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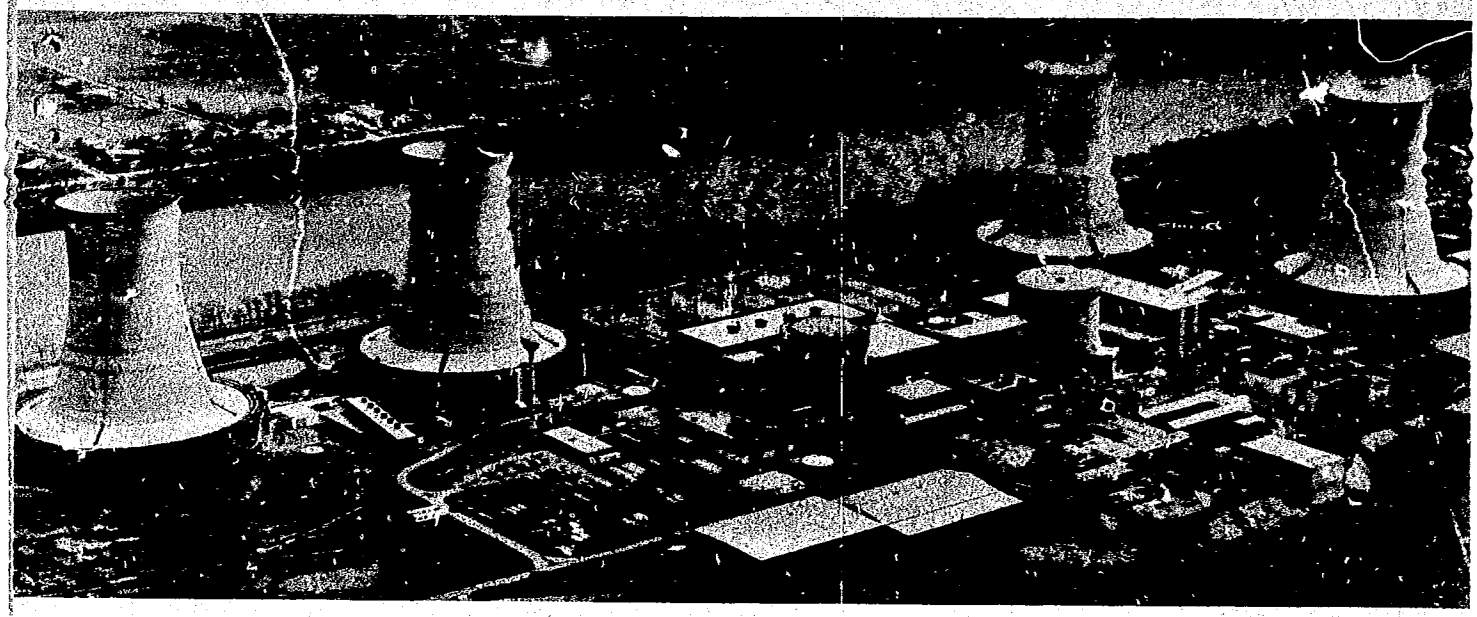

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Submerged Demineralizer System Vessel Shipment Report

MASTER

Geoffrey J. Quinn
James O. Henrie
Jess Greenborg

June 1984

Prepared for the
U.S. Department of Energy
Three Mile Island Operations Office
Under DOE Contract No. DE-AC07-76IDO1570

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SUBMERGED DEMINERALIZER SYSTEM VESSEL SHIPMENT REPORT

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ABSTRACT

Vessels containing zeolites and absorbed fission products from processing accident generated water at Three Mile Island through the Submerged Demineralizer System were found to generate radiolytic hydrogen and oxygen gases. In some vessels with high curie contents, gas generation during shipment could have resulted in flammable gas concentrations exceeding federal limits for radioactive material shipments. Tests of a catalyst bed in the vessel demonstrated that recombination of the gases back into water would permit safe shipment of the sealed vessels. Catalyst was loaded into an available screen assembly in each vessel. Vessel pressure monitoring ensured that net gas generation had stopped and that hydrogen and oxygen concentrations were kept below flammable limits. All shipments complied with federal regulations.

DISCLAIMER

FOREWORD

GEND-035 is a report of the combined Waste Immobilization Program efforts of General Public Utilities Nuclear Corporation, Rockwell Hanford Operations, and EG&G Idaho, Inc., for the U. S. Department of Energy. For readability of data, the authors used the U. S. Customary and British Imperial systems of units and the International System of Units where applicable.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of all those associated with this project and report. In particular, T. C. Runion, J. H. Pletscher, H. F. Sanchez, and D. T. Chung of EG&G Idaho, Inc.; J. K. Reilly of the Department of Energy; J. J. Galanto, B. G. Smith, and F. Telenko of General Public Utilities Nuclear Corporation; A. Viera, Bechtel North American Power Company; B. D. Bullough, G. A. Huff, C. R. Reichmuth, R. E. Smith, and D. G. Wilkins of Rockwell Hanford Operations; G. Bryan, D. E. Knowlton, and D. H. Siemens of Battelle Pacific Northwest Laboratory; H. O. Charnock and P. R. Clements of Westinghouse Hanford Company; and members of the Submerged Demineralizer System Vessel Shipping Task Force.

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SUBMERGED DEMINERALIZER SYSTEM VESSEL SHIPMENT REPORT

INTRODUCTION

The Submerged Demineralizer System (SDS) was constructed at Three Mile Island Unit 2 (TMI-2) to process the accident generated water and remove radionuclides, principally cesium and strontium. The system operates on an ion exchange process that uses as its active ingredients inorganic zeolite molecular sieve media. Radioactivity loadings on the expended zeolite were generally much higher than those for organic ion exchange wastes generated at normal commercial nuclear power plants.

After the start of SDS processing in June 1981, the expended SDS zeolite vessels were to be shipped to Richland, WA, for use as test materials in U.S. Department of Energy (DOE) waste immobilization research and development (R&D) programs. However, before the vessels could be shipped to the DOE national laboratories for study, radiolytic gas production in the vessels had to be characterized and quantified. In some vessels, H_2 and O_2 gases from radiolytic decomposition of water were being generated at rates that could have reached flammable gas concentrations during shipment. Federal Regulation 49 CFR 173.21 prohibits shipment of radioactive material which contains flammable gases.

This report describes the successful approach used to ensure safe shipment of the SDS vessels in compliance with government regulations. Specifically, a catalyst was inserted into each sealed vessel to recombine the radiolytic gases back into water (see Figure 1). The vessels were vacuum dried to enhance catalyst system performance. This report describes the testing methods General Public Utilities Nuclear Corporation (GPU Nuclear) used to determine gas generation rates, DOE laboratory testing of catalyst performance, the TMI demonstration of catalytic recombination in a radioactive vessel, demonstration of the vacuum drying system and catalyst insertion tool, preparations for subsequent shipments, and DOE R&D programs.

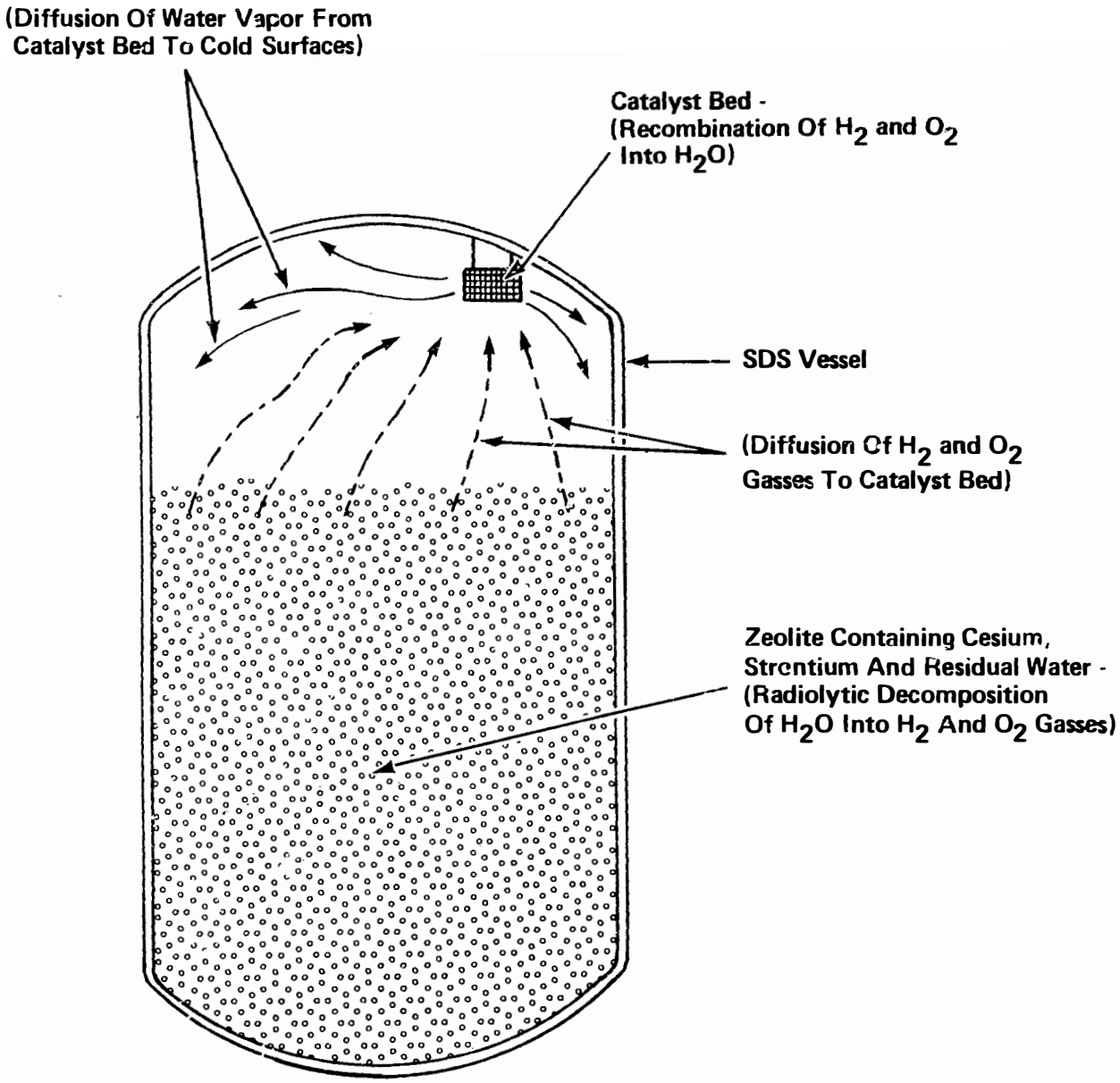

Figure 1. Diffusion recombiner system used to convert hydrogen and oxygen gases to water vapor in SDS vessels.

SDS LINER GENERATION

SDS Operations

The SDS started processing water in June 1981 and has since processed the water that was in the Reactor Building basement, the primary reactor coolant system, and several miscellaneous tanks.[1] The SDS water processing operation will continue through defueling and final decontamination of the facility. The SDS vessels contain an inorganic ion adsorption medium (demineralizer) called zeolite and are submerged in the TMI-2 spent fuel pool for radiation shielding, hence the name "Submerged Demineralizer System" (see Figure 2). The system pumps radioactive water through the zeolite beds in the vessels, leaving the radioactive contaminants, predominantly ^{137}Cs and ^{90}Sr, bound in the structure of the zeolites. Each vessel was loaded with about 8 ft^3 (227 L) of a mixture of two types of zeolites--Linde IE-95 and Linde A-51, chosen for their affinities for cesium and strontium.

Between June 1981 and May 1983, the SDS processed or reprocessed more than 2,000,000 gal (7.6×10^6 L) of accident generated water contaminated with 364,000 Ci of cesium and strontium--694,000 Ci with daughter products. (Unless otherwise noted, the use of Ci in this document will indicate curies of cesium and strontium without their daughter products.) These operations resulted in the generation of 13 expended zeolite vessels. The curie loadings of these SDS vessels are shown in Table 1. These curie loadings were determined by analysis of samples of SDS vessel influent and effluent. The accuracy of these values depends on sampling frequency and the accuracy of the analysis but are considered to be very good. The values shown in Table 1 are the result of the calculations and were not rounded to appropriate significant figures.

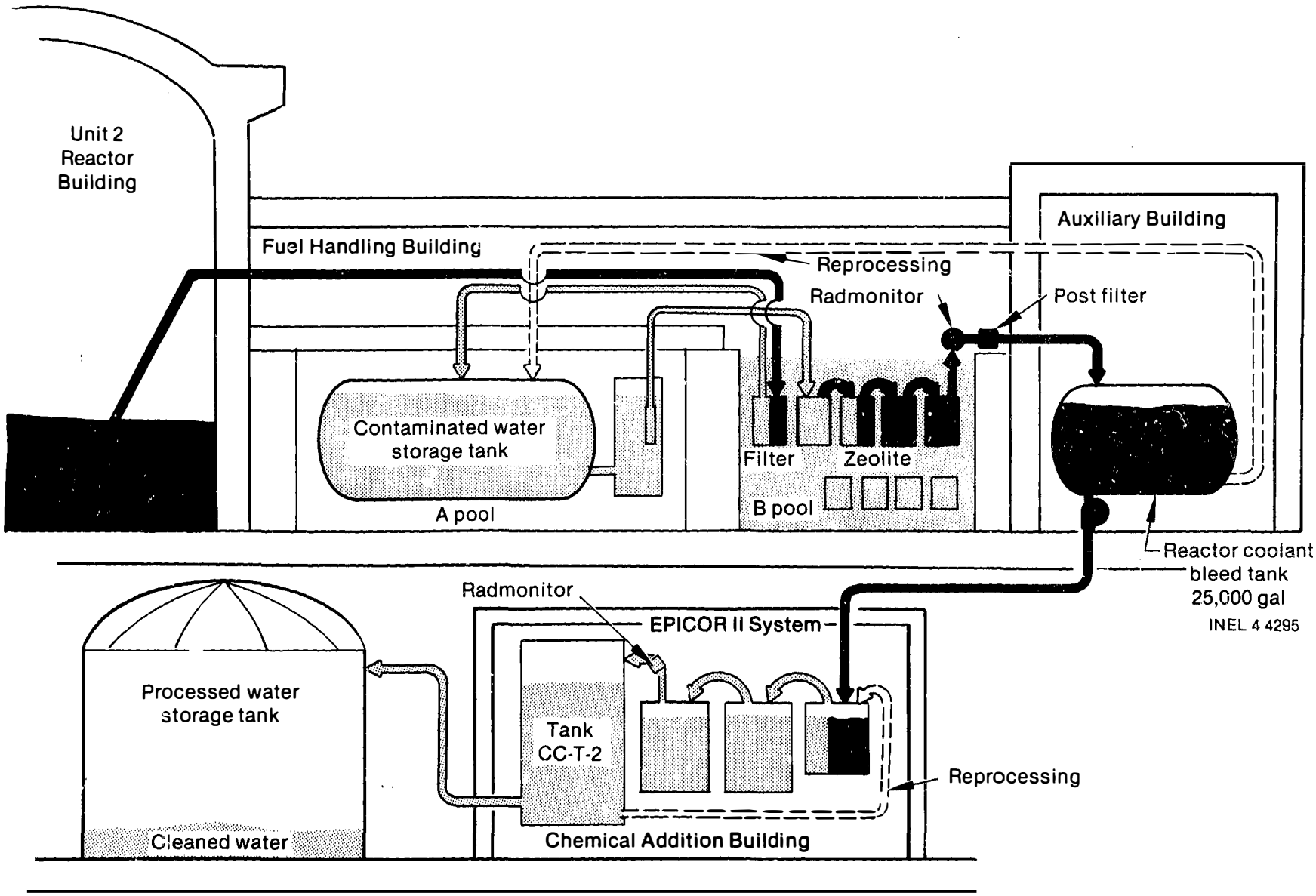

Figure 2. TMI-2 Submerged Demineralizer System.

TABLE 1. CURIE CONTENT OF SDS LINERS

Vessel	Cs (Ci)	Sr (Ci)	Total with Daughters (Ci)
D10011	44,317	2,061	88,158
D10012	57,176	2,003	112,635
D10013	49,281	1,974	97,151
D10014	28,534	2,585	59,761
D10015	5,767	1,012	12,896
D10016	57,156	1,869	112,622
D10017	30,312	1,021	59,542
D10018	2,451	309	5,273
D20022	2,599	1,006	7,198
D20026	4,036	1,343	9,692
D20027	7,084	8,124	29,732
D20028	43,333	1,660	86,334
D20029	2,127	4,863	12,705
Totals	334,173	29,830	693,699

Vessel Description

The SDS vessels are 4 ft, 5-1/2 in. (1.36 m) high, have a 2-ft (0 61-m) outside diameter, and have 3/8-in. (9.5-mm) thick walls made of 316L stainless steel (see Figure 3). Each has an internal volume of approximately 10 ft^3 (271 L). The vessels were designed to withstand 350 psig (2400 kPa) at 400°F (204°C) and were hydrostatically tested to 530 psig (3700 kPa).

Each vessel is equipped with five nozzles on the upper head. Two are zeolite fill ports, 3 in. (76 mm) in diameter and closed with standard, blind flanges that are gasketed and bolted on. The other three nozzles are flow nozzles, 1.5 in. (38 mm) in diameter and fitted with the male half of a quick disconnect coupling (Hansen with built-in check valve).

One blind flange is drilled and tapped for a 0.25-in. (6-mm) vent hose connection. A Johnson screen is welded to the inner side of the tapped blind flange to minimize the amount of zeolite fines entering the vent line.

The water inlet nozzle is a short pipe nipple 38 mm in diameter extending down from the quick disconnect coupling to an inlet spray header in the vessel. The spray header has four spray outlets to ensure, during the downflow process, an even water distribution across the top of the zeolite bed.

The water outlet line, which draws from the bottom of the vessel, consists of three, 38-mm-diameter pipe segments, two of which are straight pieces of stainless steel pipe connected by a 24-in. (0.61-m) long flexible hose of convoluted stainless steel. The flexible portion allows for thermal differential expansion of the vessel components. The lower pipe segment extends up from near the bottom of the vessel and is bevel cut on the end to allow water to flow up into the pipe. The bottom end of the pipe is screened for zeolite retention. The pipe comes up through a hole in the screen to join with the hose. The hose attaches to the upper pipe segment, which extends up through the top of the vessel to the quick disconnect coupling.

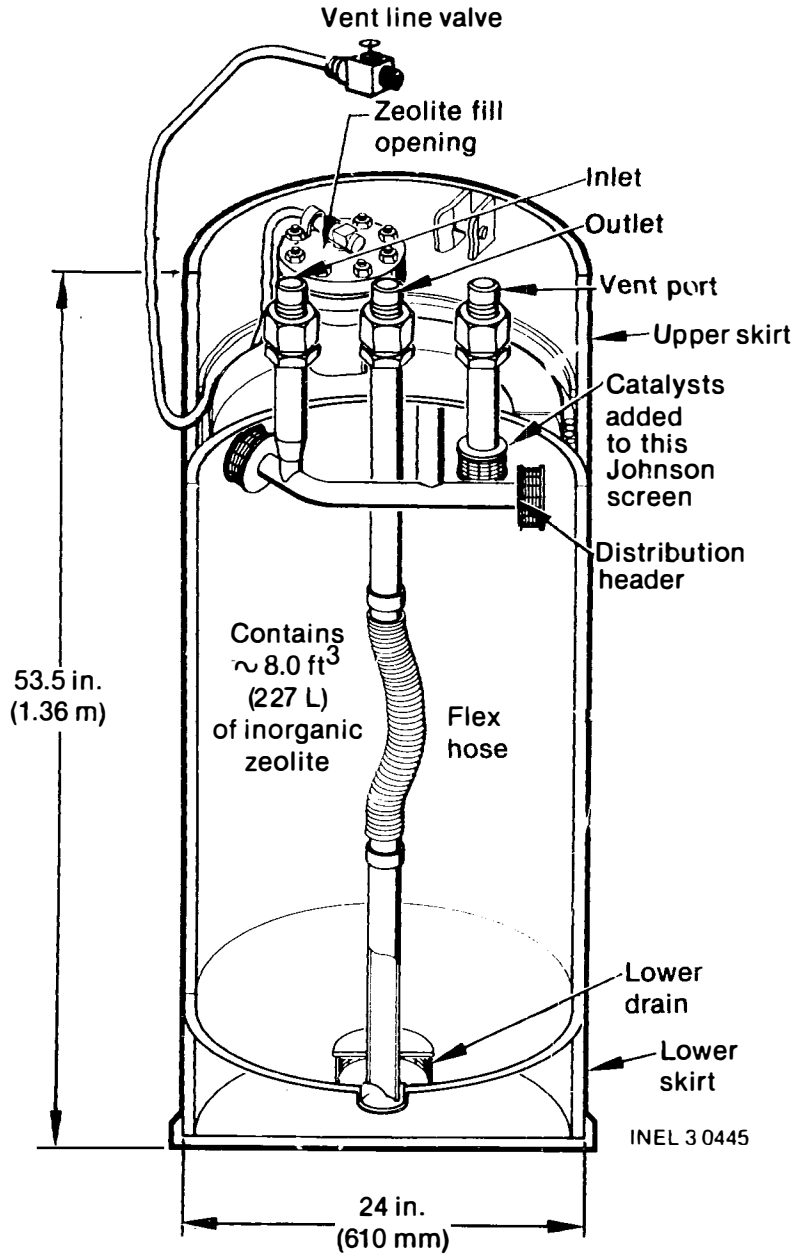

Figure 3. SDS vessel.

The vent nozzle is a short, 38-mm-diameter pipe nipple extending up through the top of the vessel A 3-in. (76-mm) diameter Johnson screen is welded around the pipe inside the vessel to retain zeolite fines. The internal volume of the Johnson screen and pipe below the coupling is approximately 14 in.^{3} (229 cm^3).

Zeolite Disposition Research and Development Programs

Following decontamination of TMI-2 accident generated water, SDS vessels containing expended, highly radioactive zeolites remained. Through a Memorandum of Understanding (MOU) between DOE and the U.S. Nuclear Regulatory Commission (NRC), DOE accepted these vessels to conduct a waste immobilization research and development (R&D) program by which it would generate information useful to the nuclear industry.[2] Specifically, the DOE R&D program was to demonstrate two waste immobilization alternatives: vitrification of SDS zeolites and monitored retrievable burial of SDS vessels in special concrete overpacks.

Shipping

Under the terms of the MOU, DOE assumed custody of the SDS vessels upon their removal from TMI. GPU Nuclear was responsible for preparing the vessels for shipment in accordance with DOE, NRC, and U.S. Department of Transportation (DOT) regulations and additional DOE requirements to facilitate the R&D program. EG&G Idaho, Inc. was responsible for shipping the vessels in accordance with DOE regulations. DOT regulations prohibit shipment of radioactive material generating flammable gas mixtures.[3] Therefore, the concentration of either hydrogen or oxygen (generated radiolytically in the SDS vessels) was required to remain below its lower limit of flammability during shipment. Hydrogen concentrations had to be less than 4.1% by volume at standard temperature and pressure (STP)--or less than 0.0018 gram moles/L of hydrogen; or oxygen concentrations had to be less than 5% by volume at STP--less than 0.0022 gram moles/L of oxygen.

Both DOE and the NRC required compliance with these DOT regulations. The Safety Assessment Document (SAD) for SDS vessel shipments required that gas concentrations in the vessels remain nonflammable for a period twice the expected shipment time.[4] The SAD required tests and measurements to verify that this condition would be met. Similarly, the NRC issued a Certificate of Compliance (COC #USA/9152/B()) for the SDS shipping cask (CNS 1-13C) with the same flammable gas specification.

EG&G Idaho found no potential adverse environmental effects in its evaluation of SDS vessel transportation.[5] Also, a risk assessment prepared by Battelle Pacific Northwest Laboratory concluded that the SDS vessel shipments "from TMI to Richland, WA, by truck can be conducted at an insignificant level of risk to the public."[6]

SDS LINER RADIOLYTIC GASES

Gas Generation Rates

Early in the design of the SDS vessels, engineers recognized that the production of gases due to radiolytic decomposition of water in the vessels would present safety concerns during in-plant storage. To prevent the buildup of gases, a vent system was incorporated into the vessel design. This vent system consisted of a valved flexible metal hose attached to each vessel. After an expended vessel was removed from service, the vent hose was uncoiled and attached to a vent header in the SDS off gas system (see Figure 4). The off gas system provided sufficient dilution flow to prevent a flammable gas mixture from accumulating. The vessel and vent system were capable of containing any H_2 combustion reactions initiated at pressures of up to 10 psig (69 kPa).

However, there was not enough information to confidently predict the gas generation rate or resulting composition and pressure in a sealed vessel during shipping. Therefore, a program was initiated to characterize the gas generation in the SDS vessels. As a part of this program, a gas sampling system was installed in the TMI-2 Fuel Handling Building beside the SDS. This system consisted of a pressure gauge and sample cylinder installed between the vessel vent hose and the SDS off gas system (see Figure 5). The sample cylinder was analyzed using the plant gas chromatograph to measure the gas composition of the evolved gases. The highest and lowest curie loaded vessels available at the time were selected for initial gas generation testing. Several vessels were tested in nondewatered and dewatered states. The dewatered state is achieved by pressurizing the vessel with nitrogen gas through the inlet nozzle to force the water through the outlet nozzle. After the vessel was connected to the gas sampling system, the gas pressure rise and the void volume for the vessel were determined. Periodic samples drawn through the sample cylinder were used to determine the gas composition. Figure 6 shows the gas generation rate in cc per hour versus the vessel curie content (curies of

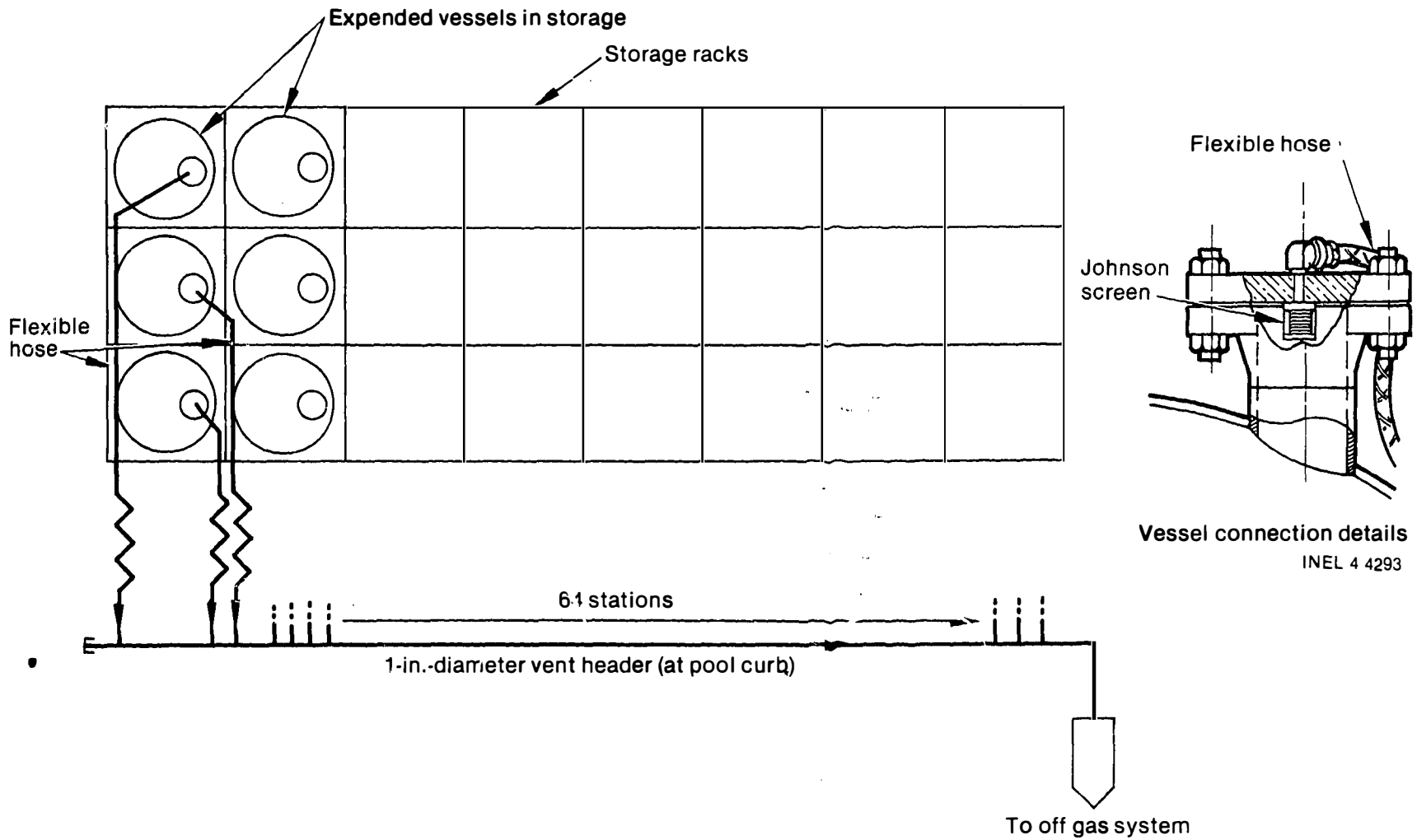

Figure 4. SDS vessel vent system. The flexible hose is a 1/4-in. inside diameter (nominal) stainless steel corrugated hose; the maximum pressure rating is 1400 psi.

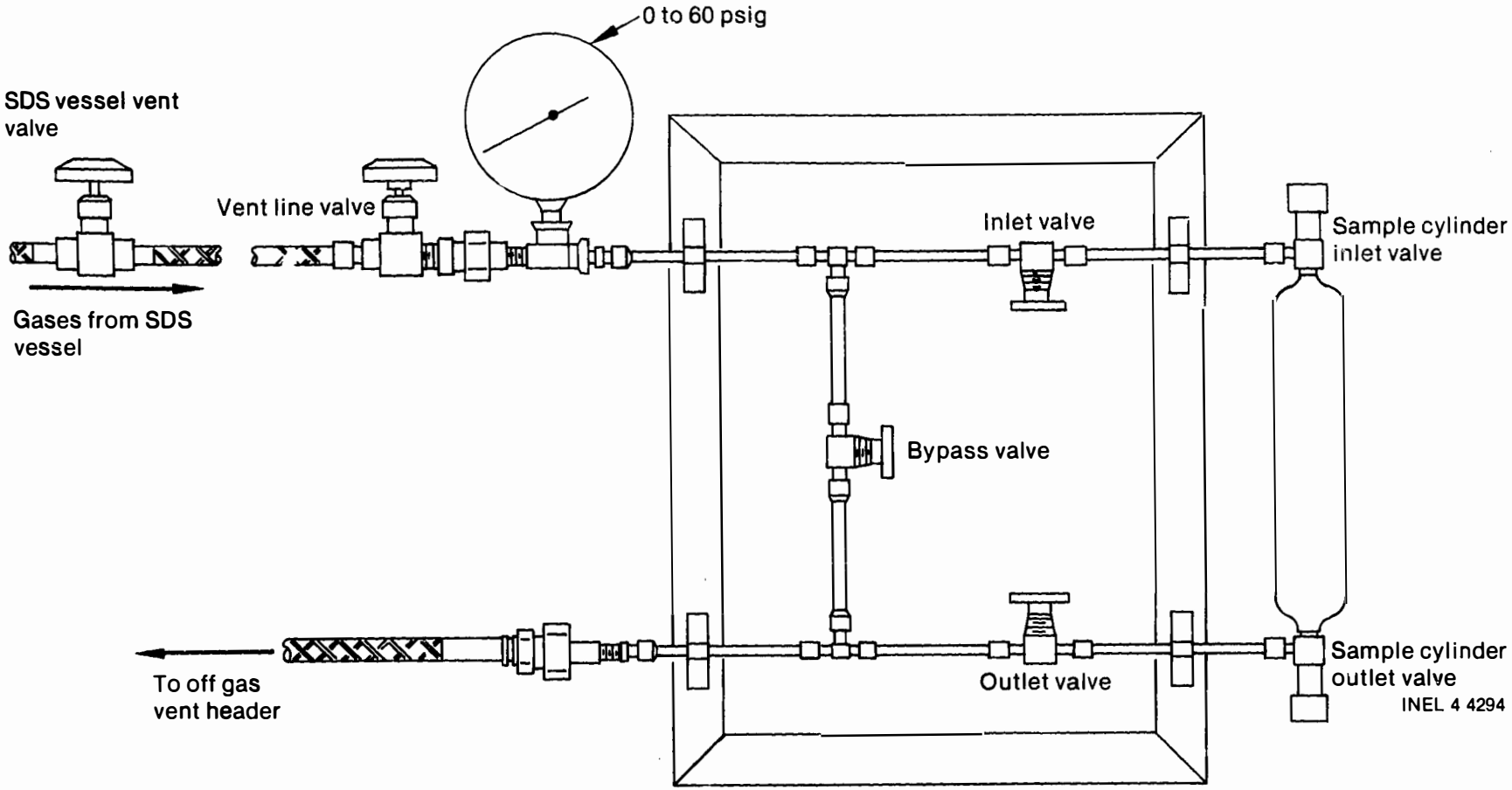

Figure 5. SDS gas sampling apparatus.

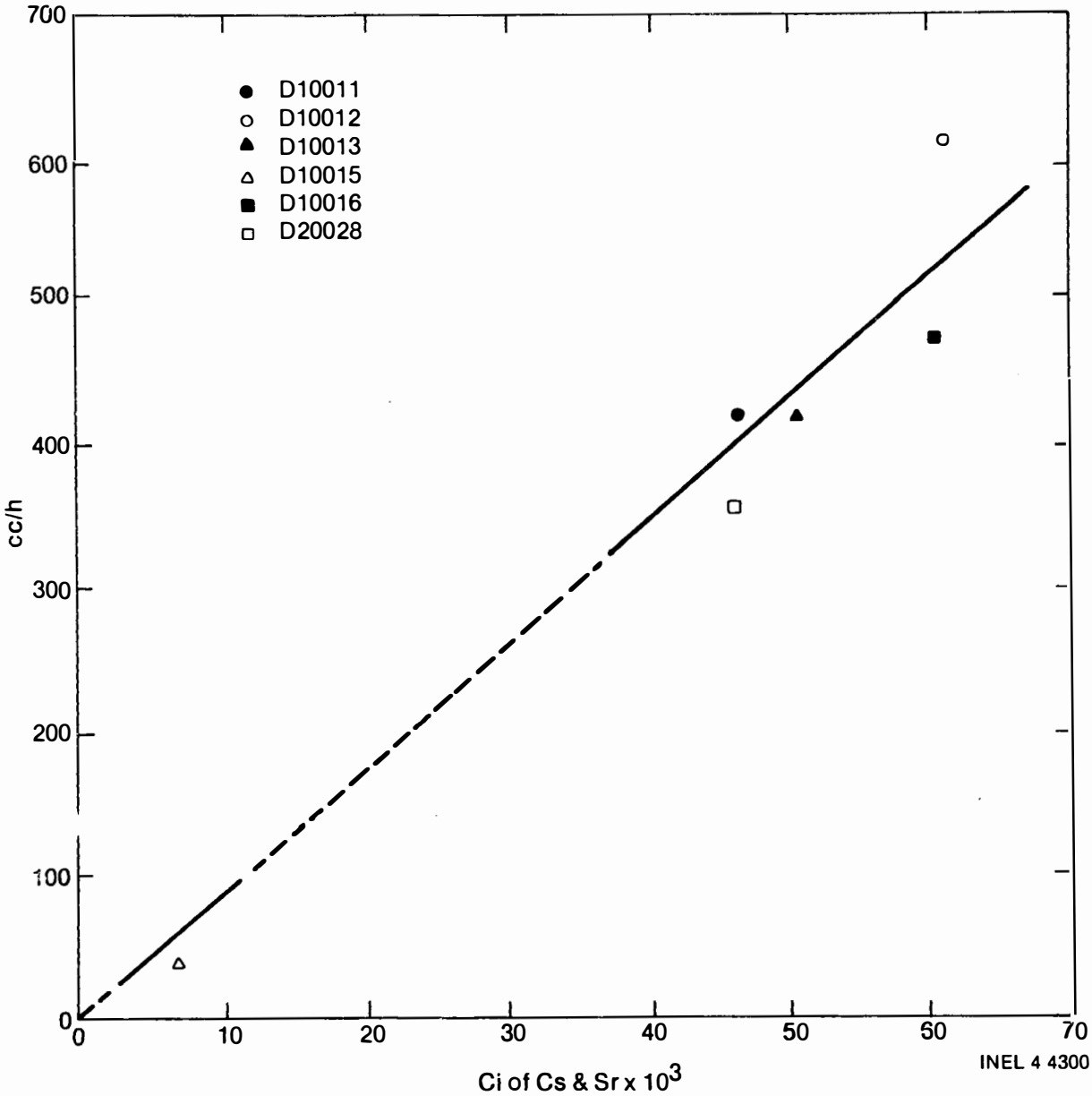

Figure 6. Total net gas generation rate versus curies of cesium and strontium. The radiolytic gas generation rate is higher. The H_2 to O_2 ratios are greater than 2. Some O_2 is being depleted (see Table A-1).

cesium and strontium) for six SDS vessels. Figure 7 shows the gas generation rate per curie of cesium and strontium versus the water volume left in the vessel for six SDS vessels. A summary of this gas generation data taken at TMI is presented in Appendix A.

The following observations were drawn as a result of the data collection program:

- The gas generation rate was proportional to the curie loading and was approximately 0.01 cc/h-Ci.

- The gas generation rate per curie was approximately proportional to the amount of water remaining in the vessel for the range from 2.8 to 5.2 ft^3 of water.

- The gas generation rate showed no sign of decreasing with increasing gas pressure. No approach toward equilibrium was observed.

- Stoichiometric gas mixtures did not immediately evolve in the vessels. The hydrogen/oxygen ratio of the resulting gas mixture was higher than stoichiometric (see Table A-1) but approaching stoichiometric with time. (Oxygen was being adsorbed or chemically bound to other elements in the system.)

The gas generation rates in SDS vessels loaded with more than 15,000 Ci, including daughter products, were sufficient to result in flammable gas mixtures by the end of the 14-day testing period (double the assumed shipping period of seven days). Since Department of Transportation (DOT) regulations prohibit shipment of radioactive materials with flammable gases, a means for suppressing gas accumulation during transport was required before the more highly loaded (greater than 15,000 Ci, including daughter products) vessels could be shipped.

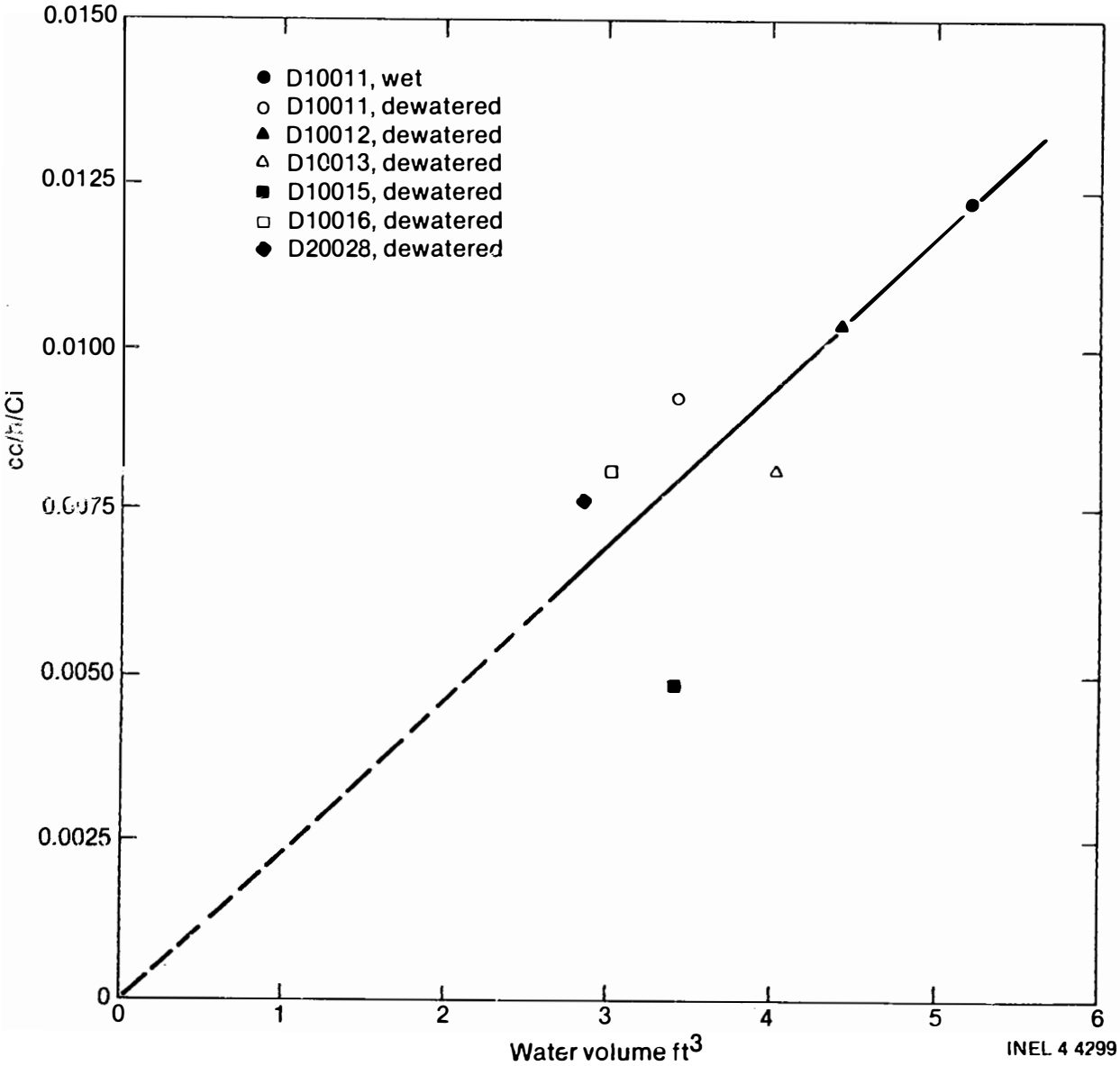

Figure 7. Gas generation rate per curies of cesium and strontium versus water volume remaining in the SDS vessel.

DOE Task Force for SDS Vessel Shipping

The generation rate of the radiolytic gases in the SDS vessels prompted a series of meetings to develop the approach that would ensure safe shipments. At the first meeting, experts from various DOE laboratories, private consultants, and representatives of EG&G Idaho and GPU Nuclear convened at TMI to discuss the configuration of the SDS vessels, gas generation rates, and gas composition results for these vessels. The current DOE, NRC, and DOT shipping regulations also were reviewed. The following list of methods to consider for preparing vessels for safe shipment was generated during this meeting:

- Shipping the vessels in casks of sufficient volume to safely dilute the generated gases
- Self drying by radiolysis, which would probably require eight years to reduce the water content to a level considered safe for shipping
- Purging or elution drying, using warm, dry gases such as N_2 or CO_2
- Suppressing radiolysis in a water-filled SDS vessel by adjusting the water to an alkaline pH by the addition of ammonia or hydrogen
- Vacuum drying, with the assistance of the self heating that accompanies radioactive decay
- Using a catalyst for gas recombination, along with vacuum drying.

The consensus of the meeting attendants was that mixtures of H_2 and O_2 gases from radiolytic decomposition of residual water in SDS vessels could be controlled at nonflammable levels by using catalytic gas recombiners. The catalyst recommended for gas recombination testing was commercially available palladium-coated porous alumina pellets. The

catalyst pellets were to be introduced into the SDS vessel by either of two means. The preferred method was to load the catalyst into the Johnson screen cup through the quick disconnect coupling on the vessel's vent nozzle. The alternative was to insert a catalyst bed through one of the 76-mm flanged fill ports. (Appendix B lists alternatives for preparing SDS vessels for shipment.)

DOE supported the catalyst testing and provided a vacuum drying system for preparing the vessels for shipment to DOE laboratories. Vacuum drying was required to ensure removal of the free standing water which could wet and thereby deactivate the catalyst if, in the event of a shipping accident, the liner were turned upside down. Vacuum drying also was expected to reduce the gas generation rate by removing water available for radiolysis. Shipping with a vacuum in the vessel was recommended to enhance diffusion of H_2 and O_2 to the catalyst bed and diffusion of water vapor from the bed.

VACUUM DRYING AND CATALYST RECOMBINER TESTING

Rockwell Hanford Operations (Rockwell), a DOE contractor, tested the processes of vacuum drying and catalytic recombination of hydrogen and oxygen. The tests simulated pertinent transport conditions--normal, abnormal, and accident-related--that could occur during actual shipment. These tests were performed at the Hanford site using a nonradioactive SDS vessel.

Simulated Transport Conditions

Normal Shipping Conditions

The SDS vessels would be evacuated (so that only the gases being generated remained) and sealed for shipment. Pressure inside the SDS vessel would be the equilibrium pressure of the generated gases plus the vapor pressure of water at the vessel shell temperature. A set of recombiner tests was conducted with the vessel initially evacuated to the vapor pressure of water. The criterion for a successful test was an inside vessel pressure that did not exceed 21 kPa for 40 h. At 21 kPa, if a burn of stoichiometric gas (67% hydrogen and 33% oxygen) occurred in the SDS vessel, the resulting peak pressure would be less than one atmosphere.

Abnormal Conditions

The SDS vessels were tested under the following two abnormal conditions:

1. Vessel leakage: If the SDS vessel develops a leak, permitting gas to enter the vessel, but the shipping cask remains sealed, the vessel and shipping cask would reach an equilibrium pressure of about one-half atmosphere. The criterion for a successful test was a pressure rise of less than 2.8 kPa for 40 h, starting at one-half atmosphere.

2. Vessel and cask leakage: If the shipping cask and SDS vessel both leak, air will enter the vessel, and the pressure inside the vessel will rise to one atmosphere. Gas produced inside the vessel could escape the vessel and shipping cask. Hydrogen accumulation in the vessel should be less than 4%. A series of tests starting at one atmosphere was considered successful if the hydrogen concentration in any gas vented from the vessel contained less than 2% hydrogen during a 40-h test period.

Accident Conditions

The SDS vessels were tested under the following three accident conditions:

1. Inverted shipping cask: During a transport accident, the SDS vessel in its shipping cask could be turned upside down. The recombiner would be surrounded by a bed of zeolite--a significant barrier to diffusion of hydrogen and oxygen to the catalyst. For this test, the SDS vessel remained sealed at the vapor pressure of water. The criterion for a successful test was a vessel pressure of less than 21 kPa for 40 h.

2. Inverted shipping cask with vessel and cask leakage: The assumed conditions originally were to have been shipping cask inversion and SDS vessel leakage. But because the atmospheric pressure test is a more stringent test, the cask was also assumed to leak rather than to reach an equilibrium pressure of one-half atmosphere. Therefore, the SDS vessel was vented during the test. The test was considered successful if gas vented from the vessel had a hydrogen concentration of less than 2% during a 40-h test period.

3. Inverted shipping cask with vessel of wet zeolite: The inverted test at atmospheric pressure was repeated but with very wet zeolite. Only a minimal amount of water was removed by vacuum

drying it from the zeolite after the vessel was drip dried with nitrogen gas. The criterion for a successful test remained the same as for the previous test.

Vacuum Drying

Test Objective

A series of tests was conducted to determine the effectiveness of removing water by vacuum drying the zeolite bed. The tests were performed on a nonradioactive SDS vessel containing a zeolite bed at room temperature and two 150-W heaters to simulate radioactive decay heat. Two existing connections, 38 mm and 6 mm in diameter, on the SDS vessel were connected to the vacuum system to be tested to determine the water removal rate for each connection size. Zeolite contains appreciable amounts of bound water. The residual water content, both bound and unbound, was quantified as a function of vacuum drying time.

Experiment

The SDS vessel loaded with zeolite was mounted on a 3300-kg platform scale. Water was added to completely fill the vessel and was left to stand overnight to saturate the zeolite. The vessel was dewatered by adding nitrogen gas through vent port C to force water out through drain port B (see Figure 8). The nitrogen was applied until the 2-m^3 nitrogen bottle was exhausted, as is done according to the procedure used at TMI.

The vacuum was connected to the 6-mm flex vent hose, which was attached to one of the 76-mm flanges on top of the SDS vessel. With the vacuum connected, the mass of the SDS vessel and pressure inside the vessel were recorded as functions of time.

The vessel was again filled with water and dewatered using nitrogen gas. The vessel was connected to the vacuum system with a 38-mm-diameter, 12-m-long pipe. Mass and pressure as functions of time were again recorded.

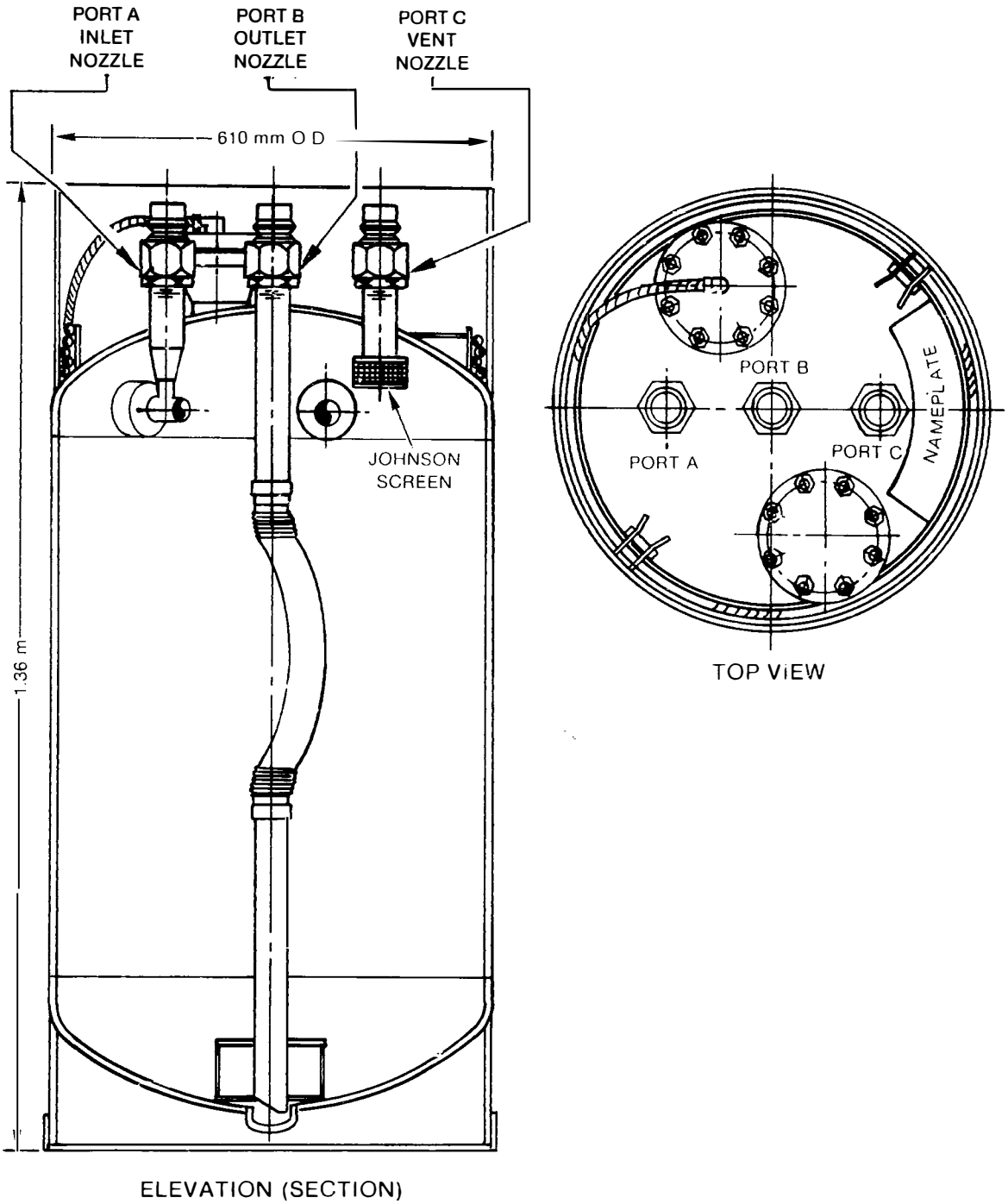

Figure 8. Cutaway and top views of an SDS vessel.

Radioactive decay heat was simulated with two 150-W resistance heaters mounted in the 76-mm flanged ports. The heaters had an active length of 30 in. (762 mm), a 0.63-in. (16-mm) diameter, and extended nearly the full depth of the zeolite bed. Thermocouples were added at various locations in the zeolite bed and on the external vessel shell. Vessel mass, pressure, and temperature were recorded as functions of time.

Test Results

Test 1 (6-mm Vent Line). Results of the vacuum drying test using the 6-mm vent line are shown in Figure 9. The SDS vessel was at ambient temperature during this test. Water removal rate was 3 lb (1.4 kg) per day over the six days of the test. Pressure in the vessel remained constant at the vapor pressure of water. This removal rate was too slow, as expected, and the test was terminated.

Test 2 (38-mm Vacuum Line Without Heat). Figure 10 presents the results of vacuum drying the SDS vessel through a 38-mm-diameter pipe, 12 m long--the approximate distance between the SDS vessels and vacuum system at TMI-2. No heaters were used; the vessel was at ambient temperature. The pressure spikes shown in Figure 10 were due to mechanical problems with the vacuum pump. Line resistance to flow was no longer the controlling factor, as evidenced by the decrease in pressure shown in Figure 10 as compared to pressure shown in Figure 9. Water removal was hindered as the vessel and its contents were subcooled by the rapid evaporation process. The test vessel was not submerged in water--as is the case at TMI--so heat transfer to the vessel was reduced. Temperatures measured inside the zeolite bed were below 0°C near the end of the drying period. However, even under these conditions, three times more water was removed through the 38-mm pipe than through the 6-mm vent line in a 160-h period.

Test 3 (38-mm Vacuum Line With Heat). The final vacuum drying test was done using the 38-mm line connection to the vacuum system and two 150-W heaters installed in the vessel. Results are shown in Figure 11.

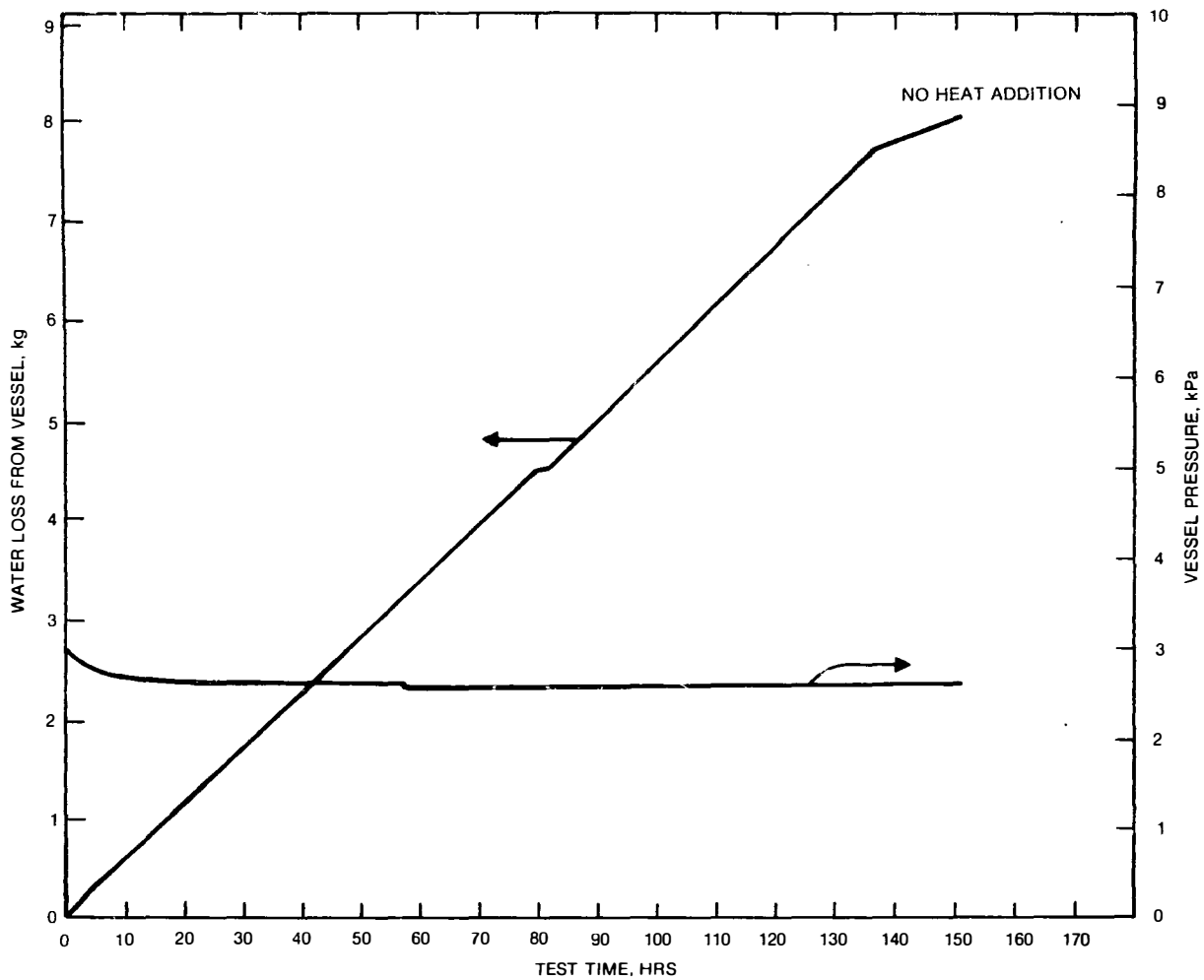

Figure 9. Water loss and vessel pressure for the pumping test with the 6-mm line.

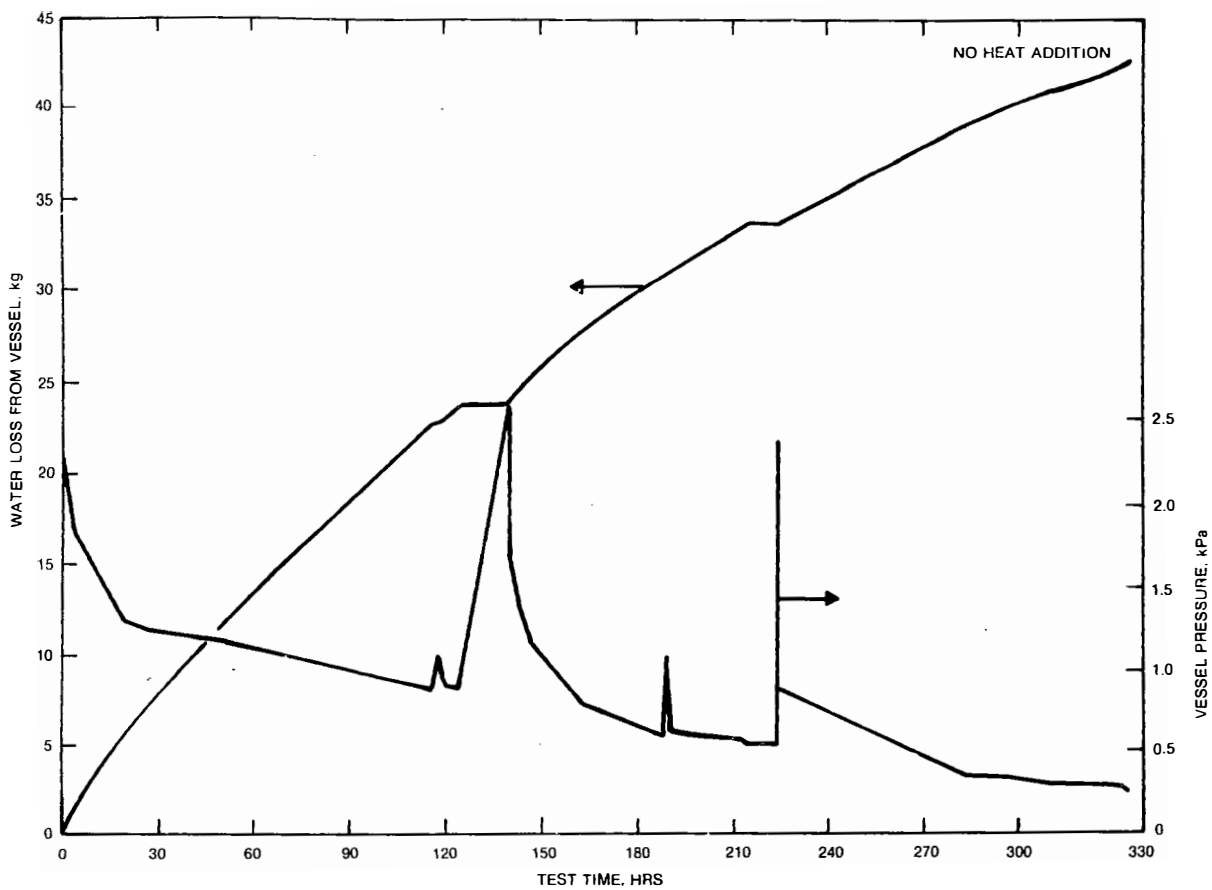

Figure 10. Water loss and vessel pressure for the pumping test with the 38-mm line.

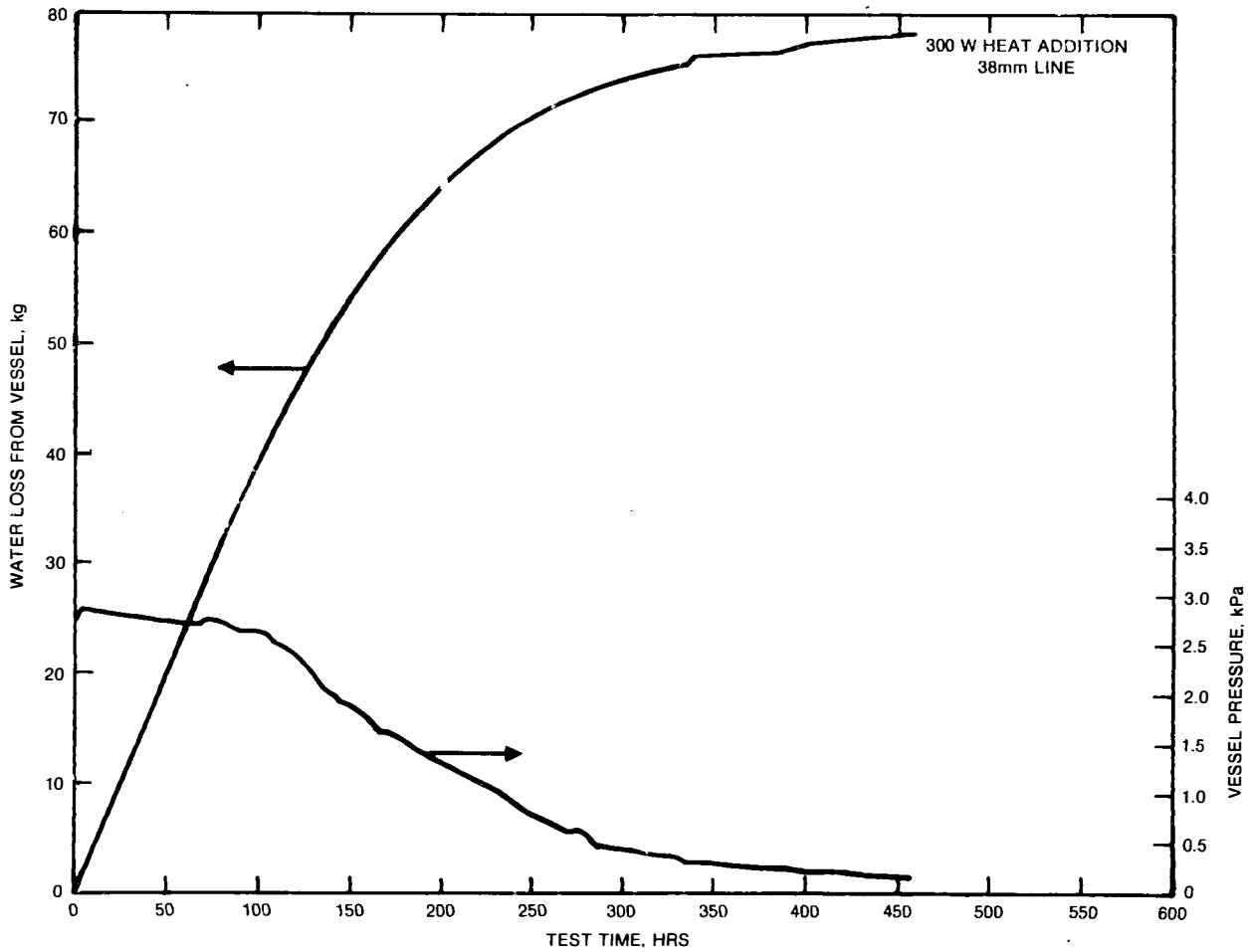

Figure 11. Water loss and vessel pressure for the pumping test with heat addition.

The heat greatly increased the rate of water removal. The partial pressure of water over the zeolite was increased because the heaters raised the temperature of the zeolite. The peak temperature near the center of the zeolite bed was 350°C while the lowest temperature, at the edge of the bed, was 27°C. This increased the water removal rate for any given pressure in the vessel as can be seen by comparing Figures 10 and 11. Approximately 50% of the bound water and all of the unbound water was removed with 19 days of vacuum drying. After the drying test, samples taken from the zeolite were analyzed and found to contain 8.7% water, dry basis. Water content was determined by weight loss upon heating to 500°C.

Using steady state heat transfer calculations and the HEATING 5 computer code, the thermal conductivity of the relatively dry zeolite while under vacuum was determined to be 0.14 W/m°C.

A total weight balance of the contents of a typical SDS vessel showed 315 lb (143 kg) of bone dry zeolite, 268 lb (122 kg) of loose water that could be blown out by nitrogen gas dewatering (drip drying), 100 lb (45 kg) of unbound water that could be removed by a second drip drying and minimal vacuum pumping, and 100 lb (45 kg) of loosely bound to tightly bound water that could be left attached to the zeolite during shipment and storage.

Catalytic Recombination

Test Objective

Rockwell has designed and used catalytic recombiners in homogeneous solution type research reactors. These closed systems were effective in recombining hydrogen and oxygen for time periods of more than 25 years. The objective of the test work described in this report was to determine the hydrogen concentration inside an SDS vessel fitted with a catalytic recombiner under a variety of conditions that simulate the expected transport and potential accidents. Another objective of the test was to determine if catalyst in the existing vent port Johnson screen would give satisfactory recombiner performance. Adequate performance requires

sufficient catalyst to recombine the gases and enough open screen space to permit diffusion of the gases and water vapor to and from the catalyst bed.

Experiment

An electrolysis unit was used to generate stoichiometric quantities of hydrogen and oxygen at the test pressure. Lithium hydroxide was used to increase conductivity of the water in the electrolysis unit. Calibration was performed by collecting the generated hydrogen and oxygen separately in volumetric flasks. The measured generation rates agreed with the theoretical production rates calculated from the observed amperage. A total of 236 g of Englehard Type D catalyst (palladium on alumina) was added through Port C. This port contains a 38-mm pipe that protrudes into the SDS vessel and is open to the vessel atmosphere through a Johnson screen. Open area of the Johnson screen is 7.7 cm^2.

A second type of catalytic recombiner was also designed and built for possible installation in one of the flanged fill ports of the SDS vessel. The recombiner was in the shape of a cylinder and had about 130 cm^2 of open screen area.

Hydrogen and oxygen were mixed, then fed to the SDS vessel through Port B, introducing the gas at the vessel bottom. For the inverted test with minimal vacuum drying, the hydrogen and oxygen were introduced at Port A. For atmospheric pressure testing, a wet test meter was used to measure the volume of gas expelled from the SDS vessel. The wet test meter was connected to the 6-mm hose for the upright test and to Port B for the inverted test.

The vacuum pump was a VWR Scientific Model D-500 (double stage rotary vane). Hydrogen concentrations were determined by gas chromatography; a 2% hydrogen gas standard was used as a calibration source. Pressure was read from a 0-100 kPa Leybold-Heraeus Logarithmic vacuum gauge.

Test Results

Test 1 (With Catalyst, Vacuum Dried Zeolite, and Vessel Upright and Inverted). The first catalytic recombination test followed the heated vacuum drying test. The upright vessel was evacuated to a pressure of 3.8 kPa. Stoichiometric hydrogen and oxygen were fed to the vessel at a total rate of 3 L/h. Pressure in the vessel rose to about 5 kPa and then leveled off as shown in Figure 12. This corresponds to the vapor pressure of water at room temperature. The vessel was then inverted and the test repeated. The results were essentially the same as for the upright vessel.

Test 2 (With Catalyst and Vessel at One-half Atmospheric Pressure). The recombination test was repeated with the vessel in an upright position at a total pressure of one-half atmosphere. The pressure-time relationship is shown in Figure 13. There was a slight decrease in pressure during the 40-h test. The lack of an observable pressure rise indicated that the feed gas was recombined successfully.

Tests 3 and 4 (With Catalyst and Vessel at Atmospheric Pressure). To simulate an accident whereby the liner and cask both leaked, two tests were done with the vessel vented to the atmosphere through a wet test meter.

The first atmospheric pressure test was done with the liner upright and the zeolite bed dry. Figure 14 shows the volume of gas expelled from the vessel. The rate of hydrogen and oxygen feed was cut in half after the first 5 L of gas were expelled, and the exit gas was sampled for hydrogen concentration; none was found. After each additional 5-L expulsion, samples were taken and analyzed for hydrogen. Again, none was found. Ten liters of gas were expelled before hydrogen reached the recombiner in sufficient quantities to start the recombination reaction. The thermocouple in the catalyst bed showed a temperature rise corresponding to the start of recombination. Gas was observed to move into and out of the vessel with fluctuations in vessel temperature caused by fluctuating (day to night) room temperatures.

The second atmospheric pressure test was done with the liner inverted and the zeolite slightly dried. A total of only 29 lb (13 kg) of unbound

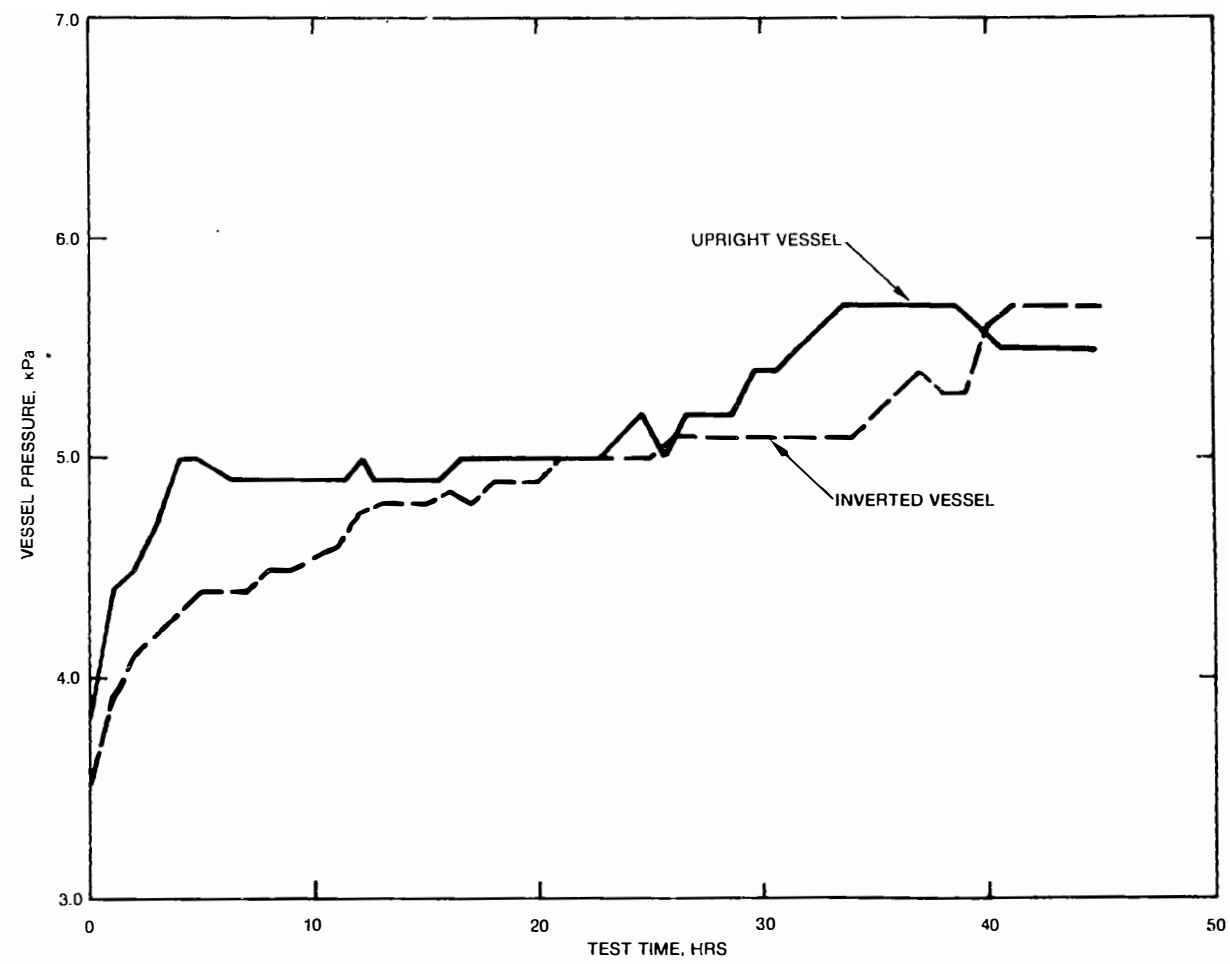

Figure 12. SDS vessel pressure for the vapor pressure recombiner tests.

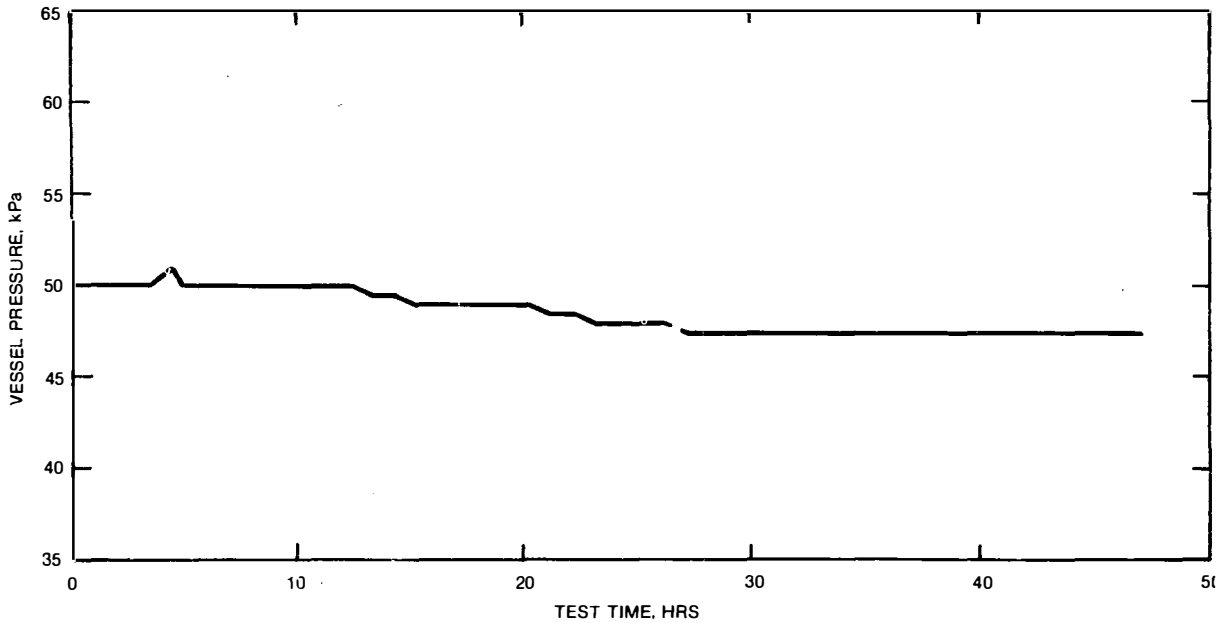

Figure 13. SDS vessel pressure for the one-half atmosphere recombiner test.

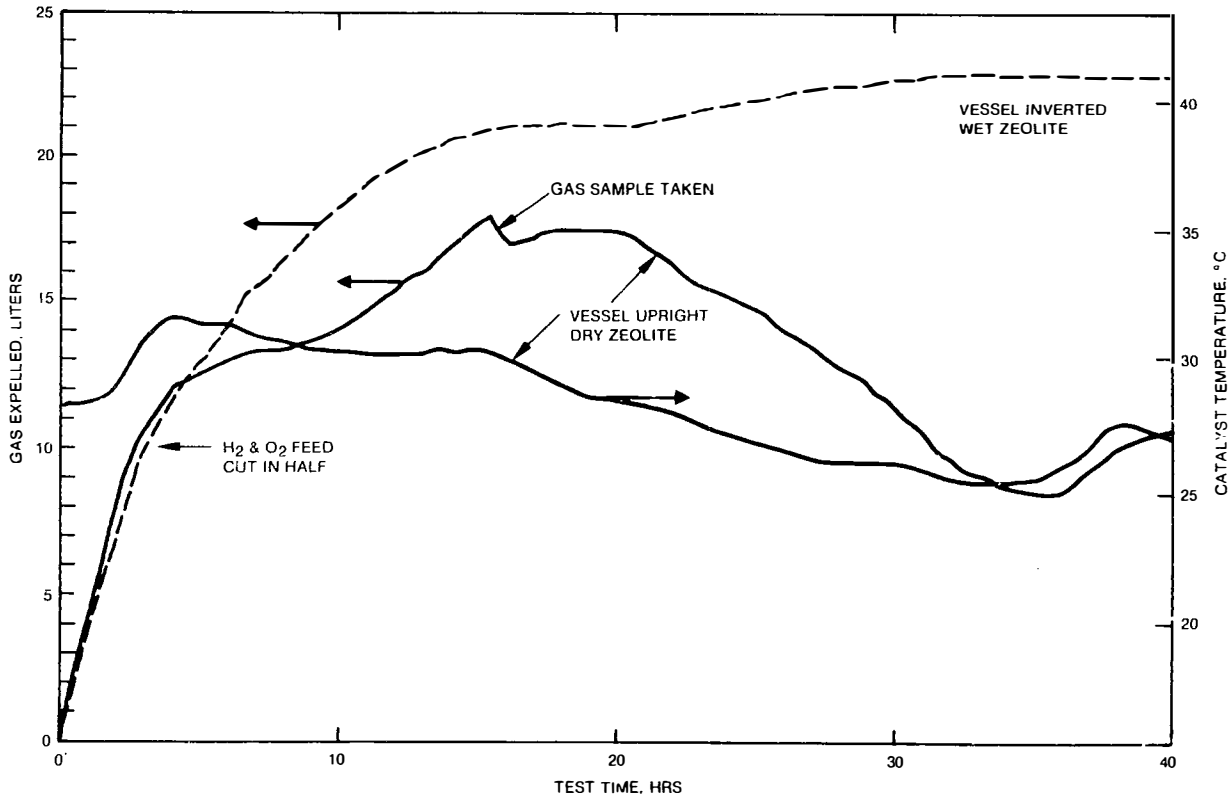

Figure 14. Volume of gas expelled for the one atmosphere recombiner tests.

water was removed from the zeolite. Results of this test are also shown in Figure 14. Again, about 10 L of gas were expelled before recombination started. The hydrogen and oxygen feed rate was cut in half after 10 L were expelled. Gas samples were taken after the initial 10 L were expelled and after each additional 5 L of gas were expelled. One percent hydrogen was detected in one sample, and the remaining samples contained no detectable hydrogen.

Test 5 (TMI Procedures). The procedure and equipment for use at TMI for vacuum drying the vessels and loading catalyst were demonstrated in a water pool at the Hanford site. The test vessel was placed underwater as the SDS vessels are dewatered at TMI. Tools were designed and fabricated by Rockwell to load the catalyst into Port C and to apply the vacuum to the submerged SDS vessel.

The test proceeded with dewatering the test vessel, followed by vacuum drying for 24 h to remove minimal amounts (about 5 kg) of unbound water. The vessel was vented to the atmosphere, and 236 g of catalyst were added in Port C through the tool. The SDS vessel was evacuated to the vapor pressure of water. Vacuum drying was continued for 4 h to remove pool water that may have leaked in on the catalyst. Operation of the catalytic recombiner was demonstrated by feeding 3 L/h total of hydrogen and oxygen to the SDS vessel through a tool connected to Port B. The recombiner operated satisfactorily as shown by the pressure-time plots in Figure 15. The tool connecting the vessel to the electrolysis system had a slight air leak and caused the pressure to rise during the test. The leak rate has been backed out of (subtracted from) the observed pressure and also plotted in Figure 15. The recombiner operated satisfactorily when the zeolite was quite wet, but it performed better with dry zeolite.

Westinghouse Hanford Company (Westinghouse) designed and built the skid-mounted vacuum system for use at TMI-2. The Westinghouse system was used to evacuate the SDS vessel during the underwater test. The vacuum system performed satisfactorily during the test.

In summary, these tests demonstrated vacuum drying, catalyst loading, and catalytic recombination under simulated conditions expected at TMI-2.

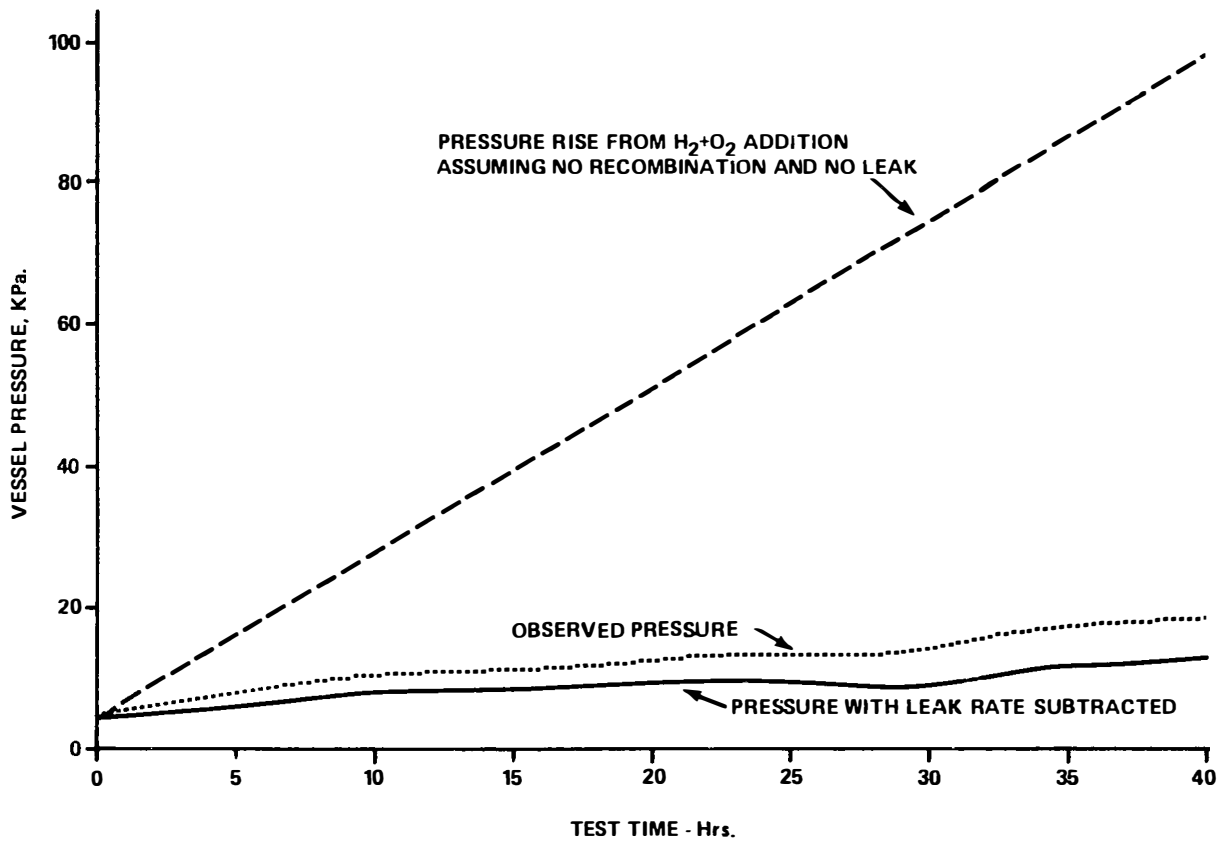

Figure 15. SDS vessel pressure for the underwater recombiner test.

TMI SITE PREPARATIONS

When plans were developed to use a catalytic recombiner in the SDS vessels, DOE agreed to supply the vacuum drying system, which Westinghouse then designed and fabricated. At the same time, Rockwell conducted its tests on the recombiner, and GPU Nuclear approved Westinghouse's vacuum system design, obtained NRC approval of the system's safety evaluation and operating procedure, and prepared the TMI-2 facility for the equipment.

Design Criteria

Westinghouse, Rockwell, GPU Nuclear, and EG&G Idaho prepared a Functional Operational Requirements Document (FORD) for the vacuum system so that its design by Westinghouse would be coordinated with GPU Nuclear's preparations for its installation. This document delineates the requirements for the system's design, fabrication, and delivery. Specifically, the document required the system to remove, by vacuum drying, essentially all moisture that could be removed from the SDS vessels at the ambient temperature of the TMI-2 spent fuel pool. The equipment was sized to remove moisture at the maximum practical rate using the 6-mm vent hose connection or a 38-mm quick disconnect coupling connection.

The document also specified the use of:

- Skid-mounted equipment with a maximum width of 20 in. (50.8 cm)
- A flexible hose connection from the vacuum drying tool on the SDS vessel to the GPU Nuclear-supplied hard piping and from the piping to the skid
- A flexible hose connection from the vacuum system discharge to GPU Nuclear-supplied off gas system piping
- Stainless steel equipment to minimize contamination

- Filters upstream of the vacuum pump to protect it from radionuclide contamination and downstream of the pump to protect the off gas system from oil contamination

- 115 V, single phase, 60 Hz electrical power

- Connections for nitrogen and argon gas bottles (bottles supplied by GPU Nuclear).

The FORD also specified process requirements for vacuum pump performance, pipe sizing, filter performance, and sampling capability; for mechanical equipment material, welding, and stresses; and for operating conditions, service life, maintenance, instrumentation, cleanliness, documentation, and Quality Assurance. Shielding was specified to limit the dose rates to 1 mR/h above background at one foot from the system.

Installation

GPU Nuclear installed the vacuum skid (Figure 16) beside the TMI-2 spent fuel pool B, which contains the SDS (see Figure 17). The vacuum skid was piped to the dewatering station and connected with a flexible hose to the catalyst addition and vacuum drying tool (Figure 18). The vacuum skid was also connected to the storage rack manifold, which had connections for six vent hoses to the vessels in storage. The piping and instrumentation diagram for the system is shown in Appendix C.

Acceptance Criteria

The criteria for preparing SDS vessels for safe shipment using catalytic recombination are based on Department of Transportation concentration limits for flammable gas mixtures in a radioisotope shipment and on Rockwell's tests and recommendations. These criteria are:

1. There will be less than 0.0018 gram moles of H_2/L or less than 0.0022 gram moles of O_2/L in an SDS vessel during shipment

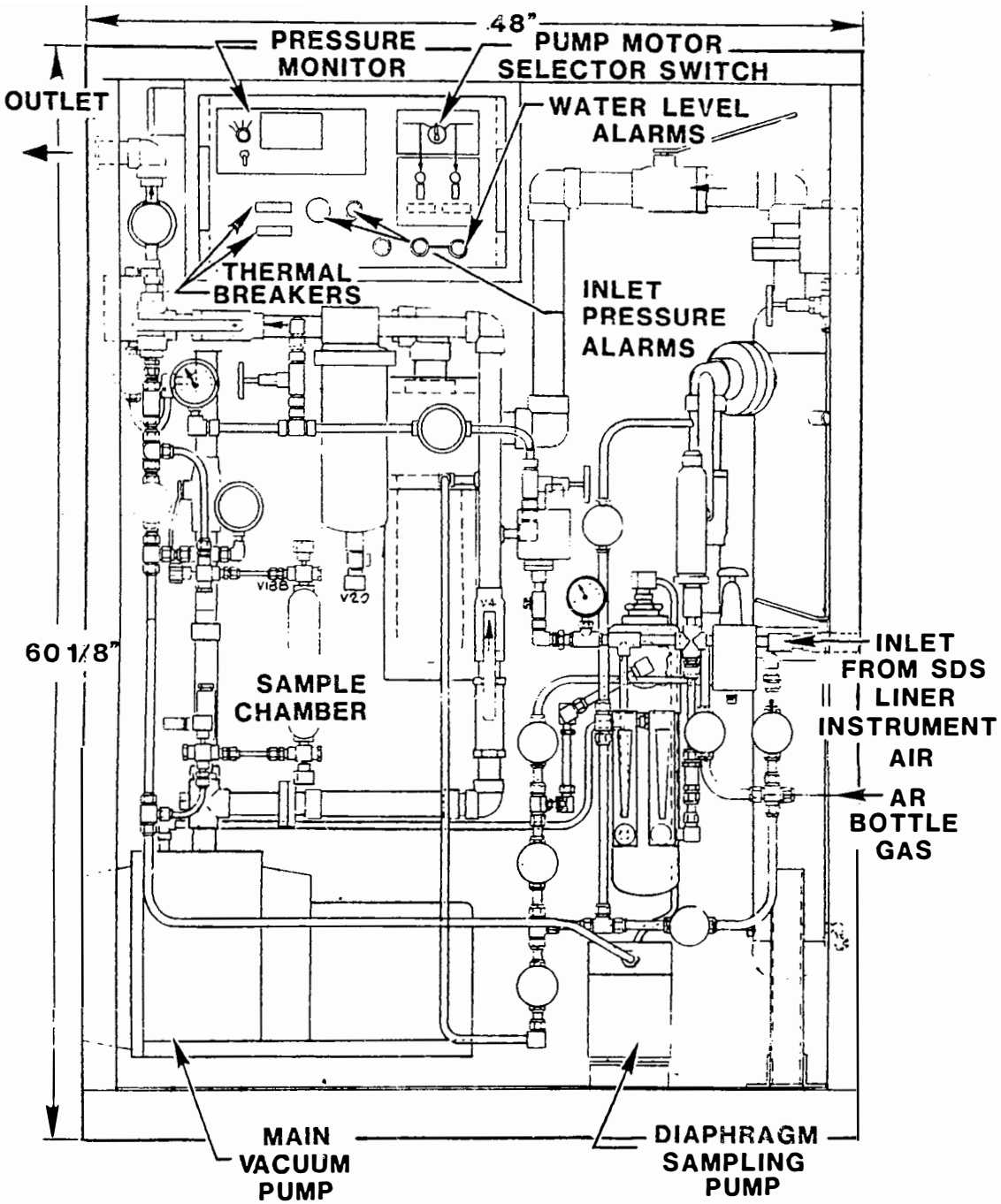

Figure 16. An illustration of the vacuum system built for TMI by Westinghouse Hanford Company.

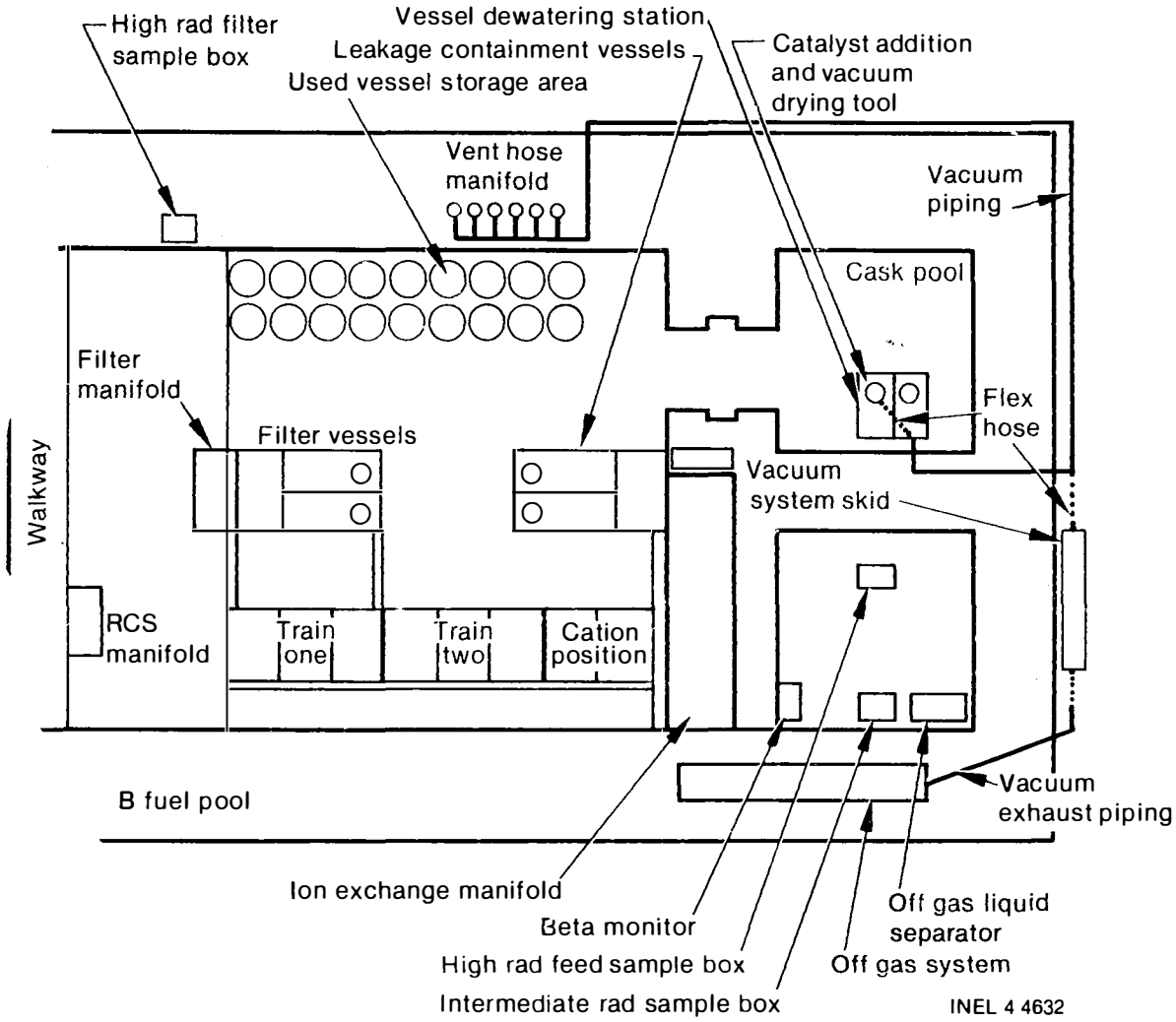

Figure 17. Arrangement of the SDS vacuum system around spent fuel pool B.

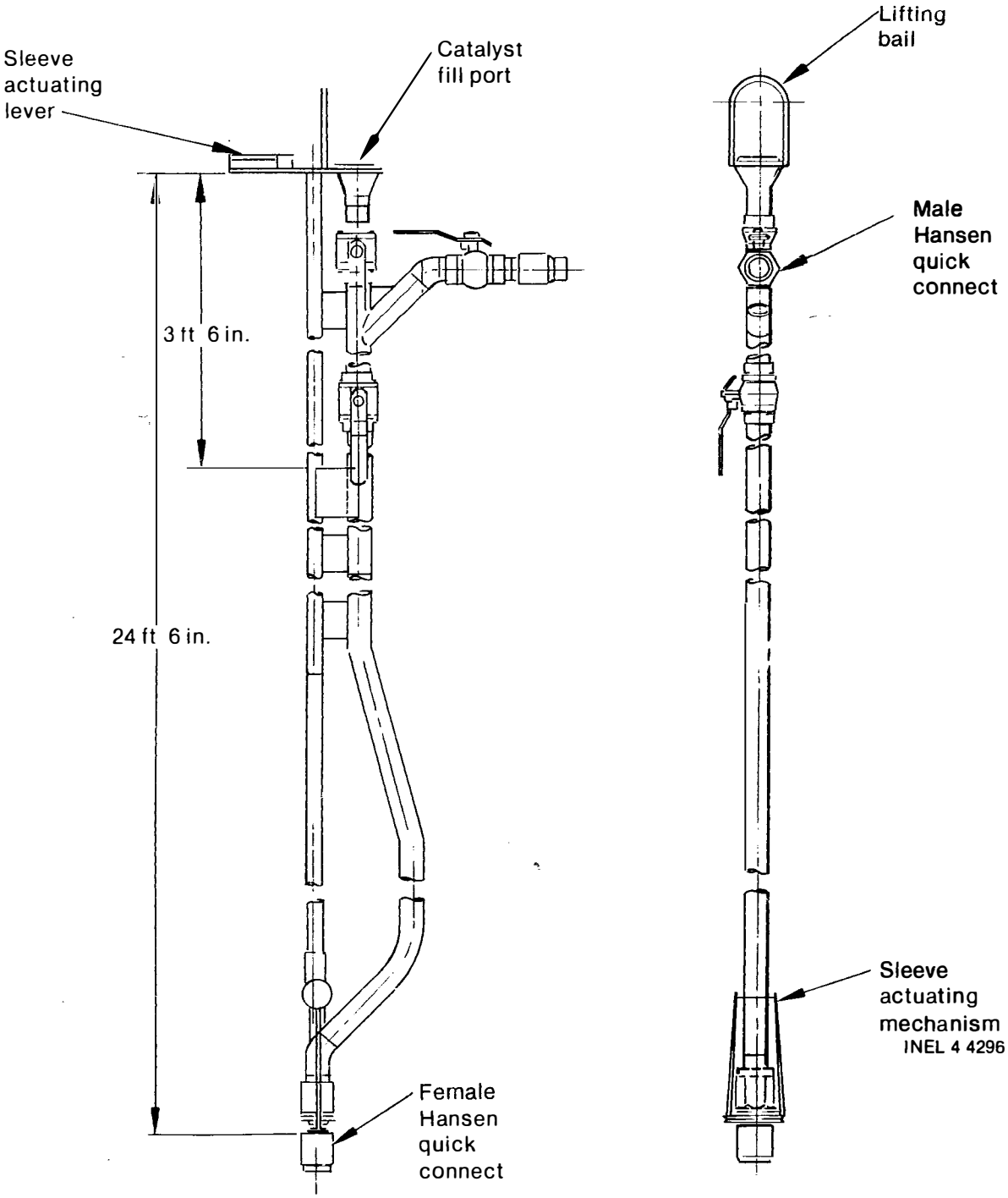

Figure 18. Side views of the TMI catalyst addition and offgassing tool.

2. The residual water content will be less than 100 lb (45 kg) for both bound and unbound water

3. A sufficient amount of catalyst pellets will be inserted into the vessel during catalyst addition.

The gram mole limit for hydrogen (0.0018 gram moles H_2/L) ensures there will be less than 4.1% hydrogen by volume at standard temperature and pressure (STP), which is its lower flammability limit. Similarly, with 5% oxygen by volume at STP--its lower flammability limit for hydrogen-oxygen mixtures--there would be 0.0022 gram moles/L.

The limit on residual water content ensures that the catalyst will not be submerged if the vessels are inverted. The residual water content limit of 100 lb (45 kg) was considered conservative since the test demonstrated recombination in an inverted vessel containing 169 lb (77 kg) of water.

The addition of catalyst to fill the vent nozzle and screen assembly ensures that an inverted vessel would have sufficient catalyst up in the screen to recombine the radiolytic gases. The nozzle and screen assembly combined can hold up to 236 g or about 5900 of the 3-mm-diameter, 3-mm-long pellets, which is at least 10 times the amount necessary to recombine gases in an SDS vessel with the highest radiolytic gas generation rate.

Operating Procedures

Based on the described test program and preliminary operating procedures by Rockwell and Westinghouse, GPU Nuclear developed the operating procedures by which the recombiner and vacuum system would be used at TMI-2. Following are the general steps for vacuum drying, catalyst addition, and recombination performance evaluation:

1. Remove the vessel from storage and weigh

2. Dewater the vessel with nitrogen gas and reweigh

3. Install the vacuum drying and catalyst addition tool on the SDS vessel and reweigh

4. Vacuum dry the vessel until the residual water content drops below 100 lb

5. Shut off the vacuum system and vent the vessel to the atmosphere using valves on the tool

6. Add catalyst pellets and remove the tool

7. Evacuate the vessel through the 6-mm vent hose for 4 h

8. Shut off the vacuum system, and isolate the vessel at a vacuum

9. Monitor the performance of the catalytic recombination using a pressure gauge

10. Obtain gas samples to confirm gas concentrations.

Additional steps required for preparing a vessel for shipment after confirming the catalyst performance are described in the upcoming section on shipments using catalyst recombiners.

TMI TESTS

To demonstrate vacuum drying and catalyst addition, a nonradioactive or "cold" demonstration test was performed at TMI. To demonstrate catalytic recombination of radiolytic gases, a radioactive or "hot" demonstration test was also performed.

Cold Test

A nonradioactive SDS vessel was vacuum pumped with the Westinghouse-supplied vacuum system and the Rockwell-supplied catalyst addition and vacuum drying tool. During the five-day vacuum drying test, a total of 55 lb (25 kg) of water was removed, which was more than the expected 10 lb/day (4.6 kg/day).

The procedure for adding catalyst requires opening both full port ball valves on the catalyst addition tool and slowly pouring the pellets down through the tool. This method ensures that all the pellets have sufficient downward momentum to bounce through the check valves of the quick disconnect coupling at the bottom of the tool. Pellets poured quickly tend to pile up and get lodged on the valve seats. If this happens, not all the pellets will be inserted and water will enter the submerged vessel during tool removal. The tests and subsequent vessel processing confirmed the reliable insertion of the catalyst.

Hot Test

The hot demonstration of vacuum drying, catalyst addition, and catalytic recombination of radiolytic gases for a radioactive SDS vessel was performed at TMI-2 using the highest curie content vessel available, 01001 2, with a total of 112,635 Ci. This vessel was dewatered and placed in the expended vessel storage area in November 1981. The hot test then began in November 1982 with the vessel in this condition. The vessel was brought from storage and weighed. GPU Nuclear calculated the residual water content in the submerged vessels by subtracting from the scale

reading the weights of the empty vessel, dry zeolite, and rigging, and then adding the bouyant force. For example, the residual water content of 101 kg (221 lb) for vessel D10012 was obtained by taking the scale reading of 289 kg (636 lb) minus 326 kg (717 lb) for the empty vessel, minus 148 kg (326 lb) for dry zeolite, minus 27 kg (60 lb) for the rigging, plus the bouyant force of 313 kg (688 lb).

The vessel was then dewatered again. The scale reading after dewatering was 545 lb (247 kg), for a reduction of the residual water to 129 lb (59 kg). The catalyst addition and vacuum drying tool was added to the vessel, and the assembly was reweighed. The tool added approximately 146 lb (66 kg); accurate measurement could not be made with the tool attached. The 38-mm flex hose attached to both the tool and the hard piping prevented exact weighing. The measurements made during vacuum drying with the tool did provide reasonable estimates for relative water removal between weighings since care was taken to position the vessel, tool, and hose in the same way for each measurement.

The residual water content of vessel D10012 during vacuum drying is shown in Figure 19. The vacuum system performed as expected for both the amount of water removed per day and for system pressure versus time. Six days of vacuum drying reduced residual water content to 81 lb (37 kg), which was below the acceptance criterion level of 100 lb (45 kg). The acceptance criterion regarding catalyst addition also was met, with less than 1% of the pellets remaining in the tool after removal. However, water in-leakage during tool removal after the first vacuum drying campaign prompted a change in the operating procedure to minimize such in-leakage in future operations. The change was to pressurize the vessel to 10 psig during tool removal to counterbalance the force of the water above the valve in the coupling during closure. The water that entered the vessel after the tool was first removed was vacuum dryed during a second three-day drying campaign (see Figure 19). With a 10-psig positive pressure in the vessel, little water entered during the second tool removal operation. To ensure the catalyst was adequately dry after possible water in-leakage during tool removal, a 4-h vacuum drying period followed using the 6-mm vent hose before the vessel was isolated for subsequent pressure monitoring.

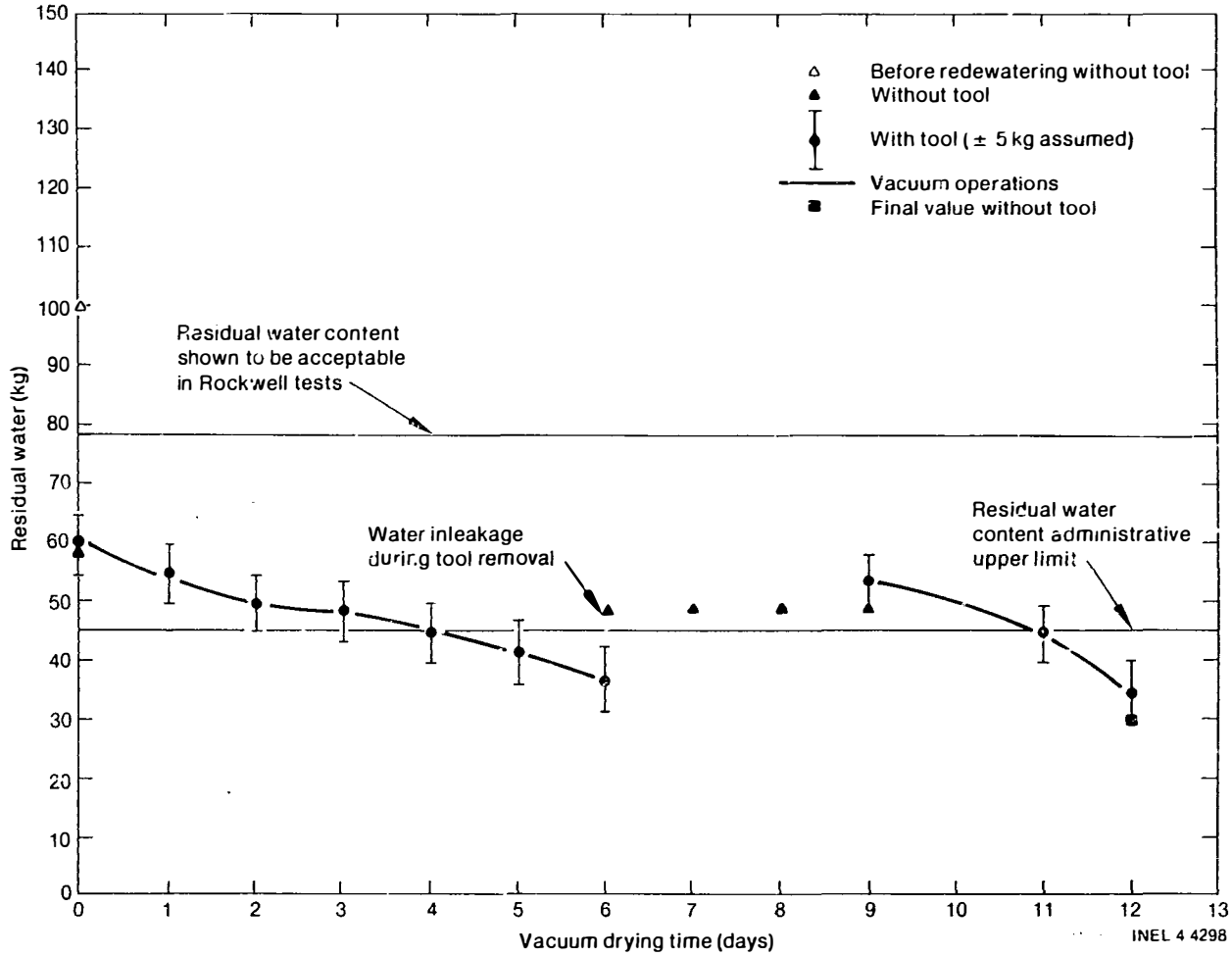

Figure 19. Residual water content in SDS vessel D10012 versus vacuum drying time.

Pressure monitoring of vessel D10012 continued for 14 days to satisfy DOE and NRC requirements that a flammable gas mixture would not develop in the vessel during an observation period twice that expected for shipping (seven days expected). By using the highest loaded vessel for this demonstration, engineers proved the safety of applying catalytic recombination to future, lower curie content vessels. And based on this demonstration, a shorter monitoring period was sufficient to confirm proper catalyst functioning.

The pressure history for vessel D10012 after catalyst addition is shown in Figure 20. The successful performance of the catalytic recombination process is shown by the difference in expected pressure rise (based on early GPU Nuclear testing documented in Appendix A) and the observed pressure. Control of vessel pressure during monitoring demonstrates that the catalyst recombination process was successful in controlling the generation of flammable gas mixtures produced from radiolysis of residual water in SDS vessels. The observed pressure rise during the 14-day monitoring period was due in part to air in-leakage, which was not corrected until after the monitoring period was over. Results of gas sample analysis confirmed that there was air in-leakage, as shown later in Table 4.

Using the gas sample result, the amount of H_2 in the vessel at the end of 14 days was calculated to be 0.0003 gram moles of H_2/L, which is less than the Department of Transportation flammable gas limit of 0.0018 gram moles of H_2/L. This information confirmed the conclusions obtained from the pressure data.

The air leak was located and repaired, after which a second monitoring was performed. The vessel was evacuated and pressure monitored for four days; results are also shown in Figure 20. This curve shows initial buildup of radiolytic gases, followed by a sharp drop in pressure due to initiation of the recombination process as the catalyst bed dried.

The successful hot demonstration of vacuum drying, catalyst addition, and radiolytic gas recombination at TMI-2 was a major milestone which permitted the start of routine shipment of expended, high curie content SDS vessels for DOE research and development program use.

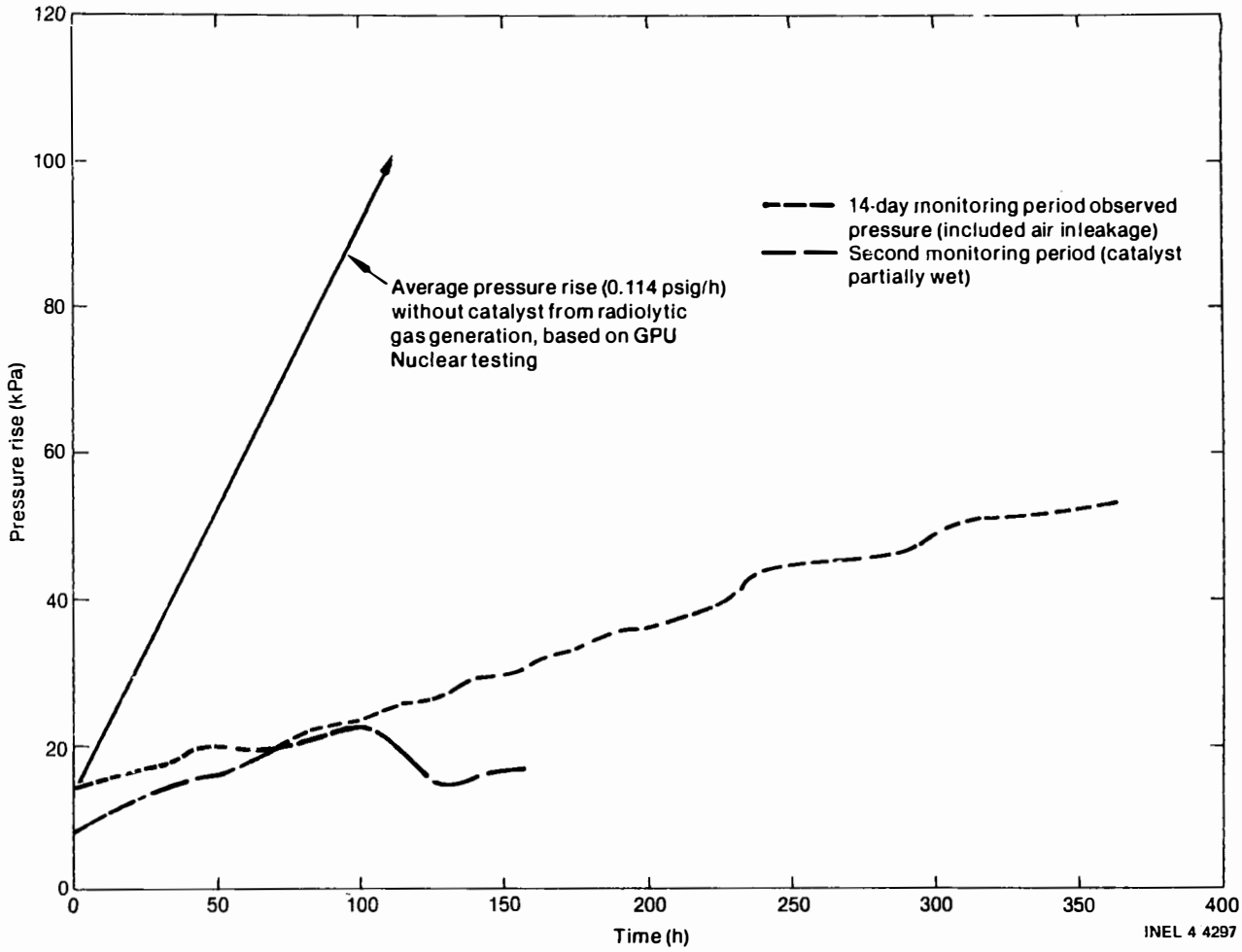

Figure 20. Pressure rise in SDS vessel D10012 versus time for the 14-day monitoring period and second monitoring period.

SHIPMENTS

All SDS vessel shipments have been in compliance with Department of Transportation flammable gas criteria. The first expended SDS vessel (D10015) was shipped without catalyst recombiners because the gas generation rate was sufficiently low. All other SDS vessels (14 vessels to date) have been prepared with catalyst recombiners.

Shipment Preparation

Low Curie Vessel

The first SDS vessel to be shipped from TMI was vessel D10015, with a total of 12,896 Ci, including daughter products. The gas generation data for this vessel are provided in Appendix A. The gas generation rate was low enough, even assuming stoichiometric gas production from this nonstoichiometric vessel, to permit safe shipment during a period twice the expected shipping time without using a catalyst to recombine the radiolytic gases. Nitrogen gas was used to dewater the vessel and to inert the vessel and shipping cask at atmospheric pressure.

Shipments Using Catalyst Recombiners

The first SDS vessel shipped using a catalytic recombiner was vessel D10012, which had been used in the TMI site radiolytic recombination demonstration. To facilitate acceptance of this vessel for retrievable burial by Rockwell, GPU Nuclear performed the following steps:

1. The vessel was re-evacuated to 1 psia (7 kPa).

2. A rupture disc and filter assembly was installed at the end of the hose.

3. The vent hose valve was opened and the valve handle removed.

4. The vessel was placed in the submerged shipping cask, and the vent hose was coiled on top of the vessel.

5. A lifting bail was installed on the vessel's lifting lugs.

6. The cask's lid was placed on top of the cask, and the cask was lifted from the pool. Personnel obtained a sample of the water that was drained from the cask and performed a contamination level check.

7. While inerting the cask for shipping, technicians confirmed the cask drain was not plugged.

Subsequent SDS vessels were prepared for shipment in the same manner as D10012. The dewatering data for these vessels are shown in Table 2. After dewatering and catalyst addition, the pressure rise during the catalyst performance monitoring period showed the effectiveness of the catalyst in controlling gas pressure increases by recombining hydrogen and oxygen back into water. Table 3 shows the initial pressure, final pressure, pressure rise, and length of the monitoring period for each vessel.

Although the pressure rise data established the catalyst's performance, gas samples were obtained after each vessel's monitoring period. Table 4 shows the gas sample analysis results for each vessel. The samples containing N_2 experienced air in-leakage during the sampling procedure--except for vessels D10012 and D10016, which had air in-leakage during their observation periods. Note that the catalytic system kept hydrogen concentrations well below the 4.1% lower flammability limit, and therefore the shipments were in compliance with federal regulations.

In SDS vessels where the gas generation is near stoichiometric, hydrogen concentrations will increase slowly as hydrogen is used to combine with the oxygen back to water vapor. At some unknown hydrogen overpressure, the gas generation would be expected to stop by back

TABLE 2. SDS VESSEL DEWATERING DATA

Vessel Number	Residual Water Content					
	Starting Weight		After Redewatering		After Vacuum Drying	
	(lb)	(kg)	(lb)	(kg)	(lb)	(kg)
D10012	221	100	129	59	67	30
D10016	136	62	105	48	65	30
D10013	208	96	134	61	63	29
D10017	131	60	119	54	51	23
D10018	150	68	117	53	62	28
D20027	92	42	84	38	60	27
D20028	136	62	134	61	56	25
D10014	122	55	115	52	19	9
D10011	145	66	142	65	68	31
D20026	419	190	161	73	81	37
D20022	143	65	120	55	76	35
D20029	333	151	130	59	76	35
D20031	79	36	55	25	23	10
D20037	59	29	41	19	22	10

TABLE 3. PRESSURE RISE DURING CATALYST PERFORMANCE MONITORING PERIOD

Vessel Number	Initial Pressure (kPa)	Final Pressure (kPa)	Increase in Pressure (kPa)	Monitoring Period (h)
D10012				
first[a]	13.6	55.9	42.3[b]	336
second[c]	7.8	15.3	7.5	114
D10016	7.2	41.3	34.1[b]	138
D10013	6.1	8.2	2.1	54
D10017	6.5	7.8	1.3	92
D10018	6.5	8.2	1.7	133
D20027	6.8	9.5	2.7	91
D20028	7.2	7.8	0.6	108
D10014	7.5	9.2	1.7	120
D10011	6.5	6.5	0	48
D20026	6.8	9.9	3.1	90
D20022	6.1	10.6	4.5	107
D20029	7.2	11.9	4.7	80
D20031	9.2	10.2	1.0	480
D20037	7.5	10.6	3.1	163

a. First catalyst performance monitoring period.

b. High pressure increase resulted from air in-leakage in the pressure monitoring system above the water level. See gas analysis in Table 4.

c. Second catalyst performance monitoring period.

TABLE 4. GAS SAMPLE RESULTS AFTER CATALYST PERFORMANCE MONITORING PERIOD (IN VOLUME PERCENT)[a]

Vessel Number	Sample Number	H_2	O_2	N_2	Comment
D10012	1	0.34	2.86	13.95	Air leak into system
	2	0.50	6.55	29.57	Air leak into system
	3	0.67	5.38	25.88	Air leak into system
D10016	1	0.17	0.67	5.21	Air leak into system
	2	0.17	1.01	6.22	Air leak into system
D10013	1	<0.03	<0.44	<0.81	--
	2	<0.03	<0.44	<0.81	--
D10017	1	0.03	0.55	1.68	--
	2	0.07	<0.22	<0.42	--
	3	0.10	<0.22	<0.42	--
D10018	1	0.05	21.0	78.3	Air leak into sample
	2	0.27	1.23	7.39	Air leak into sample
D20027	1	0.03	<0.29	1.02	--
	2	0.13	<0.29	<0.52	--
D20028	1	<0.02	<0.29	<0.64	--
	2	<0.02	<0.29	<0.64	--
D10014	1	0.18	0.84	<0.66	--
	2	0.44	<0.29	<0.66	--
D10011	1	<0.02	1.68	6.55	Air leak into sample
	2	0.03	5.21	20.50	Air leak into sample
D20026	1	<0.02	<0.37	1.04	--
	2	<0.10	<0.37	0.62	--
D20029	1	0.17	<0.50	3.19	--
	2	0.17	1.85	9.41	Air leak into sample
D20022	1	0.34	0.50	2.18	--
	2	0.34	0.50	2.69	--
D20031	1	0.27	0.67	4.59	--
	2	0.50	1.08	4.92	--
D20037	1	0.17	<0.34	<0.67	--
	2	0.34	<0.34	<0.67	--

a. The vessel atmosphere was diluted with argon gas prior to sampling. The gas sample analysis results were normalized and reported on a one-atmosphere basis. Each number preceded by a less than sign is the lower limit of detectability for that sample. This number is provided in cases where the actual volume percent measured is less than this limit.

reactions involving hydrogen. During early testing at TMI, no reduction in gas generation rate was found when vessels were allowed to pressurize to 24.7 psia of hydrogen rich mixtures from radiolytic gas generation (see Appendix A).

Net Gas Generation Rate Versus Residual Water Content

During preparation of SDS vessel D10013, additional data on gas generation rate versus residual water content were obtained. After this vessel was removed from storage, it was weighed and found to have a residual water content of 208 lb (96 kg). The vessel was then inerted at atmospheric pressure with nitrogen and the pressure monitored for 80 h. From the data obtained, the gas generation rate was calculated to be 592 cc/h. At that rate and for 51,000 Ci of cesium and strontium, the gas generation rate per curie was 0.0116 cc/h-Ci.

The vessel was vacuum dried to a residual water content of 63 lb (29 kg). It was isolated at a vacuum without any catalyst added. Pressure was monitored for 62 h. The gas generation rate was calculated to be 423 cc/h, resulting in a generation rate per curie of 0.0083 cc/h-Ci.

The earlier GPU Nuclear study (see Appendix A) indicated an approximately linear relationship between gas generation rates per curie of cesium and strontium and vessel water content from 2.8 to 5.2 ft^3, the range for residual water after bulk removal with N_2. The D10013 data indicate this relationship does not hold at lower vessel water contents. The explanation may be that residual water collects in the bottom of the vessel, which is away from the high radiation zone.[7] The presence of this water does not contribute proportionally to hydrogen and oxygen generation. Vacuum drying removed residual water from the bottom of the vessel, leaving about the same amount of bound water in the zeolite at the top of the bed where the radioactivity is concentrated and where most of the radiolysis takes place.

Transport

EG&G Idaho assumed responsibility for the GPU Nuclear prepared SDS vessel shipments at the TMI site boundary. Each shipment was completed without incident. Teams of two specially trained and qualified drivers consistently made the trips from TMI to Richland, W', in less than three days.

Figure 21 shows a drawing of the SDS shipping cask, and Figure 22 shows the cask tied down to the trailer.

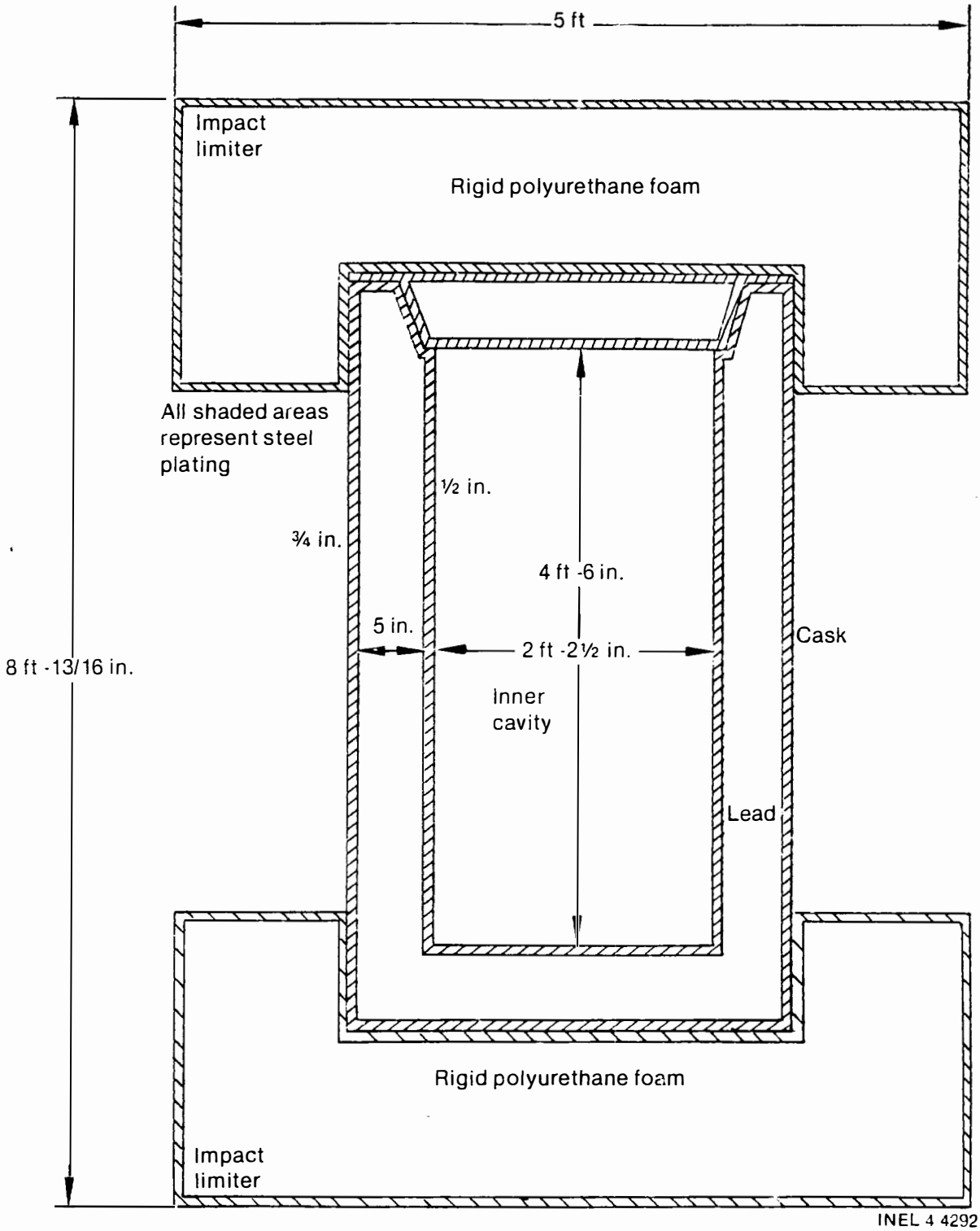

Figure 21. A simplified schematic of the CNS 1-13C shipping cask.

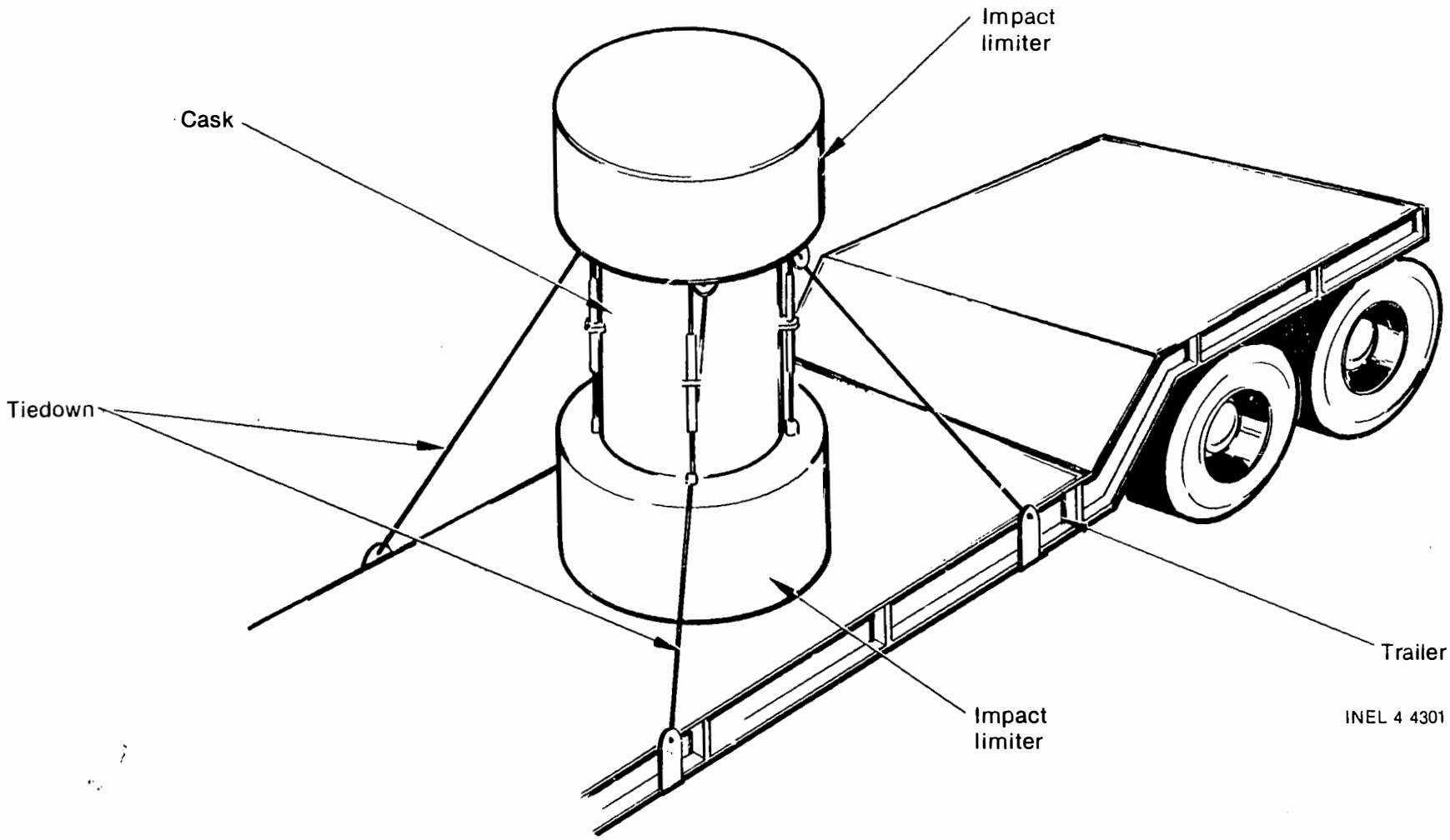

Figure 22. The tie-down system for the CNS 1-13C shipping cask.

DOE RESEARCH AND DEVELOPMENT PROGRAMS

Zeolite Vitrification Demonstration Program

Vessels D10012, D10015, and D10016 were shipped to Pacific Northwest Laboratory for use in vitrification experiments. The contaminated zeolite was removed from the vessels, glass formers were added, and the mixture was placed in special stainless steel canisters. A full-scale, in-canister melting process was then used to vitrify the material. In this process, the canister serves as the container for the solidified (glass) final waste product. Program details are presented in References 7, 8, 9, and 10.

Dry Handling and Monitored Burial Demonstration Program

The other ten vessels, listed in Table 1, were sent to Rockwell for experiments demonstrating remote dry handling techniques and monitored burial in special concrete overpacks. The remote transloading from shipping cask to concrete overpack proved to be cost effective. The transloading was conducted in the T-Plant rail tunnel, remotely from the shielded cab of the canyon traveling crane, and observed through optical systems and closed circuit television. No significant problems were encountered in any of the transloading operations. Shipping cask handling and decontamination costs were minimized by avoiding underwater handling.

After transloading each SDS vessel into its concrete overpack, it was transported by truck to a nearby burial trench, into which it was placed using a truck-mounted crane (see Figure 23). The overpack was then buried at least 9 ft underground, below the sand and rock material previously removed from the trench.

One of the SDS vessels, D10011, and its overpack will be specially instrumented for long-term burial monitoring. The monitoring equipment includes two vessel pressure transducers, four vessel shell thermocouples, 12 overpack thermocouples, four backfill thermocouples between overpacks, and two gas sampling lines to monitor the air in the overpack above and below the vessel for moisture and contamination.

Figure 23. Workers remove the lifting sling from an overpack containing an SDS vessel in its retrievable burial position.

Figure 24 shows the arrangement of the SDS vessel, concrete overpack, and instrumentation for burial. The pressure transducers are radiation resistant, high temperature devices with radiation resistant cables terminating in the instrument enclosure. The two sampling lines are 6-mm stainless steel tubes terminating in the instrument enclosure.

This burial package will be monitored weekly for the first two months, monthly for the next four months, bimonthly for the following six months, quarterly for the following three years, and then semiannually until monitoring is terminated. Analysts expect the temperature will rise slowly, with a maximum of less than 350°F peaking in about three-and-a-half years. The system pressure is expected to rise slowly from a partial vacuum to one atmosphere, due to small leaks and a low net hydrogen gas generation rate, and then remain at a slightly positive pressure.

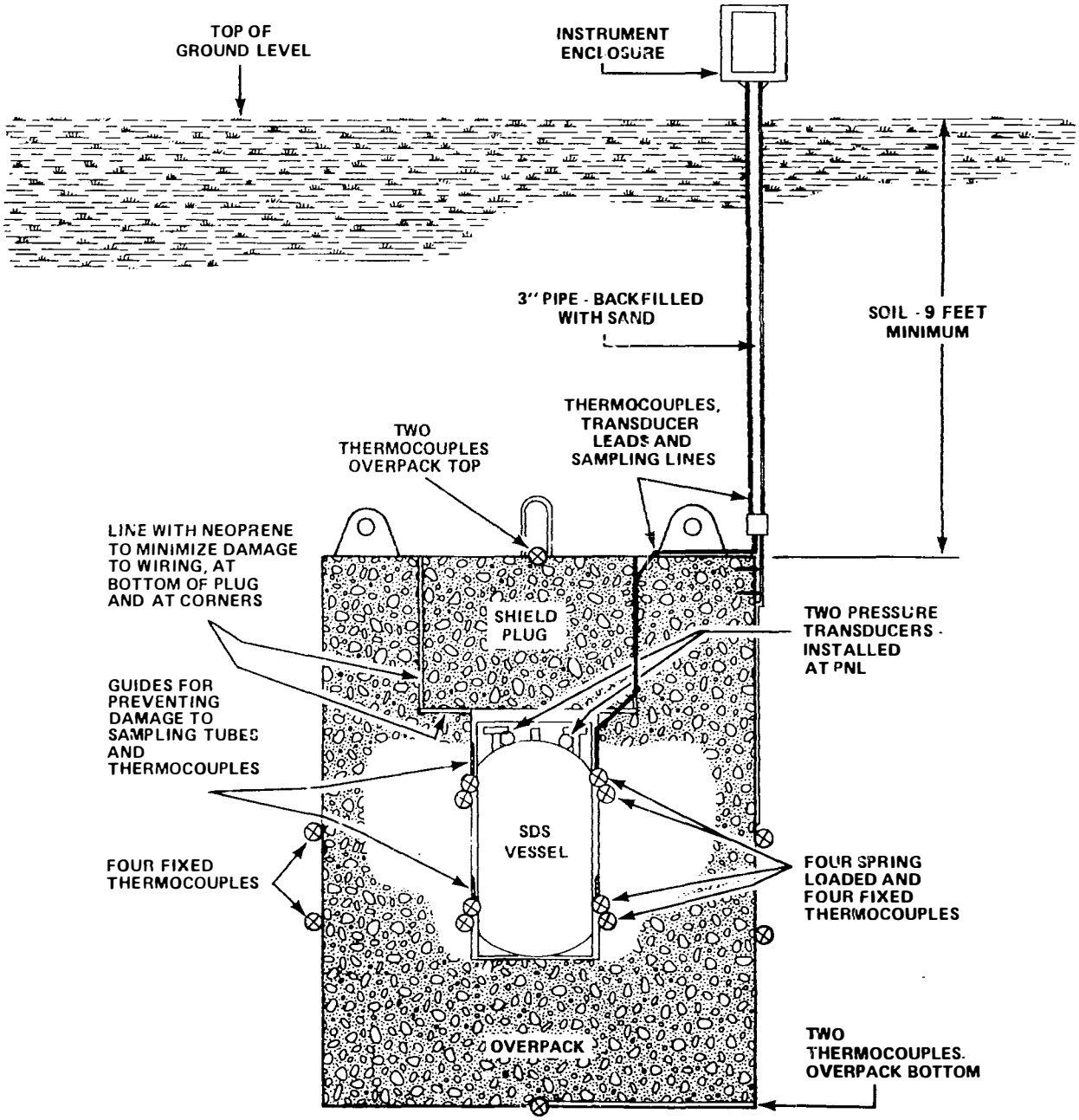

Figure 24. An instrumented SDS vessel and modified overpack in their burial position.

CONCLUSIONS

The overall SDS process has proved to be very effective, particularly considering safety issues and needs to keep radiation exposure levels as low as reasonably achievable, in removing, concentrating, handling, shipping, and safely storing fission products from the contaminated water which had been in the TMI-2 Reactor Building. Radiolytic gas generation from the concentrated fission products on the zeolites was recognized before system startup and characterized after the first vessels were removed from service. Catalyst testing at more than twice the observed maximum gas generation rate established the performance of recombiners in SDS vessels. Implementation of the vacuum drying and catalyst addition process at TMI successfully demonstrated radiolytic gas control by recombination for the vessel with the highest amount of radioactivity. Hydrogen and oxygen concentrations in each vessel were maintained within acceptable limits. All shipments complied with federal regulations and were conducted without incident.

REFERENCES

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3. 49 CFR 173.21--Forbidden Materials and Packages.

4. S. R. Adams, Safety Assessment Document for Shipment of Submerged Demineralizer System Liners from Three Mile Island, Pennsylvania, to Richland, Washington, SD-B-82-006, April 1982.

5. H. W. Reno and R. L. Dodge, Environmental Evaluation of Transportation of 10 to 20 Submerged Demineralizer System Liners to Richland, Washington for Interim Storage, March 1982.

6. R. H. V. Gallucci, A Risk Assessment for the Transportation of Radioactive Zeolite Liners, PNL-4032, January 1982.

7. G. H. Bryan et al., Summary of Radioactive Operations for Zeolite Vitrification Demonstration Program, GEND-038, January 1984.

8. G. H. Bryan et al., Zeolite Vitrification Demonstration Program Nonradioactive Process Operations Summary, GEND-024, September 1982.

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11. S. P. Queen, Preparations to Ship EPICOR Liners, GEND-029, June 1983.

12. B. W. Mercer and W. C. Schmidt, Storage of Long-Lived Fission Products on Alumino-Silicate Zeolites, AEC Access #14466, Report RL-SR-58, 1965.

APPENDIX A

GAS GENERATION DATA

APPENDIX A
GAS GENERATION DATA

GPU Nuclear initiated gas generation measurements immediately following removal of the first SDS vessel from the waste processing train. A gas sampling system was installed adjacent to the vessel storage area. This system consisted of a pressure gauge and sample cylinder installed between the vessel vent hose and the SDS off gas system (see Figures 4 and 5 in the main body of the text). The gas collected in the sample cylinder was analyzed using the plant gas chromatograph. As the testing progressed, the highest and lowest curie loaded vessels available at the time were selected for testing. Several vessels were tested in nondewatered and dewatered states. After the vessel was connected to the gas sampling system, the gas pressure rise and the void volume for the vessel were determined. Periodic samples drawn through the sample cylinder were used to determine the gas composition.

The following data resulted from these measurements:

1. Figure 6 in the main body of the text shows gas generation rate versus curie content. The gas generation rate is proportional to curie content (neglecting second order effects such as oxygen absorption) and was estimated to be 0.01 cc/h-Ci.

2. Figure 7 in the main body of the text plots the measured gas generation rate (on a per curie basis) against the best estimate of residual water in the vessel. Gas generation is somewhat proportional to water content for the range of 2.8 to 5.2 ft^3.

3. Table A-1 lists the average observed gas generation rate (averaged over the entire observation time). Also listed are the observed H_2/O_2 ratios (averaged over the collected samples) and the observed peak H_2 and O_2 concentrations. Several items are worth noting.

TABLE A-1. RADIOLYTIC GAS GENERATION IN SDS VESSELS

Vessel	Cs & Sr Approximate Activity (Ci)	Gas Void Volume (ft^3)	Vessel Condition	Average Observed Gas Generation Rate (psig/h)	Average Observed Gas Generation Rate (cc/h)	Peak Observed Gas Vol. Percent[a] H_2	Peak Observed Gas Vol. Percent[a] O_2	Average Observed Mole Ratio (H_2/O_2)
D10011	46,000	2.24	Wet	0.140	559	74	21	3.2
	46,000	4.0	Dewatered	0.0589	421	60	22.6	2.7
D10012	59,000	3.0	Dewatered	0.114	613	84	16	5.2
D10013	51,000	3.4	Dewatered	0.0688	418	72.6	25.3	2.9
D10015	6,800	4.0	Dewatered	0.00487	33	8.1	0	Infinity
D10016	59,000	4.4	Dewatered	0.061	476	70	24	2.8
D20028	45,000	4.6	Dewatered	0.0430	353	--	--	3.7

a. Balance is N_2.

First, the gas generation rate is calculated from the measured pressure rise rate and measured vessel volume (determined by measuring the pressure drop associated with drawing multiple sample cylinder gas volumes) using the assumptions of the perfect gas law, Henry's law, and isothermal conditions. The pressure measurements and analyses required to obtain the gas generation values reported herein are estimated to have an accuracy of plus or minus 20%. The assumptions used in these analyses would tend to place the reported values in the lower portion of the estimated error band. The gas generation rates listed in Table A-1 may be 20% low.

Second, radiolysis gas is pure H_2 and O_2. As such, peak H_2 and O_2 gas concentrations are functions of the test time and number of samples withdrawn. The test pressure was limited to 10 psig. The test procedure resulted in frequent vessel venting to atmosphere which reduced the inventory of N_2 and enhanced H_2 and O_2 concentrations.

Third, the gas that accumulated in vessel D10015 was primarily hydrogen (see Table A-1). A scrap of plastic (a pipe end cover) was found in this vessel during the vitrification process. It appeared that radiolytic oxygen combined with this organic material as it decomposed. This is consistent with observations of other vessels containing wet, radioactive, organic materials.[11]

4. Figure A-1 plots the recorded experimental data taken on vessel D10011 (dewatered). Other vessels had similar gas generation properties, as summarized in Table A-1.

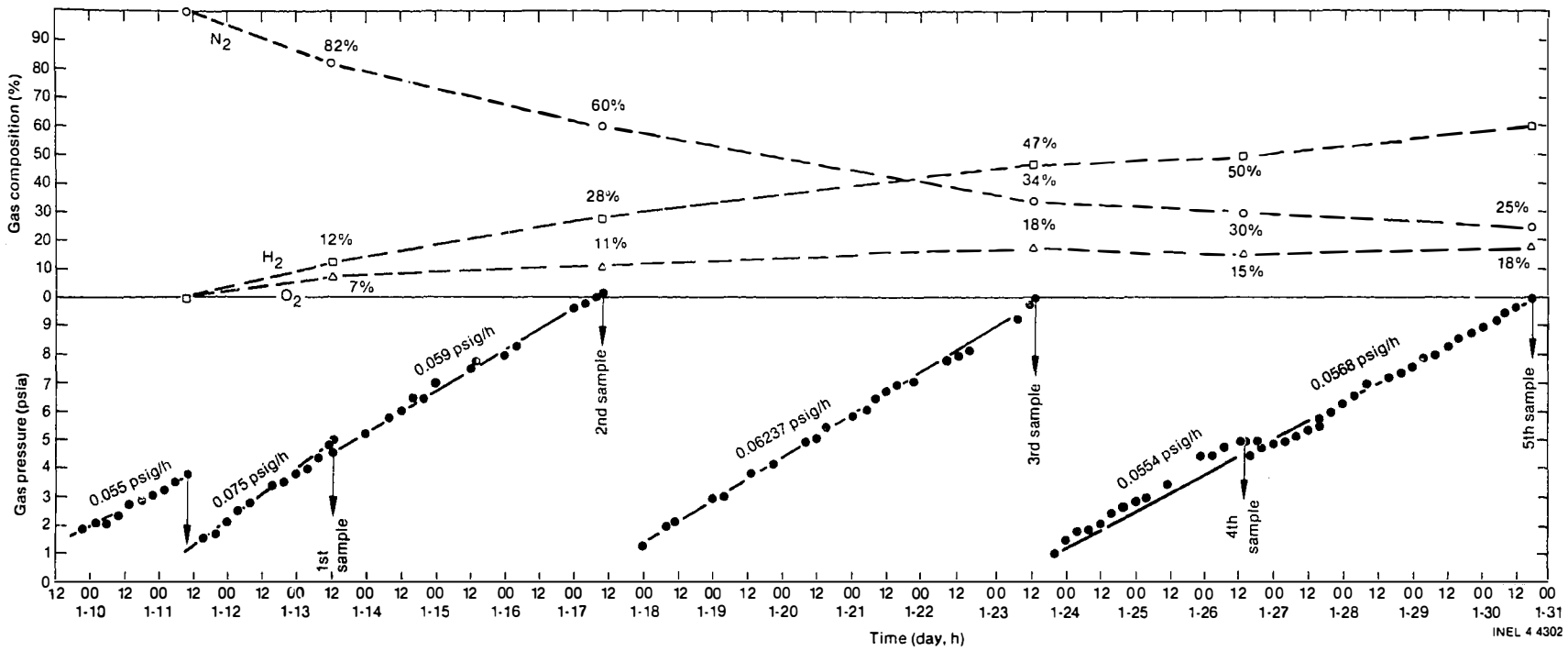

Figure A-1. SDS vessel D10011 gas generation dewatered.

In conclusion, a fully loaded SDS vessel (59,000 Ci of cesium and strontium) generates between about 500 and 700 cc/h of radiolytic gases. The gas generation rate is somewhat dependent on the amount of residual water in the vessel after drip drying. The generation rate would decrease as water is radiolytically decomposed or evaporated from the upper part of the bed where most of the radioactive cesium and strontium isotopes are located. These results are in basic agreement with the previously published data of 1.8 cc/h/W which equates to about 520 cc/h at 59,000 Ci of cesium and strontium (289 W).[12]

APPENDIX B

ALTERNATIVES FOR PREPARING SDS VESSELS FOR SHIPMENT

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1. Remove the water by radiation decomposition.

2. Pressurize vessel with inert cover gas.

3. Pressurize vessel with hydrogen alone or hydrogen-CO mixture.

4. Fill with some other liquid which contains no hydrogen.

5. Put a strip or grains of hydrogen recombiner catalyst on the bed surface or elsewhere in the upper vessel.

6. Add an oxidizer to the bed.

7. Remove the water by air flow at essentially pool temperature.

8. Remove the water by vacuum pumping.

9. Provide an inert storage dilution vessel.

10. Combination of #2 and #9.

11. Remove (separate) oxygen from ex-vessel portion of gas in #9 and #10.

12. Remove with air flow at higher temperature.

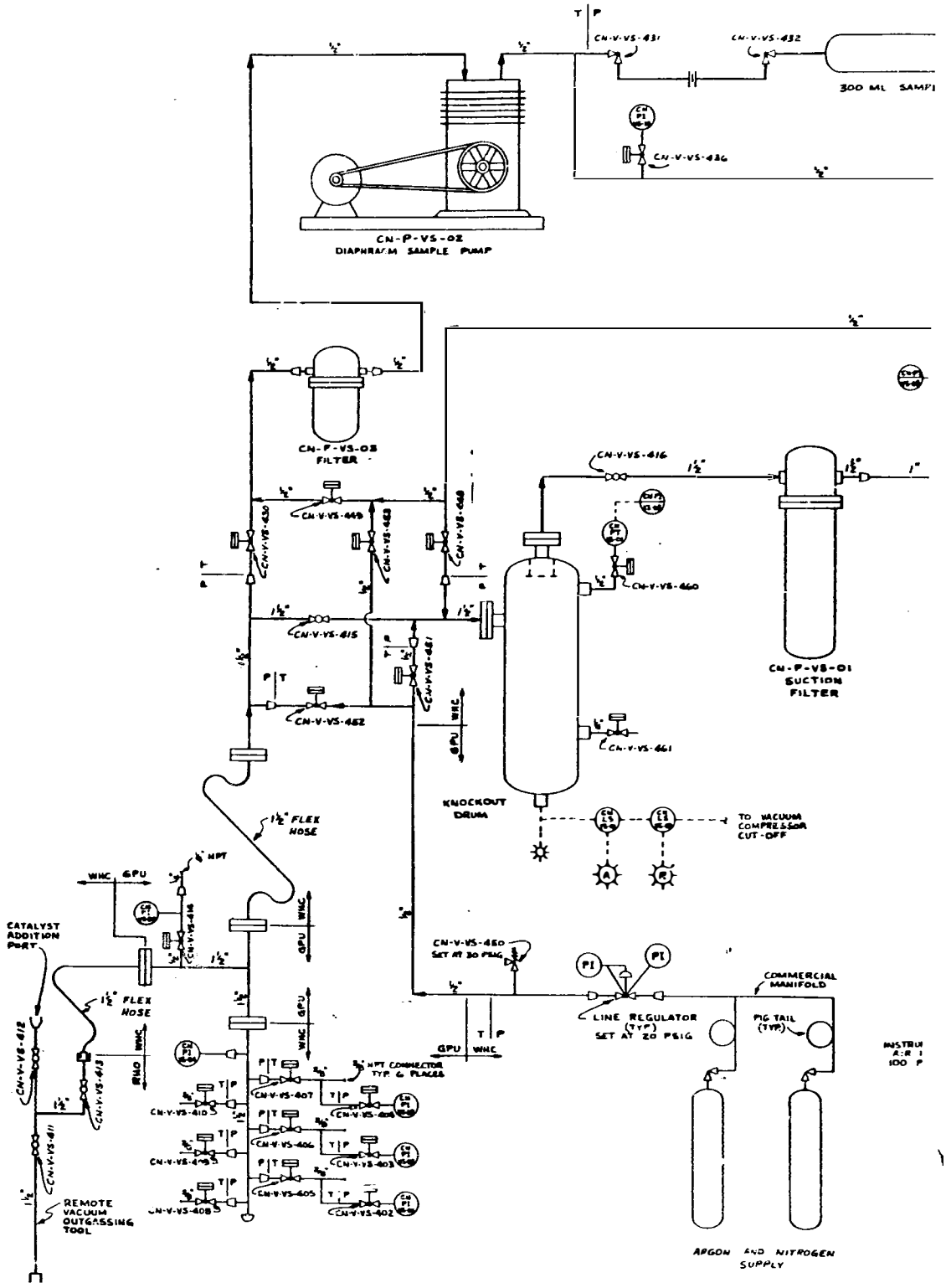
13. Combination of #8 and #12.

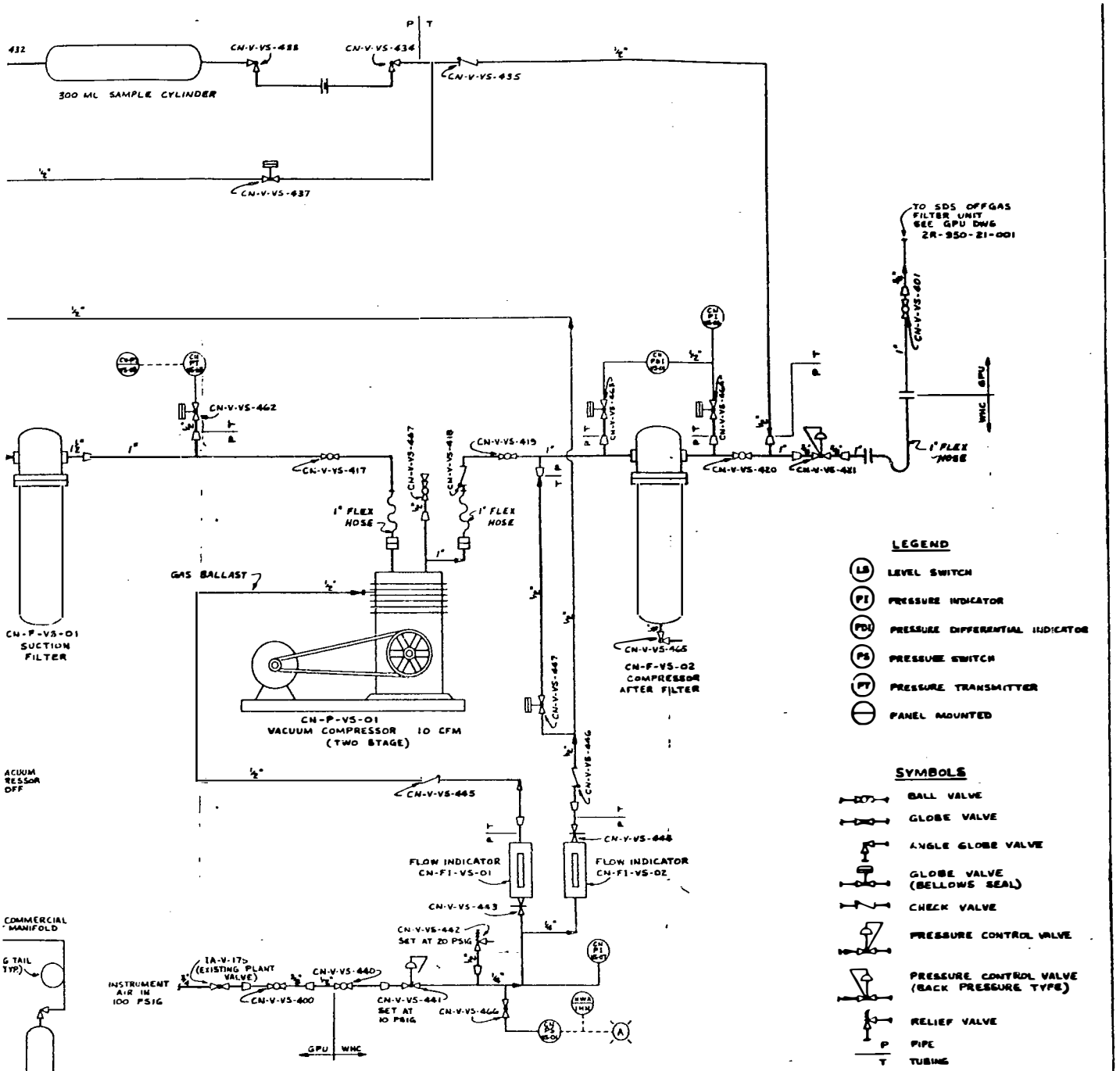
14. Use an exiting gas in #2, #9, #10, and/or #11.

15. Drying and/or elution of the resin by a gas other than air.

APPENDIX C

PIPING AND INSTRUMENTATION DIAGRAM FOR SDS LINER VACUUM OUTGASSING AND DRYING SYSTEM


CN-V-VS-431
CN-V-VS-432
300 ML SAMPL
CN-V-VS-436
CN-P-VS-02
DIAPHRAGM SAMPLE PUMP
CN-F-VS-03
FILTER
CN-V-VS-416
CN-V-VS-449
CN-V-VS-430
CN-V-VS-463
CN-V-VS-448
CN-V-VS-460
CN-V-VS-415
CN-V-VS-461
CN-V-VS-462
CN-P-VS-01
SUCTION
FILTER
KNOCKOUT
DRUM
TO VACUUM
COMPRESSOR
CUT-OFF
1½" FLEX
HOSE
WHC
GPU
CATALYST
ADDITION
PORT
CN-V-VS-412
CN-V-VS-413
CN-V-VS-411
REMOTE
VACUUM
OUTGASSING
TOOL
CN-V-VS-460
SET AT 30 PSIG
LINE REGULATOR
(TYP)
SET AT 20 PSIG
COMMERCIAL
MANIFOLD
PIG TAIL
(TYP)
ARGON AND NITROGEN
SUPPLY
CN-V-VS-407
CN-V-VS-406
CN-V-VS-405
CN-V-VS-410
CN-V-VS-409
CN-V-VS-408
CN-V-VS-404
CN-V-VS-403
CN-V-VS-402



NOTE:

½" AND ABOVE — STAINLESS STEEL PIPE w/ SOCKET WELD FITTINGS.

½" AND BELOW — STAINLESS STEEL TUBING w/ COMPRESSION FITTINGS.

EQUIPMENT CONNECTIONS — NPT

RECORDS/INFO. ONLY

NOT FOR CONSTRUCTION

DWG NO	TITLE
H-3-48566	WESTINGHOUSE HANFORD COMPANY SDS P&ID-THE VACUUM OUTGASSING AND DRYING SYSTEM

REFERENCE DRAWINGS

JHA 8-23-92 DRAWN

CHECKED

DESIGN LEADER

CHIEF ENGINEER

MANAGER APPROVAL

ENG MECH

Nuclear

P&ID SDS LINER VACUUM OUTGASSING AND DRYING SYSTEM

DWG. NO. 2D-950-21-003 REV. 0

SCALE: NONE

AUTHORIZATION NO.