 20,000, respectively. The difference between these values is not considered significant, indicating the absence of a strong volatilization/condensation loss mechanism for cesium isotopes. Overall, off-gas particulate entrainment was found to be too high to allow aerosol size distributions to be established. This high aerosol off-gas loading is most likely due to a malfunctioning sintered metal filter housing.

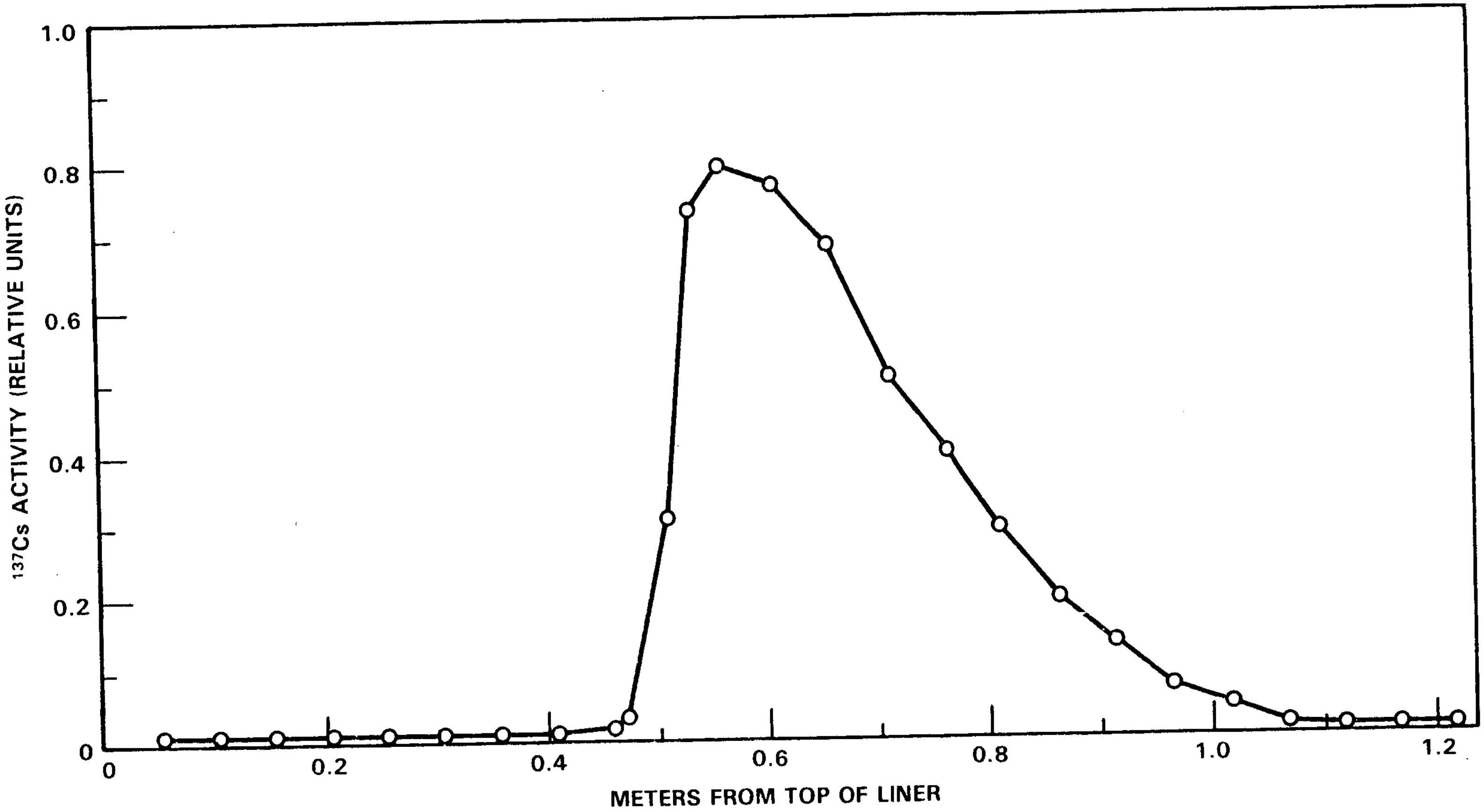

FIGURE 11. Cesium-137 distribution across zeolite liner--activity profile is typical of all TMI liners received.

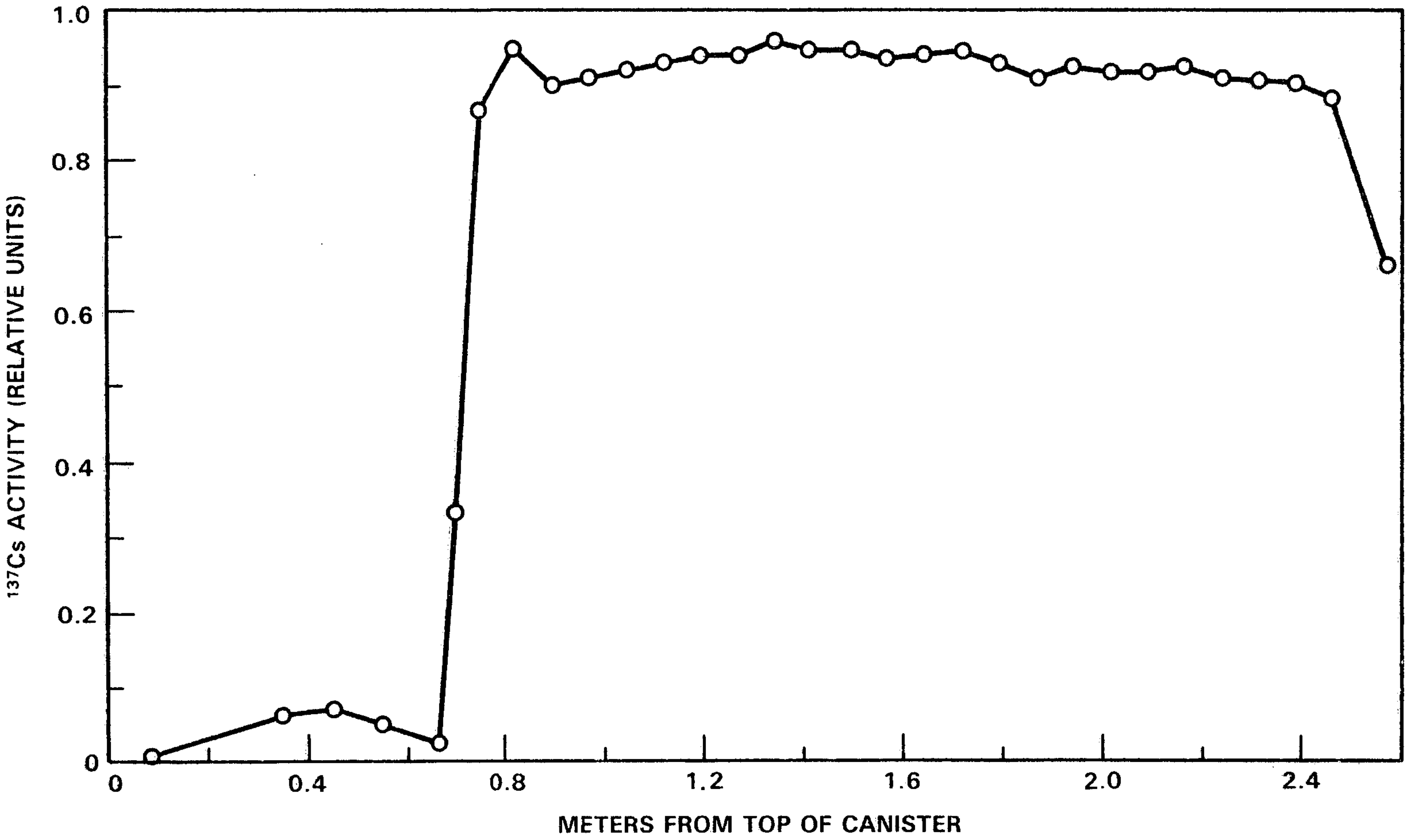

FIGURE 12. Cesium-137 distribution across vitrified ZVDP glass product canisters

Tritium in the form of water vapor is the only significant gaseous radioactive effluent generated by the vitrification of TMI zeolite waste. Since water possesses a DF = 1 for all glassification processes, the impact of tritium emissions from zeolite waste vitrification will depend both on the specific activity and quantity of water in the candidate feed.

The radioactive uniformity of the glassified TMI zeolite was established using γ-ray canister scanning techniques. In all cases, a homogeneous product was observed.

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