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Evaluation of Special Safety Issues Associated with Handling the Three Mile Island Unit 2 Core Debris

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ABSTRACT

This document reports the results of recent tests and analyses evaluating safety concerns relating to Three Mile Island Unit 2 (TMI-2) core debris pyrophorocity, radiolytic hydrogen and oxygen, and the potential for steam generation in shipping canisters during a fire. Recommendations drawn from these results include the following: (1) hydrogen-oxygen recombiners should be installed in each core debris canister, (2) water should be removed from each canister by drip drying (no vacuum pumping is required), (3) the maximum weight of the loaded, dewatered canisters and the minimum volume of gas/vapor in each canister should be controlled and measured by weighing before and after dewatering, (4) a cover gas of approximately two atmospheres of argon should be added to each canister, (5) each canister should be weighed and pressure checked prior to shipping, (6) the shipping cask should be designed to limit the temperature of the canister contents after the standard hypothetical accident (fire) such that the design pressure of the canister/cask will not be exceeded, (7) provisions should be made for canister venting during long-term storage and for cask venting in the event of an overpressure condition resulting from an "extended" fire, and (8) some pyrophoricity testing of samples taken during defueling should be conducted to assure adequate safety-related information during canister opening.

ACKNOWLEDGMENTS

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1.0 INTRODUCTION

The March 28, 1979, loss-of-coolant accident at the Three Mile Island Unit 2 (TMI-2) nuclear reactor caused significant damage to the 177 fuel assemblies in the reactor core. This damaged fuel is to be placed in canisters and shipped to the Idaho National Engineering Laboratory (INEL) for research and subsequent disposal.

Rockwell Hanford Operations (Rockwell) was assigned by the U.S. Department of Energy and EG&G Idaho, Inc., to assist those parties and the General Public Utilities Nuclear Corporation (GPUNC) in evaluating and resolving safety concerns relating to pyrophoricity, radiolytically generated hydrogen and oxygen, and the potential for steam generation in core debris canisters during an accidental fire. Criticality studies are being completed by other organizations and are not part of this work.

This document provides a description of methods, techniques, configurations, and conditions that maximize safety and minimize cost and schedule needs while resolving these safety issues.

2.0 PYROPHORICITY

Finely divided metal from a variety of sources is present in the TMI-2 core debris. Zircaloy, cadmium, indium, silver, and stainless steel have all been identified. Zircaloy, an alloy containing 98% zirconium, originated primarily from the fuel pin cladding. Approximately 23,000 kilograms (kg) of zirconium was originally contained in the reactor core; it is believed that about half of this zirconium was oxidized (Henrie and Postma 1983) and most of that was degraded to rubble. Similarly, it is believed that about half of the 93,000 kg of uranium oxide was overheated, fractured, reduced to rubble, and mixed with the other core debris. An early estimate of the particle size distribution of the rubble (Henrie et al. 1983) still appears to be reasonably consistent with more recent estimates based on core debris samples. On that basis, about 80,000 kg of the fuel debris may be in the form of full or partial fuel assemblies, frozen agglomerates, or in pieces (>1 in. or 2.5 cm) too large for removal with hydraulic vacuuming techniques. About 40,000 kg of the debris is probably in rubble sizes less than 1 in. (2.5 cm). Possibly half of that debris is trapped in the matrix between the fuel pins of reasonably intact fuel assemblies and is likely to be removed with those assemblies. Only about 5,000 kg of the debris is believed to be less than 800 micrometers (μm) in size. Assuming that some of this will be retained in "knockout" canisters and that some will remain trapped within the matrix of fuel assemblies, it is likely that less than 3,000 kg of debris will be removed in "filter" canisters.

The pyrophoricity potential of the segregated core materials is limited primarily to the fine particles. Any intact or partially intact fuel assemblies and other large pieces and the coarse rubble (greater than a few hundred micrometers) have a very low potential to be pyrophoric (Cooper 1984). The fine materials (less than a few hundred micrometers) that are found primarily in filter canisters have the greatest pyrophoricity potential, considering only their size. However, even for the fine materials, the potential for pyrophoricity is very small since essentially all of the particles are almost certainly already well oxidized. Of seven small samples of core debris examined by differential thermal analysis (DTA) calorimetry techniques at Rockwell, only one oxidized significantly, indicating that it was not well oxidized prior to performing the analysis. The oxidation occurred between 500 and 900 °C.

2.1 PYROPHORICITY OF ZIRCONIUM

Numerous published laboratory experiments have proven that the presence of water does not change the ignition temperature of zirconium (Cooper 1984). Once wet zirconium reaches its ignition temperature, it can extract oxygen from water, liberating hydrogen in the process. Whereas dry zirconium burns with a quiet, white-hot flame, wet zirconium burns violently, tossing burning debris into the air.

Despite the inability of water to raise the ignition temperature and despite the violence of combustion of wet zirconium, water is still universally used to stabilize powdered zirconium. The water successfully acts as a heat sink and typically prevents the zirconium from reaching its combustion temperature. The amount of water used is generally greater than 25% of the weight of zirconium. If the water is allowed to boil away during extended heating, the zirconium can burn as described above.

The effectiveness of water as a heat sink was dramatically illustrated by an experiment in which pyrophoric powder (in a drum) was covered by water and the drum was placed between four drums of dry powder. The dry powder was ignited, and the resulting heat melted the central drum down to the water line but did not boil away enough water to ignite the wet zirconium powder.

As a consequence of these and other experiments, the following simple handling and storage recommendations for zirconium powder have evolved. (These are not necessarily applicable to TMI-2 core debris.)

1. Handle and collect all fines (<850 µm) under water.

2. Separate zirconium powder from other combustible materials.

3. Maintain a low moisture content (<3% by weight) or submerge completely.

4. Avoid use of CO_2 or water fire extinguishers.

5. Avoid dust accumulations.

6. Avoid ignition sources.

7. Use solid diluents (such as sand, oxides of uranium, etc.) in a one-to-one or greater ratio.

8. Use argon (or other noble gas) as a cover gas.

9. Provide pressure relief for closed systems to minimize rupture potential.

10. Separate zirconium work areas from other work areas.

11. Exercise extreme care in opening sealed containers.

12. Avoid high temperatures (typically those above the ambient boiling temperature of water).

Massive pieces of zirconium metal may be safely stored for long periods in or out of water. (Massive pieces are defined as sheets 0.3 mm thick or thicker and fragments or pieces whose smallest dimension exceeds 3 mm.)

For small particles greater than 60 μm, submerged storage is advised to minimize the chance of a significant temperature rise.

For pure zirconium and zirconium alloy powders less than 60 μm, storage under water and/or inert gas is mandatory.

2.2 PYROPHORICITY TESTS AT ROCKWELL

Rockwell has completed a number of laboratory investigations to identify the combustion behavior of finely divided zirconium under drip-dry* and bound-water-only** shipping conditions. The conclusion drawn from these investigations are that <u>wet</u> zirconium fines do not burn when struck by a spark in an atmosphere of argon with less than 3 vol% oxygen or in an argon atmosphere <u>initially</u> containing 3% oxygen and 4% hydrogen (although, for unknown reasons, the hydrogen and oxygen did react). <u>Vacuum-dried</u> zirconium fines showed no reaction to a spark in an argon atmosphere containing 3% oxygen and 4% hydrogen. <u>Wet</u> zirconium fines can burn in an argon atmosphere with more than 3% oxygen. No reaction occurred when a spark was struck in an argon atmosphere to fine zirconium powder that was wetted with a solution of hydrogen peroxide (an intermediate in the radiolytic production of hydrogen and oxygen). From these results it appears advisable to maintain materials that might be pyrophoric in an argon atmosphere with less than 3% oxygen.

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*Drip-dry denotes the wet condition of a previously submerged substance after the water has been allowed to drain.
**Bound-water-only denotes the wet condition of a substance after the free (unbound) water has been removed.

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2.3 REACTIVITY OF THREE MILE ISLAND CORE DEBRIS

The TMI-2 core debris is not believed to be pyrophoric. Six characteristics tend to mitigate pyrophoricity in the TMI-2 core debris.

- Zircaloy-clad fuel pins and zircaloy cladding hulls have been demonstrated to be noncombustible (burning is not self-supporting).

- Most of the core debris consists of UO_2 and ZrO_2, which are not combustible.

- Most of the core debris (UO_2 and ZrO_2) acts as a solid diluent that reduces the combustibility of any pyrophoric metal particles.

- The particulate matter in the core debris was heated to high temperatures during the loss-of-coolant accident. Any reactions that occur at a high temperature should already have occurred.

- Considerable oxidizing, melting, alloying, and agglomerating of metals occurred in the loss-of-coolant accident so that pure metal fines are probably relatively scarce.

- No mechanical processes that produce unoxidized fine materials have occurred. Therefore, fresh (unoxidized) metal surfaces should be relatively scarce. If the defueling process creates fresh metal surfaces and particularly if it creates very small chips and fines such as from sawing and grinding operations, the pyrophoricity potential would be increased.

The planned core debris environment during removal, handling, and shipping essentially eliminates any pyrophoricity potential during these periods.

- The core debris will be placed in canisters while under water.

- An inert gas will blanket the core debris in the canisters after dewatering.

These core debris characteristics and environmental controls provide a reasonable basis for believing that no pyrophoricity incident will be encountered while handling the core debris. If any pyrophoric condition is encountered during the testing program, it would not impact the defueling and shipping procedures currently being considered; however, it could significantly affect procedures during canister opening, when the debris could be exposed to air.

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3.0 HYDROGEN GENERATION

Radiolytic hydrogen and oxygen gas generation from wet core debris is considerably different than that from undamaged irradiated fuel assemblies. First, the undamaged fuel exposes the surrounding water primarily to gamma (γ) radiation since the fuel cladding effectively shields the water from the alpha (α) and beta (β) radiation. The irradiated core debris emits α, β, and γ radiation into the water. A high fraction of the radiolytic hydrogen and oxygen in TMI fuel canisters will be generated from the β radiation.

The second significant difference between the gas generation rates from undamaged fuel assemblies and the gas generation rates from the TMI core debris is in the amount of water in close contact with the material. During the shipping of clean, undamaged fuel assemblies, essentially no water is in close contact with the fuel. Decay heat drives moisture away from the fuel rods, and the moisture condenses on cooler surfaces. The condensate drains to the side or bottom end of the cask where radiation levels are lower. The fraction, F (see appendix A), of the ionizing radiation absorbed in the water is thereby lowered, and less radiolytic gas is produced. Conversely, fine core debris particles trap a considerable amount of water, which is difficult to remove. Since this water is in close contact with the debris, a much higher F factor is realized and hydrogen and oxygen are produced at a much higher rate. An evaluation of these qualitative conditions indicates that the two factors together could increase the radiolytic production rate of hydrogen and oxygen gases in canisterized, moist core debris by several orders of magnitude over that of undamaged fuel assemblies having the same irradiation and cooling histories.

Calculations indicate a probable-maximum hydrogen-plus-oxygen generation rate of 0.11 liters/hour* (L/h) (0.076 L/h of hydrogen and 0.038 L/h of oxygen) per 800 kg of TMI-2 core debris (see appendix A). This probable-maximum gas generation rate would be reduced if either the F factor (the fraction of the total ionizing radiation that is absorbed in water) or the G value (the net number of gas molecules generated per 100 electron volts (eV) of ionizing radiation absorbed in water) could be reduced. The F factor of 0.2 (Turner 1968) would be reduced if the core debris in each canister were dried. However, the degree of dryness necessary to keep hydrogen and oxygen concentrations below flammable limits is extreme. The extent of canister drying is further discussed in section 6.

The G value of 0.44 (Turner 1968) would eventually decrease under conditions where some or all of the oxygen being radiolytically generated is chemically removed (scavenged) by the oxidation of some of the core debris or by the insertion of an oxygen scavenger such as carbon steel wool or hydrazine. This potential reduction in the G value would result from excess hydrogen causing back-reactions. At some unknown hydrogen overpressure,

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*Standard conditions, 1 atm pressure and 0 °C temperature, are intended throughout the report unless specifically noted.

there would be no net generation of hydrogen or oxygen. Since the extent of oxygen scavenging by the core debris is unknown and since the hydrogen overpressure required to prevent the net generation of hydrogen and oxygen is unknown, it appears that, without further experimental evaluation, involved regulatory agencies would not be likely to permit consideration of the eventual reduction in the G value.

The peak-to-average factor (the ratio of peak energy from the fuel debris in a canister to the energy in the same quantity of average fuel debris) of 1.9 is used. This factor, which is based on calculated peak-to-average values in the undamaged TMI-2 core, appears to be conservative because the core debris from the upper half of the center (most highly active) elements was degraded and scattered during the accident. This high peak-to-average factor also provides an allowance for the possible concentration of radioactive materials resulting from the hydraulic segregation of particles during the accident and during the core debris removal process.

As noted in the preceding paragraphs, each of the factors affecting the hydrogen-oxygen generation were selected based on conservative estimates and resulted in the probable-maximum generation rate. Conversely, if these factors were selected based on much less conservative estimates, the calculated gas generation rate would be reduced by a factor of at least 2 but probably not more than 10.

The pressure and gas concentrations for various canister loadings after 88 days (twice the planned shipping time) are shown in figure 1. The curves are based on a hydrogen-plus-oxygen generation rate of 0.11 L/h per 800 kg of debris and the assumption that none of the gases are recombined or otherwise removed. Note that if the hydrogen or oxygen gas concentrations were to be kept below their lower limits of flammability (4% for hydrogen or 5% for oxygen) for the 88-day period, the ratio of the volume of wet core debris to the canister empty volume would have to be limited to less than 15%. To avoid exceeding the 3% oxygen limit suggested in section 2.2 on the basis of pyrophoricity control, the volume of wet core debris in a canister would be limited to 10%. To make better use of the canister volume, other means of gas control, including drying, the addition of oxygen scavengers, and the addition of hydrogen-oxygen gas recombiners, have been considered (sections 6 and 8).

4.0 WATER VAPOR PRESSURIZATION FROM A POTENTIAL FIRE ACCIDENT

In any closed system containing gas and water, as the temperature is increased, the pressure increases correspondingly. If there is sufficient water in the system such that the water vapor remains saturated, the pressure is easily predicted for any given temperature by applying standard gas laws and adding water vapor pressure values in accordance with standard steam tables. The dashed line in figure 2 shows this temperature-pressure

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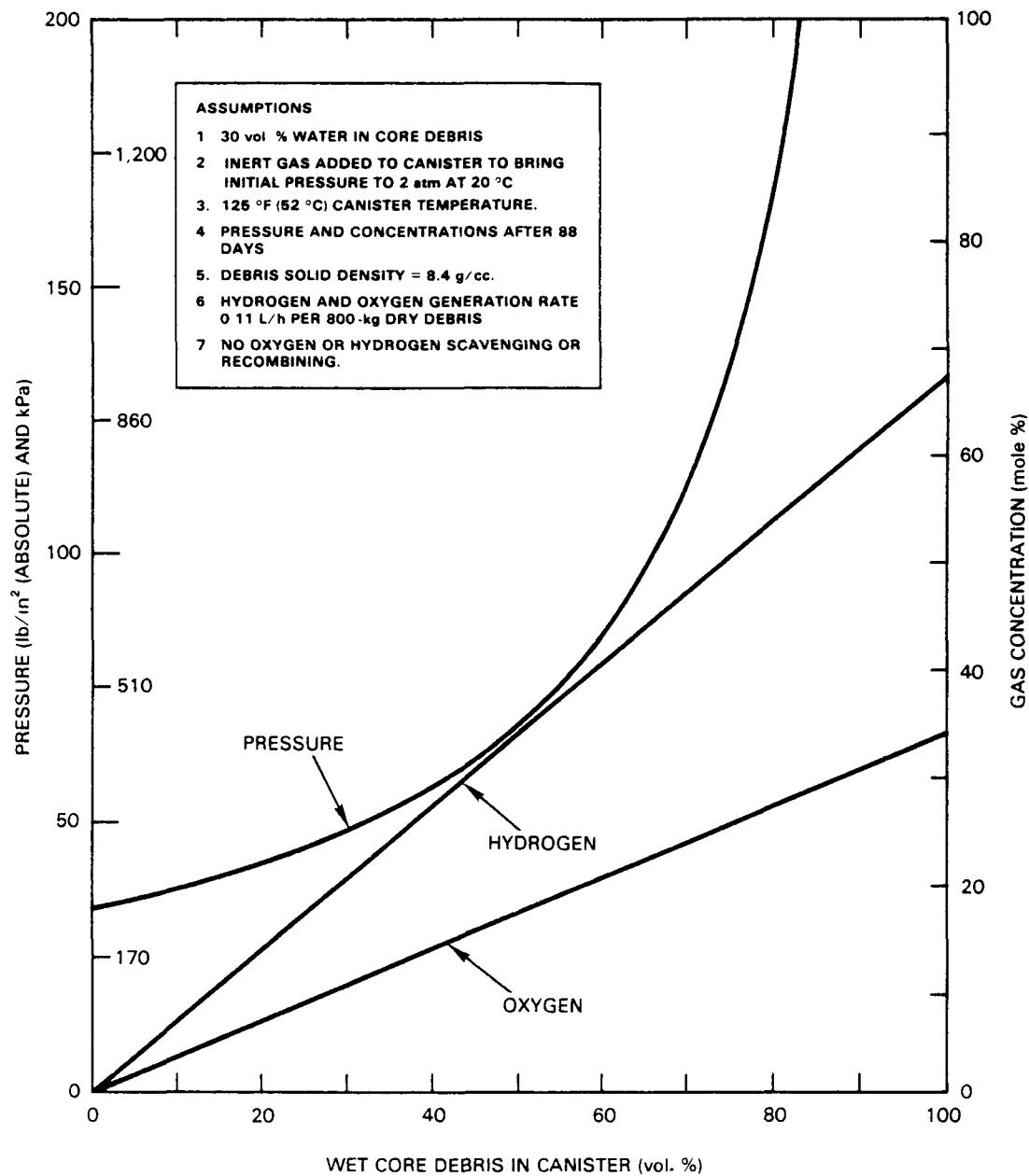
Figure 1. Pressure and Gas Concentration Versus Volume
Percent of Wet Core Debris in Canister after 88 Days.
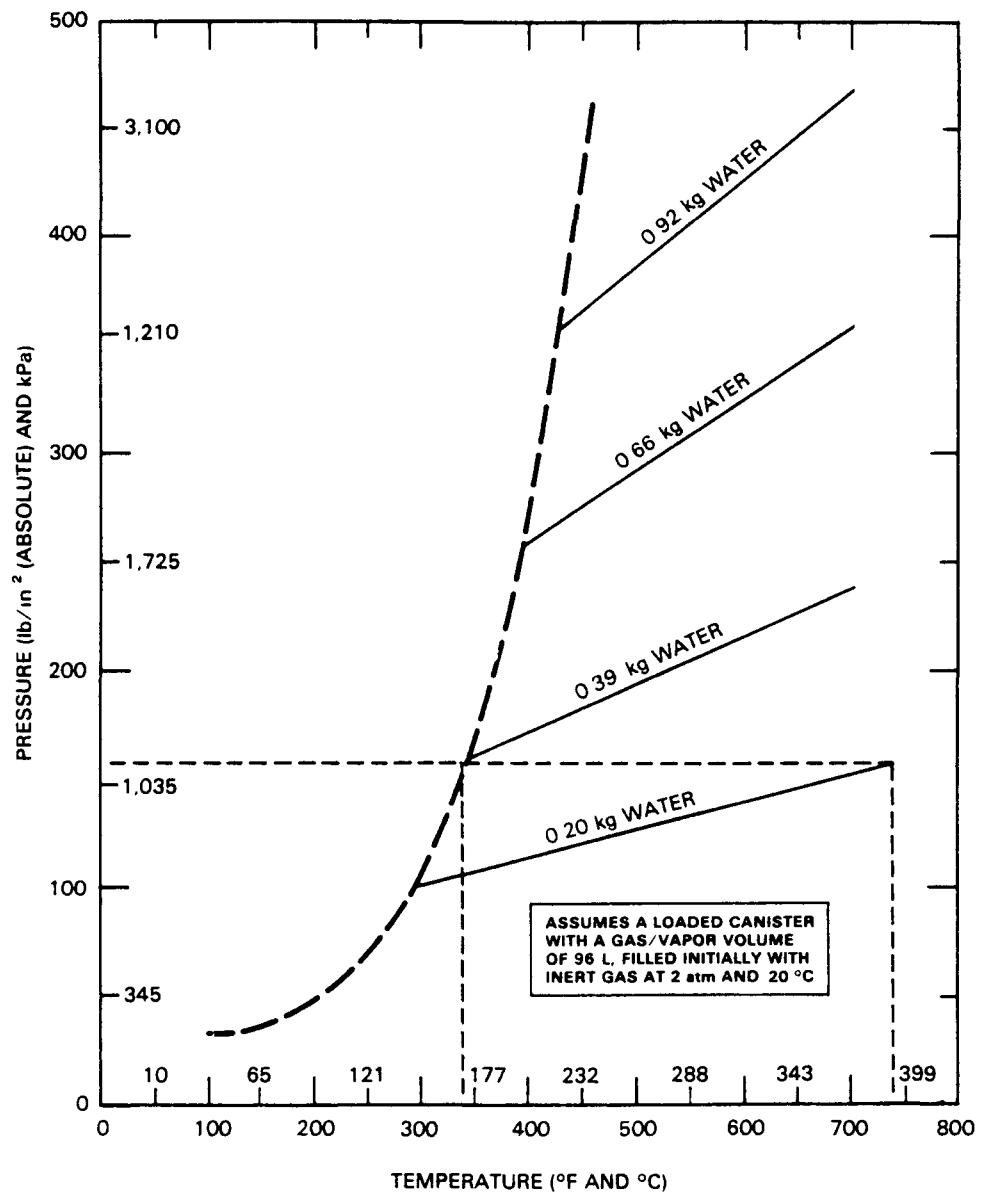
Figure 2. Temperature Versus Pressure for Various
Amounts of Water in a Loaded Canister.

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relationship for any closed, saturated system, starting at 2 atmospheres (atm) of inert gas and water vapor at 20 °C. If the amount of water in a closed system is limited such that all of the liquid water is converted to vapor and then superheated, the pressure increases more slowly as temperature increases. Examples of these conditions are shown by the solid lines in figure 2 for a loaded canister having a 96-L void space and for various limited amounts of water in the canister. Note that the amount of water allowed in a canister would be very restrictive (less than 1 kg) if a water limit were used as the primary method of keeping pressures within reasonable limits. This method is discussed further in section 6. Limiting canister and cask pressures by designing the shipping cask to limit internal temperatures in the event of an accidental fire is discussed in section 9.

5.0 CANISTERS AND SHIPPING CASK

Three types of canisters, each 14 in. (35.6 cm) in diameter by 150 in. (381 cm) in length, are planned for shipping and storing the core debris (Jacks 1984). They are termed fuel, filter, and knockout canisters, and their physical features are described in appendix B. As shown in appendix B, the fuel canister has the smallest inside free volume. When loaded to the established dewatered weight limits, the remaining gas/vapor (void) volume is much less in the fuel canister than in the filter or knockout canisters. Due to limited void volume, radiolytic gas generation would increase the pressure in the fuel canister much more rapidly than in the filter or knockout canisters. Since all three of the canister types have the same 150-lb/in^2 gage (1,135 kPa) design pressure rating, the fuel canister characteristics establish the basis for any limiting conditions resulting from radiolytic gas generation.

The shipping cask being designed by Nuclear Packaging, Inc., to safely transport the TMI-2 core debris canisters is rail mounted. The loaded cask will contain seven debris canisters. To meet pertinent shipping criteria, the cask is designed to provide double containment. The canisters are not relied upon to provide a level of containment for shipping. The calculated gas volume between the seven canisters and the inner containment of the loaded cask is 295 L. The calculated gas volume between the inner and outer containments is 517 L. Initially, these volumes will be filled with approximately 1 atm of argon at 20 °C. The cask is designed such that internal temperatures will not exceed 200 °F (93 °C) after exposure to the standard hypothetical accident conditions. See section 10 of the Code of Federal Regulations (CFR), 71.73 "Hypothetical Accident Conditions," (c) "Tests," (3) "Thermal."

6.0 WATER REMOVAL FROM DEBRIS CANISTERS

Several methods of removing water from canisters have been considered. Each method has varying degrees of complexity, and each method varies in its effectiveness. The methods include the following: (1) the use of pressurized

gas for water displacement and stripping (drip drying) while the canister remains submerged; (2) method 1 (gas displacement) followed by circulation of dry, heated gas through the canister; (3) method 1 (gas displacement) followed by vacuum pumping; (4) method 3 (gas displacement and vacuum pumping) with the addition of heat; and (5) drying by heating and vacuum pumping in a shielded, dry cell. Only the last method assumes that loaded canisters would be removed from the water for debris-drying operations.

Method 1, Gas Displacement (Drip Drying)

A gas such as argon could be used to displace and strip water from the canister. Gas displacement is the easiest method of removing water. All that is required is a supply of gas, a line to carry fresh gas to the canister, a line to carry contaminated water and gas from the canister back to the canister dewatering system, and weighing equipment. Self-sealing quick-disconnect couplings could be used on the canister for remote connection of the lines. The bulk of the water could be removed from the canister by this drip-dry method. If the residual water remaining in the canisters after drip drying can be tolerated, the water removal system would be the simplest and the cost and time required for dewatering would be significantly less than for any of the following methods.

Method 2, Hot Gas Drying

A system of circulating heated, dry gas through the canister was considered. This approach is not recommended. As drying proceeds, the gas flow would tend to spread contaminated fine materials. When considering the difficulties of providing the heated gas stream, underwater insulation, and the additional filtration system required to remove radioactive particulates carried by the circulating gas, such a system was judged to be much more complex and less cost-effective than vacuum pumping (method 3).

Method 3, Vacuum Pumping

A higher degree of dryness than that provided by method 1 could be attained by vacuum pumping after drip drying. In addition to the drip-drying and weighing equipment, vacuum-pumping equipment would be required. This method would assure that the free, unbound water had been removed. However, the remaining water would not necessarily provide sufficiently low moisture levels to prevent high vapor pressure concerns resulting from the standard fire, or to prevent the radiolytic generation of large quantities of hydrogen and oxygen gases.

To demonstrate that a reasonable amount of vacuum pumping would not eliminate high vapor pressure concerns, a comparison has been made between "critical moisture," various residual water quantities, and resulting vapor pressures during a fire. Critical moisture as used herein is the average moisture content when the constant-rate drying period ends. Below the critical moisture level, the rate of drying continuously decreases. Figure 3 compares the critical moisture for

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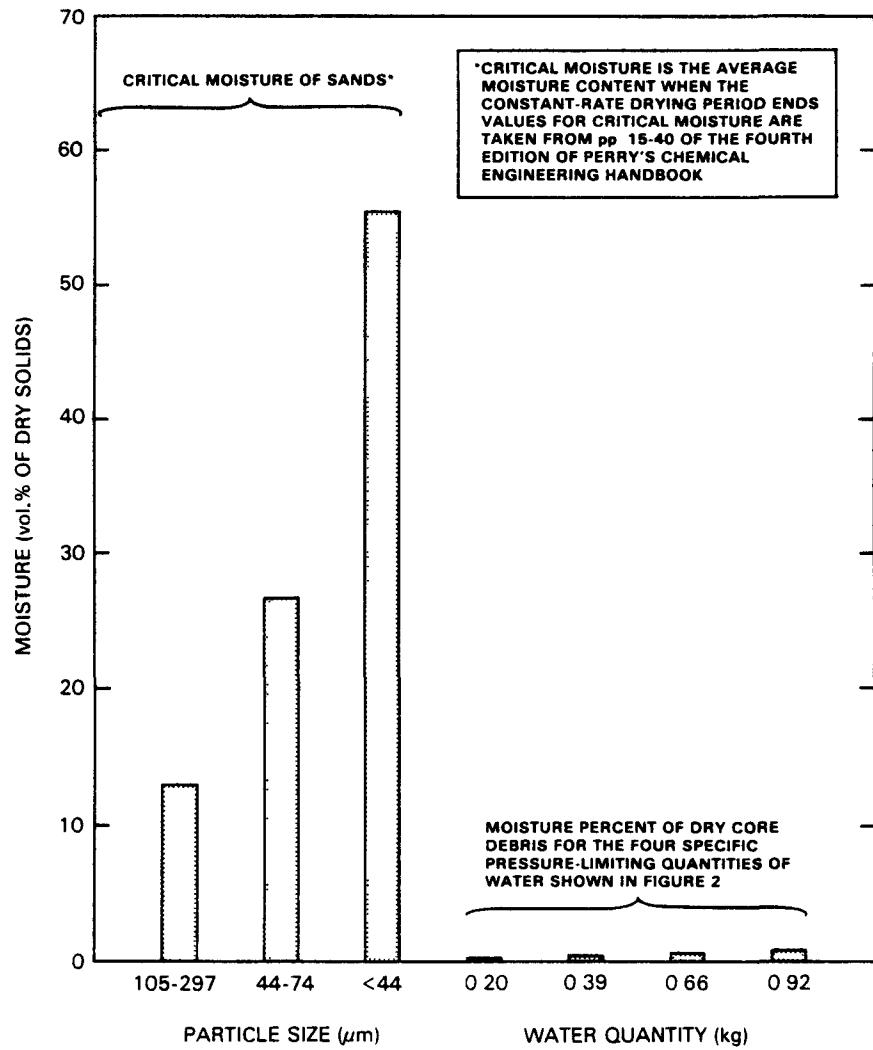
Figure 3. Comparison of Moisture Contents.

three size ranges of sand particles. The critical moisture varies from 13 vol% on a dry basis for the coarse sand to 56 vol% for the finer sand. Critical moistures of fine subsoils have been found to be in the 80- to 90-vol% region. Although the critical moisture levels for various size ranges of the core debris are not currently known, some of the finer particles will undoubtedly approach the size of fine subsoils. Even the canisters containing coarse core debris will include sizes ranging down to fine particles. Furthermore, cracks and crevices in the fuel material and cladding, through which water could have been forced from the high pressure cycling during the accident, would provide a source of water that would be difficult to remove without heat. Note that the critical moisture level even for very coarse materials (fig. 3) is much higher than the moisture level limit required to prevent overpressure at high temperatures (fig. 2).

To evaluate the length of time it might take to dry fine materials, zeolite vacuum-drying data taken by Rockwell were plotted and are shown in figure 4. Note that after drip drying and heating at 300 watts (W) and vacuum pumping for about 5 days, the critical moisture was reached. After about 18 days of heating and pumping, the rate of drying approached zero. At this point in the drying, the moisture content was still above 20%. Although zeolite is probably harder to dry than fine fuel debris, the data gained from the zeolite evaluation do give some indication of the difficulty in vacuum drying fine materials with little or no heating. Although moisture levels below 20% could surely be attained, it would be very difficult to assure that moisture below (for example) 1% had actually been attained. Thus, it would be necessary to install more extensive drying facilities to ensure that canisters of core debris were sufficiently dry to avoid high pressures resulting from a potential fire accident.

Method 4, Heating and Vacuum Pumping

A higher degree of dryness could be attained by combining heating and vacuum pumping. This would considerably complicate the drying process. Heat addition to canisters in a storage pool would require a canister cover such as a diving bell or a waterproof, insulated heating jacket. Electric heating would be complicated by potential wetting of equipment. Steam heating would be preferred but would require insulated piping. Steam heating would also minimize a potential pyrophoricity problem associated with local hot spots. Underwater heating, vacuum pumping, and the possibility of water intrusion while disconnecting vacuum ports after drying would be complex. Thus, it would be extremely difficult and certainly not cost-effective to assure that the contents of each canister would be sufficiently dry to eliminate the need for other means of preventing high pressures resulting from a potential fire and preventing flammable gas mixtures. For these reasons, underwater-heated vacuum drying was not further pursued.
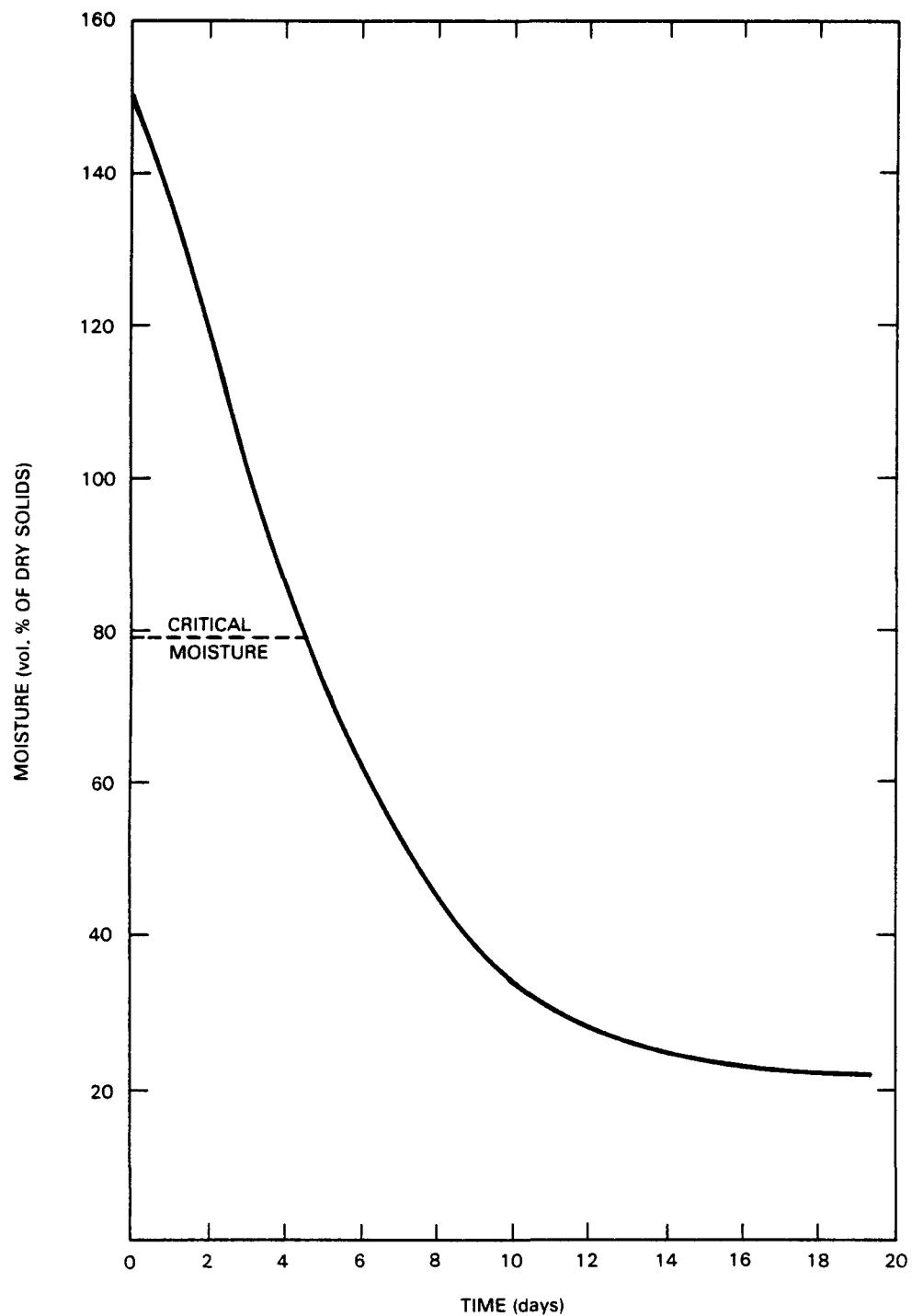
Figure 4. Vacuum-Drying Curve for Approximately 700 kg of
Zeolites with 300-W Heat Addition.

Method 5, Special Drying Facility

The last method considered for removing water from the canister would involve conducting drying operations in a completely shielded cell that has multiple heating and vacuum-pumping stations and uses remotely operated tools and equipment. This method would assure sufficient drying, eliminating the need for other means of steam and hydrogen control. However, significant heating would be necessary, and this would aggravate any pyrophoricity potential. The cost of construction of such a facility would be very high, and the construction schedule would probably delay shipping well beyond any currently planned timeframe. For these reasons, heated vacuum drying in a shielded cell was not further pursued.

If any of the first four water removal methods were used, a potential for water intrusion would exist, either from canister leaks or during the process of disconnecting the canister from the dewatering system. Water intrusion can be minimized by maintaining a higher pressure inside the canister than can exist outside the canister. The ambient pressure plus water head ($\sim$25 ft (8 m) from the water surface to the bottom of the canister) totals less than 2 atm absolute. Therefore, 2 atm (25 to 30 lb/in^2 (absolute) or 193 to 207 kPa) of cover gas in the canisters would minimize water intrusion and is recommended. To adequately assure a general level of dryness under water at the time of shipment, weighing procedures will be necessary. Each filled canister should be weighed after dewatering and capping and again just prior to shipment to detect inadvertent water intrusion.

By removing as much water as practical from the canisters, estimates of the actual amount of remaining water and debris will be improved (see appendix C). However, accountability of the fuel material in each canister to gram quantity accuracy cannot be established by canister weighing techniques.

Since tests by Rockwell (section 7) have shown that the Engelhard Deoxo-D and Atomic Energy of Canada Limited (AECL) silicone-coated catalysts perform satisfactorily starting wet (but not submerged), Rockwell recommends that the canisters be shipped with some free water remaining in the canister (method 1). However, the catalysts did not perform satisfactorily when submerged in water. Therefore, it is recommended that each canister be dewatered to a level such that the debris plus remaining water occupy no more than 50% of the volume of the empty canister. This will positively assure that at least 50% of the catalyst (100 g) is not submerged at any time after dewatering. Accordingly, based on current estimates of canister volumes and weights, it is recommended that at least 96, 141, and 152 L of water be removed from the filled fuel, filter, and knockout canisters, respectively (see appendix B). If the canisters are not overloaded, dewatering to this level can be accomplished by using argon gas to force water through a filtered dip tube. No vacuum pumping should be required. If instances occur where canisters are inadvertently overloaded (very unlikely for fuel and filter canisters), conditions would be evaluated on a case-by-case basis, and removal of free water by repeated dewatering operations and possibly even by vacuum pumping might be determined to be the most appropriate corrective action.

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7.0 CATALYST BED TESTS

A series of catalytic recombiner tests was performed by Rockwell. The tests were conducted using small (16-L gas/vapor volume) pressure vessels that simulated the shipping canisters. Electrolytic hydrogen/oxygen generators were connected to the vessels for controllable simulation of the radiolytic generation of these gases. Other connections permitted vessel purging with inert gases, temperature and pressure monitoring, and gas sampling.

The interior of each vessel was fitted with screened containers (catalyst beds) to hold specified volumes of selected catalysts. Five bed designs were used at various times during the test series. These beds permitted the testing of such parametric effects as bed volume, bed depth, and screening/gas-diffusion effects.

Four catalysts were selected to determine the relative benefits of special wet-proof and proven "industry standard" catalysts. The four catalysts tested follow:

- Engelhard Deoxo-D, palladium on alumina

- AECL silicone-coated, platinum on alumina

- AECL Teflon-coated, platinum on alumina

- Houdry, platinum on alumina.

The coated (AECL) catalysts are designed to prevent wetting of the catalytic sites while permitting gases to diffuse through the coating to reach those reaction sites. As part of the test series, the coated pellets were tested for irradiation effects and found to be susceptible to deterioration. Since the decomposition products of Teflon are potentially corrosive, only limited testing of the AECL Teflon-coated catalyst was performed. The Engelhard catalyst has an established history of good performance under irradiated conditions in a number of Rockwell-designed facilities. Testing of the Houdry catalyst was also limited and was used primarily to determine differences in recombination effectiveness between palladium- and platinum-based catalysts.

The test series was designed to evaluate handling/shipping conditions that might affect catalyst performance. Such conditions included wetted catalyst beds; submerged beds; beds poisoned with waterborne chemicals, insoluble particulates, and carbon monoxide gas (generated radiolytically from organic substances); frozen catalysts; and heavily irradiated catalysts. Tests to measure each of these effects on various sizes and shapes of catalyst beds were included in the series. The results of these efforts are summarized in the following statements.

- When catalysts were totally submerged in water, essentially no recombination occurred.

- Catalyst beds that were drained after submersion under water at 2 atm for approximately 24 h started recombining hydrogen and oxygen even in a 100% relative humidity atmosphere. Recombination rates increased with bed drying as a result of the exothermic reaction. The AECL "wet-proof" catalysts began recovery earlier than the Engelhard catalyst but were not as effective as the same volume of Engelhard catalyst in maintaining the gases at acceptable levels.

- Waterborne contaminants (synthetic cooling water with dissolved salts and particulates) had only slight, if any, effect on the catalysts. Carbon monoxide gas had temporary effects on the Engelhard and Houdry catalysts (recovery in 4 h after CO gas introduction) but had a longer lasting effect (>8 h) on the AECL catalyst.

- Irradiation of the AECL silicone-coated catalyst of 10^8 rad (a level that is approximately what is expected in the canister's 30-yr ship-store period) had definite effects on the catalyst. Microscopic examination of cross sections of the irradiated pellets indicated a spreading of degradation products into the pellet. The surface of the silicone coating appeared to be more uniform and less porous except for fissures. This condition apparently occluded reaction sites within the pellet and decreased its effectiveness as a catalyst.

- Long-term (>25 yr) Rockwell experience with the Engelhard catalyst under very high radiation exposure has shown no performance degradation and obviated further radiation testing of this material.

- Thin beds with a larger surface area exposed to the canister interior performed distinctly better than compact beds.

- Mixed-bed catalysts containing 80% Engelhard and 20% AECL silicone-coated catalysts by weight gave significantly improved performance over either catalyst alone.

- Catalyst tests starting under frozen conditions indicated unacceptably low recombination rates. However, when recombination was initiated above freezing conditions then cooled to below freezing, recombination continued until the system was shut down after 35 h.

The synergistic effect of mixtures of AECL silicone-coated and Engelhard catalysts appears to be due to the immediate recovery of the AECL catalyst from wetting effects. The AECL pellets apparently provide initial reaction sites that warm and dry the neighboring Engelhard pellets. The high recombination efficiency of the drying Engelhard catalyst then quickly brings the hydrogen and oxygen concentrations under control at levels well below that of single-catalyst beds.

Graphic results of some of the final test runs are shown in figures 5 through 9. In these tests, the nominal test conditions shown in table 1 were used. These conditions were selected to closely simulate the conditions expected in the shipping canisters. The tests indicate the effects of potential or suspected aqueous poisons in the TMI-2 core water (figures 5 and 6), radiation effects (figures 7 and 8), and catalyst type (figure 9).

Examination of figure 9 shows the distinct synergistic effect of the mixed-bed catalyst under nonirradiated conditions (lowest curve). With increased time, the catalyst would further dry and become more effective (reactive). If the catalyst were rewetted after prolonged irradiation and deterioration of the AECL silicone wet proofing, some increase in gas concentrations would be experienced. However, even then the mixed bed would perform reasonably well with only the remaining Engelhard catalyst, as shown in figure 8.

Hydrogen-oxygen recombination by the final-design catalyst bed, starting at temperatures between 5 and 10 °C, as shown in figure 10, was very similar to that at higher temperatures (approximately 20 °C) as shown in figure 9. The operating recombiner was cooled to below-freezing temperatures and still continued to perform well until it was shut down after 35 h. The 25-h period during which this time-accelerated test (0.3 L/h per 16-L void) showed excellent performance under frozen conditions is equivalent to 17 days for a loaded fuel canister (0.11 L/h per 96-L void). Further, the test was continued and the recombination rate at 77 h was 0.14 L/h, which is higher than the calculated probable-maxiumum generation rate for a loaded canister (0.11 L/h). Therefore, the tests indicate that the catalyst would maintain oxygen concentrations in a debris canister below 3% for a number of weeks under freezing conditions. A buildup of frost that looked like snow was observed on the corners of catalyst pellets after earlier tests under freezing conditions. This buildup causes catalyst performance to slowly degrade with time. When temperatures rise to above freezing, the "snow" on the pellets would melt and normal recombination rates would be restored.

8.0 HYDROGEN/OXYGEN CONTROL

The radiolysis of 18 g (1 mole) of water produces 33.6 L of stoichiometric hydrogen-plus-oxygen. In a loaded fuel canister (appendix B), this would result in hydrogen and oxygen concentrations of approximately 10% and 5% respectively, which are equal to or greater than their lower flammability limits. For safe shipment, the oxygen concentration must be kept below 5% (its lower flammability limit in hydrogen). A 3% oxygen limit is recommended for potential pyrophoricity control. To maintain 3% or 5% oxygen levels for an 88-day period (twice the planned shipping time), the percent of the empty canister volume occupied by wet core debris would have to be limited to
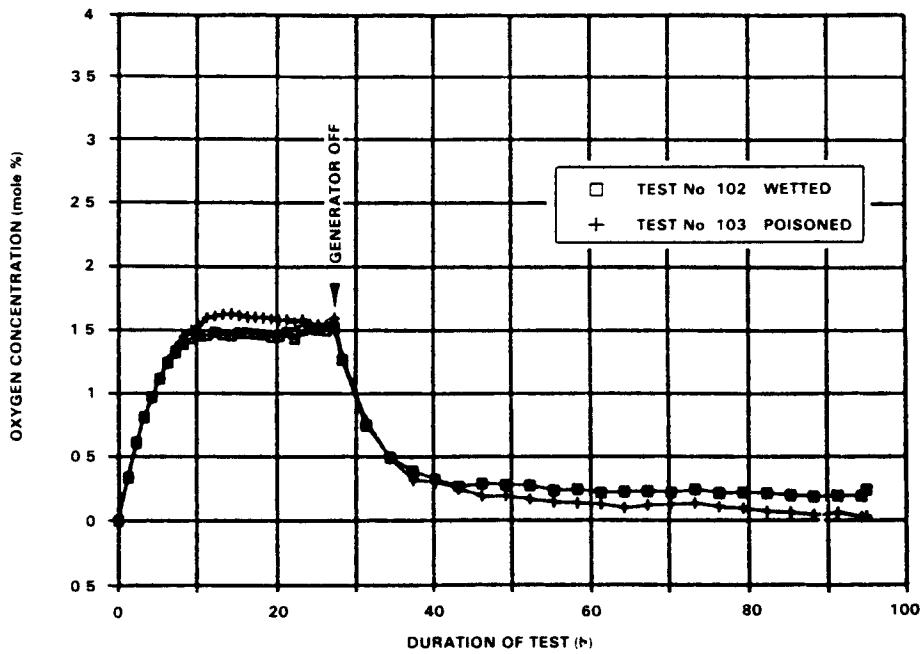
Figure 5. The Effect of Aqueous Poison on Engelhard Catalyst.
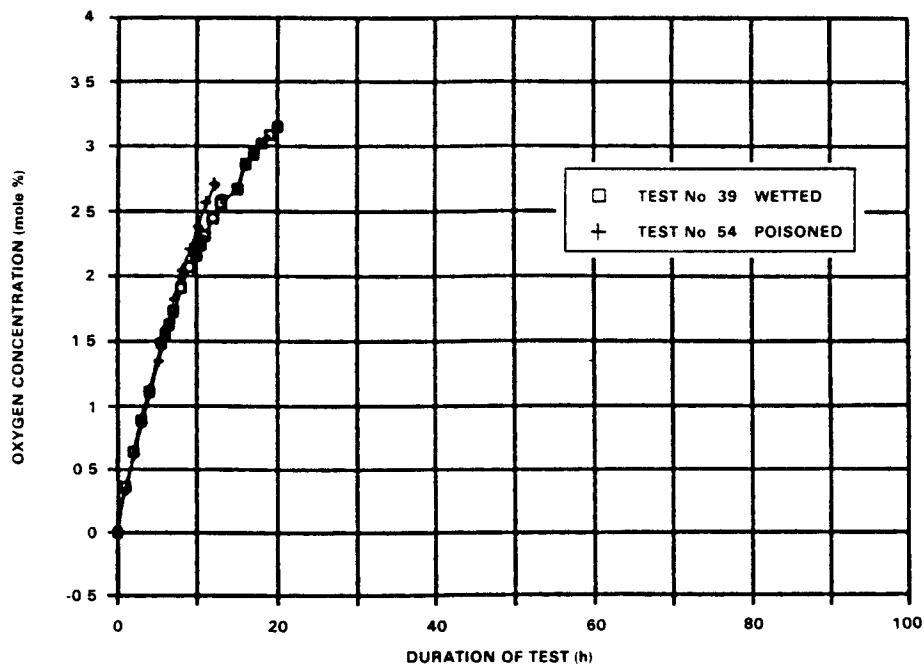
Figure 6. The Effect of Aqueous Poison on AECL Silicone-Coated Catalyst.
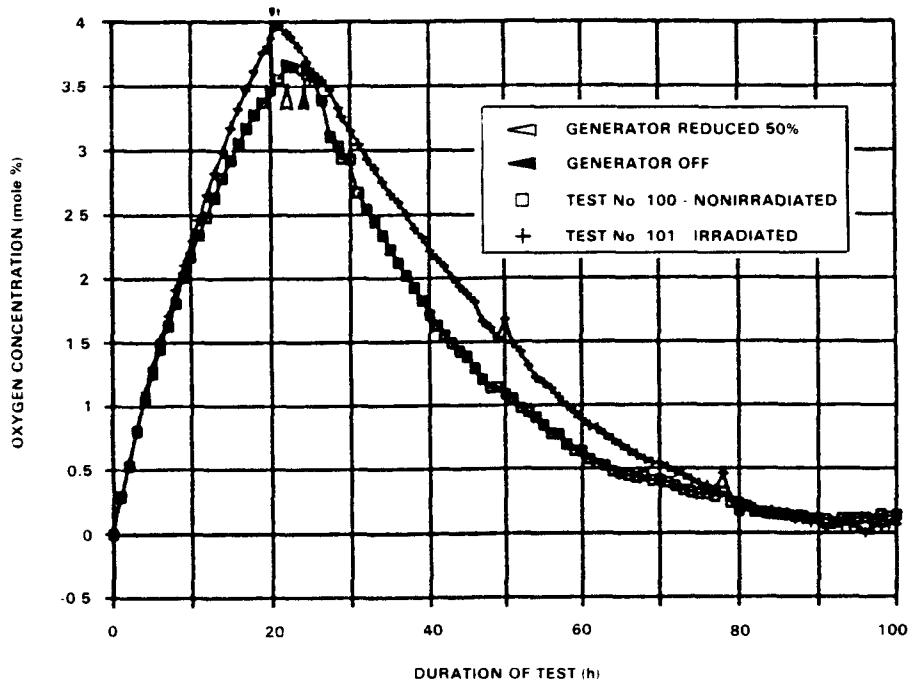
Figure 7. The Effect of Radiation on AECL Silicone-Coated Catalyst.
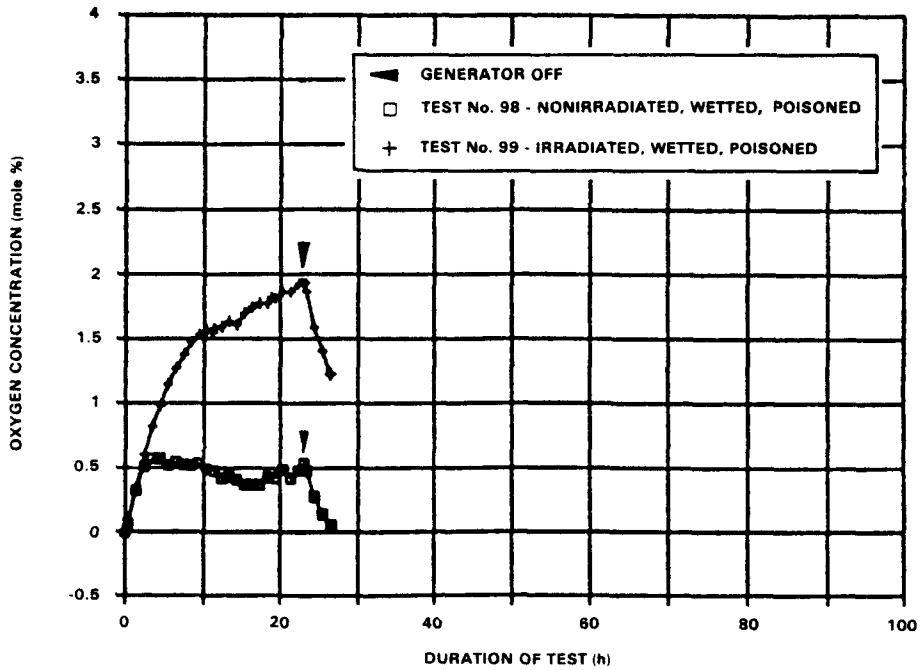
Figure 8. Final Design--The Effect of Radiation on Mixed-Bed Catalyst.

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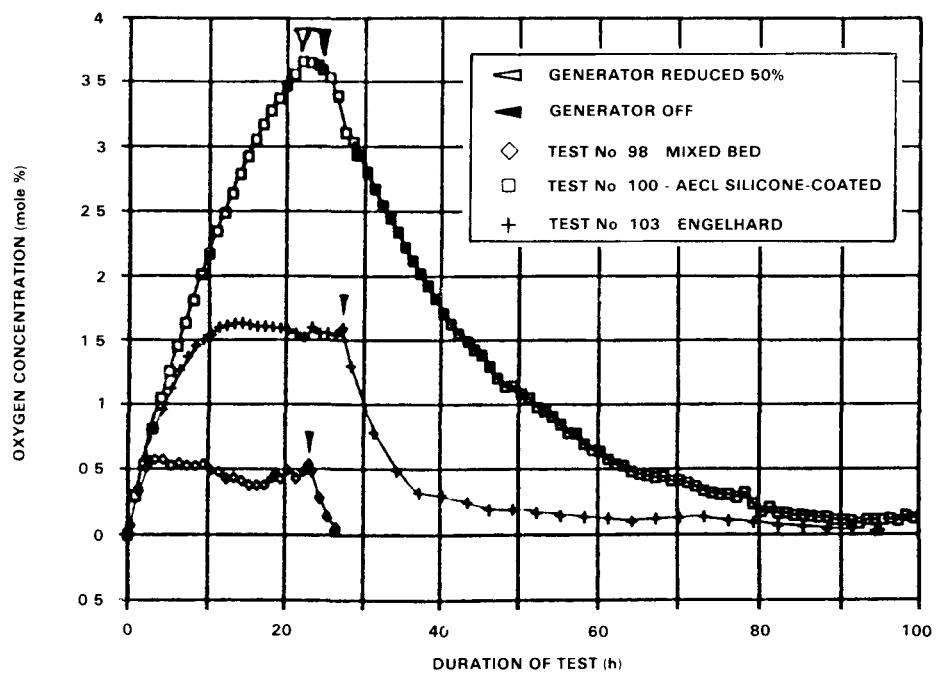
Figure 9. Final Design--Catalyst Comparison: AECL Silicone-Coated, Engelhard, and Mixed-Bed.
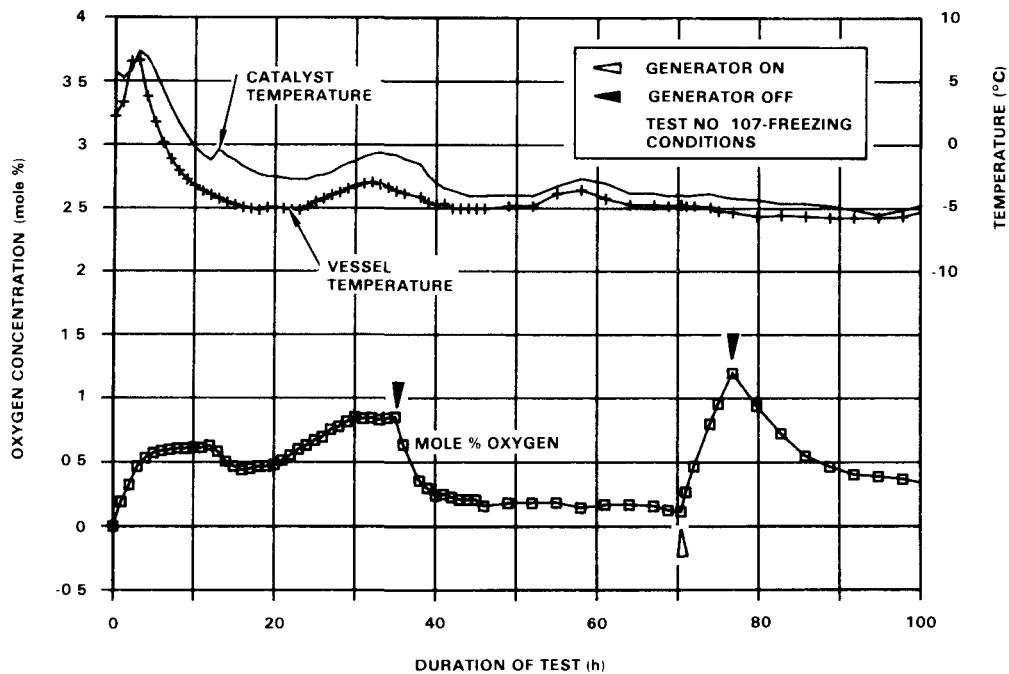
Figure 10. Final Design--Mixed-Bed Operation under Freezing Conditions.

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Table 1. Test Conditions.

General test conditions	Range tested	Nominal conditions
Pressure	0-2 atm	2 atm
Cover gas	Argon, nitrogen, air, helium	Argon
Hydrogen/oxygen generation rate	0.075-0.3 L/h	0.3 L/h
Catalyst volumes (100 g)	4.5-715 cc	∿100 cc
Bed thickness	1-3 cm	1 cm
Vessel void volume	16 L	16 L
Ambient temperature	-5 to +30 °C	∿20 °C
Poisons: aqueous	Synthetic cooling water	Synthetic cooling water
gaseous	Carbon monoxide	None added
Wetted catalyst	12-24 h submerged at 2 atm	12-24 h submerged at 2 atm

less than 10% or 15%, respectively. Since it would be too costly to ship the core debris on such a debris-limited basis, to assure significantly lower generation rates, or to provide for controlled venting at specific periods during shipment, a hydrogen-oxygen recombiner or an oxygen scavenger in each canister appears to be required.

Several types of oxygen scavengers could be used to prevent the oxygen from reaching its lower flammability limit. An example of an oxygen scavenger in liquid form is hydrazine. Hydrazine has been used in pressurized water reactor systems to remove oxygen and create a hydrogen overpressure, which causes back-reactions and prevents (at some minimum pressure) the net generation of hydrogen and oxygen. The major disadvantage of using an oxygen scavenger such as hydrazine is that it replaces the oxygen with nitrogen. The calculated net gas generation would require an increase in the design pressure of the canister/cask (unless it could be demonstrated that hydrogen overpressure would prevent the net generation of hydrogen and oxygen before reaching the design pressure). Another disadvantage is that hydrazine would be consumed as oxygen is scavenged. Approximately 40 g of hydrazine would be consumed per month if 0.038 L/h of oxygen were reacted. Hydrazine would need to be extensively tested in a stagnant system to ensure that diffusion would not limit its effectiveness. As a result of these disadvantages, the use of hydrazine was not further considered.

Another type of oxygen scavenger in solid form that could be used is carbon steel wool. However, the use of carbon steel wool in this application has not been tested. Further, carbon steel wool would be consumed as oxygen is scavenged. (Approximately 90 g of iron would be consumed per month if 0.038 L/h of oxygen is reacted.) Iron oxidation would allow hydrogen buildup in the canister, but no secondary gas would be generated, as occurs with hydrazine. Because of the uncertainties involved and the lack of any advantage over the use of catalysts, the addition of carbon steel wool was not further considered.

Catalytic hydrogen-oxygen recombiners have a long history of satisfactory use in controlling gas buildup. A series of tests evaluating catalysts and catalyst bed parameters was conducted by Rockwell. Results of this effort are reported in section 7.

Consistent with the calculated probable-maximum radiolytic hydrogen-oxygen generation rate of 0.11 L/h per 800 kg of TMI-2 core debris, the catalyst tests and evaluations provide a substantial basis for the following recommendations.

1. Two or more catalyst beds should be located in each of the TMI-2 core debris canisters such that after dewatering and closing the canisters at least 100 g of the specified mixed catalyst will not be submerged in water at any one time, regardless of canister orientation.

2. Each catalyst bed should consist of 80% Engelhard Deoxo-D nuclear grade catalyst and 20% AECL silicone-coated catalyst. Additional Engelhard catalyst should be used to fill any oversized beds.

9.0 CANISTER/CASK PRESSURES DURING SHIPMENT

Shipping regulations (10 CFR 71.4, "Definition of Maximum Normal Operating Pressure," and 71.73, "Hypothetical Accident Conditions," (b) "Test Conditions") require that the canister/cask be designed to withstand the maximum normal operating pressure at 1 yr (unless the 1 yr is reduced (to 6 mo, for example) as a result of "operational controls during transport"), followed by the standard hypothetical accident (fire). Figure 11 shows the relationship between the canister pressure and gas/vapor volume at a 200 °F (93 °C) peak temperature of the contents after the hypothetical accident. Curve (a) shows the pressure-volume relationship for the water vapor, inert gas, and hydrogen generated at a rate of 0.076 L/h (see appendix A) for 1 yr (oxygen scavenged with no secondary gas generation). Curves (b) and (c) are the same as curve (a) except that the period prior to the standard hypothetical accident has been reduced from 1 yr to 9 mo and 6 mo, respectively. Curve (d) shows the pressure-volume relationship, assuming recombiner operation and no oxygen scavenging (water vapor and inert gas only).

Note that for the weight-limited (2,940-lb or 1,336-kg) fuel canister (see appendix B, table B-1), with a 96-L gas/vapor (void) volume, the 165-lb/in^2 (gage) (1,135 kPa) design pressure is exceeded under assumption (a) of figure 11, but not assumptions (b), (c) or (d). Until pressure-rise measurements are made on loaded canisters at TMI, it cannot be shown that some or all of the oxygen will not be inadvertently scavenged. Therefore, curves (a), (b), and (c) can be more readily justified than curve (d). Curves (a), (b), and (c) are probably highly conservative since gas generation rates decrease as hydrogen overpressures increase. Further, minimum gas/vapor volumes and pressure limits on loaded canisters are not strictly required since the shipping cask provides both of the required levels of containment. Canister failure due to overpressure would not jeopardize cask integrity. If, for the worst-case cask loading, seven weight-limited fuel canisters vented to the inner containment of the cask, the total gas/vapor volume would be 967 L and the total hydrogen-plus-oxygen gas generation rate would be 0.77 L/h. Assuming that all of the oxygen is scavenged, that the hydrogen builds up for 1 yr, and that the temperature of the cask contents is raised to 200 °F by the standard hypothetical accident, the pressure in the cask inner containment would be 119 lb/in^2 (gage) (921 kPa), which is well below its design pressure. In the unlikely event of an "extended" fire (significantly more severe than the temperature and duration of the supposed fire defined in the standard hypothetical accident), the cask contents might vent to the outer containment of the cask and then to the atmosphere. The use of a melt plug, rupture disk, or other device for limiting cask pressure in an "extended" fire is recommended.
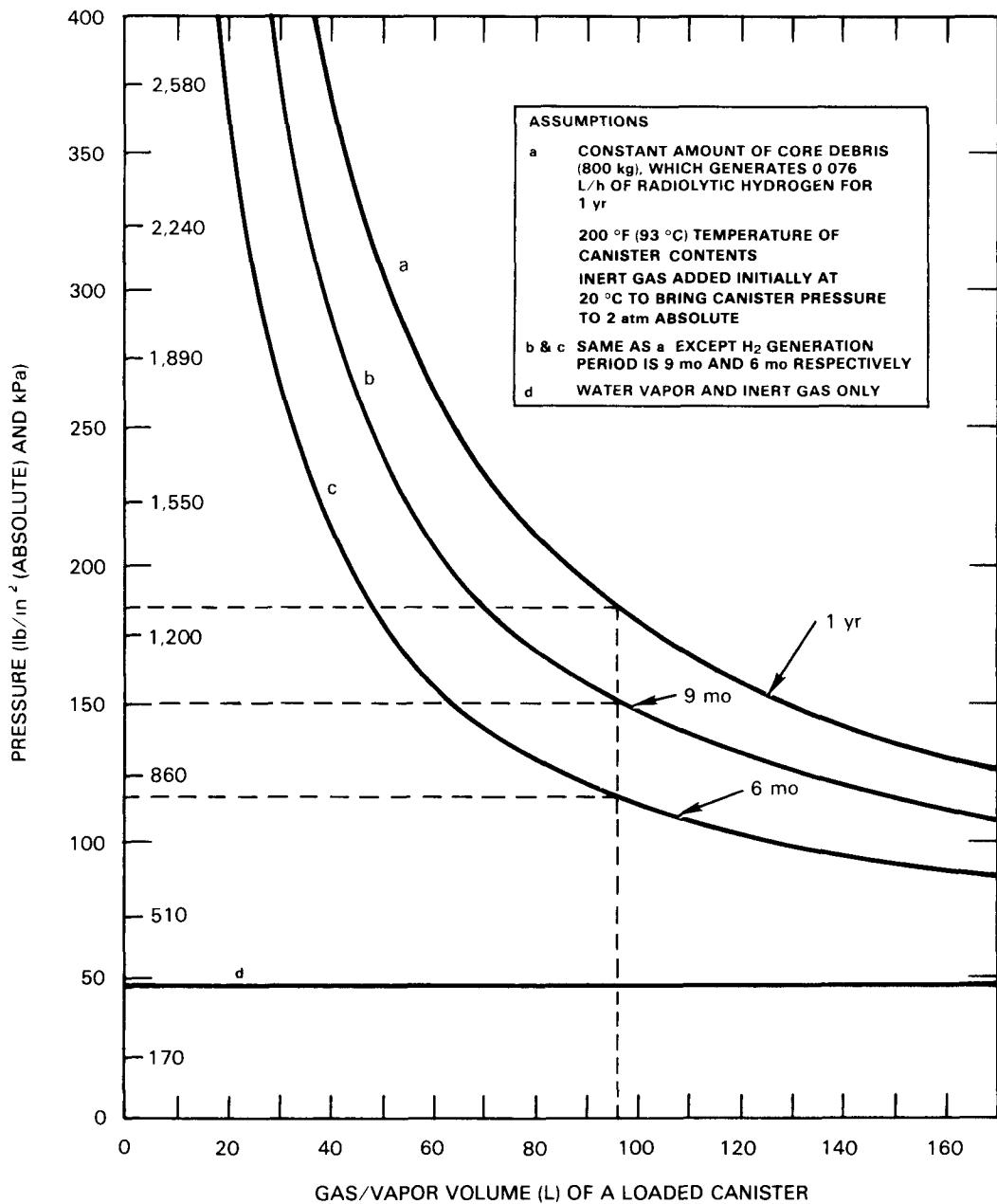
Figure 11. Canister Pressure Versus Gas/Vapor Volume.

10.0 COVER GAS

There are two reasons why having a cover gas in the canisters is more desirable than shipping the core debris under vacuum. With a cover gas, intrusion of water would be minimized while the canister is still under water. This is particularly important to ensure adequate catalytic recombination. An inert cover gas would also minimize the intrusion of air into the canisters. Air would increase any potential for a pyrophoric reaction. An inert cover gas would reduce the oxygen reaction potential to that of a metal-water reaction, which would require significant heating to initiate.

There are several desirable characteristics that a cover gas should possess for this application. The cover gas should prevent heat from being transferred quickly into the canister during a fire. One way to judge the relative ability of gases to transfer heat rapidly is to compare their thermal diffusivities. Table 2 shows the thermal diffusivities of a number of common gases. The thermal diffusivity of carbon dioxide is the lowest. The thermal diffusivities of nitrogen and argon are about an order of magnitude lower than helium.

The cover gas should allow rapid diffusion of oxygen and hydrogen toward the recombiner catalyst and water vapor away from the catalyst. Since the helium atom is smaller than that of the other gases being considered, helium would probably be best in allowing hydrogen, oxygen, and water vapor to diffuse through it. Rockwell tests have shown that oxygen diffuses through argon and nitrogen rapidly enough so that recombination is not significantly affected.

Table 2. Thermal Diffusivity
of Common Gases.

Gas	(ft^2/h)
Carbon dioxide	0.363
Nitrogen	0.780
Argon	0.706
Helium	6.15

A good cover gas can easily be contained. Helium, having the smallest and lightest molecule of the gases considered, is the most likely to escape from the canister. Argon and carbon dioxide both have molecular weights greater than air; they are, therefore, denser than air and less likely to escape. Gases can escape through metal pores (a very slow process that can be ignored), fissures, welding flaws, mechanical closures (pressure- and

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diffusion-controlled), or openings in the upper part of the vessel after the head or caps have been removed (gravity-controlled due to density differences).

The cover gas should be nonreactive with materials (gases, liquids, or solids) that the canister will contain. A literature search of zirconium pyrophoricity revealed that finely divided zirconium powder can react vigorously in both nitrogen and carbon dioxide at temperatures above 500 or 600 °C (Cooper 1984).

Finally, the cover gas should be different from air constituents so that air intrusion can be detected if for any reason chemical analyses of the cover gas must be made.

Based on the preceding reasoning, argon is recommended for the cover gas. Argon is not reactive with the core debris, is easily contained in the canister, minimizes heat transfer to the fuel debris in a fire, and is not a major constituent (0.934%) of air. Recombiner tests under 2 atm of argon indicate no significant problem with the diffusion of hydrogen and oxygen to the catalyst or the diffusion of water vapor from the catalyst.

11.0 CATALYST BED LOCATION AND DESIGN CONCEPT

Providing at least two catalyst beds in each canister allows for normal conditions of transport (horizontal and vertical canister orientations) as well as an improbable accident condition in which the canister becomes inverted for an extended period. Proper catalyst bed location prevents having both beds submerged in water at the same time.

Loading the loose catalyst pellets directly into the debris bed is not recommended since the catalyst location would be unknown, particularly during accident conditions, and could be submerged.

The concept shown in figure 12 locates small, flat catalyst beds in the upper and lower ends of each canister. This approach was selected by the canister designer.

Some cleanliness requirements will be necessary during catalyst bed fabrication. Components of this type are typically assembled under relatively clean conditions to avoid the need for extensive internal vessel cleaning after fabrication. Any cleaning solutions that will contact the catalyst must be explicitly approved in advance.

TWO 1/16-L, 3 1/2-in. (8.9-cm)-diameter
by 3/8-in. (1-cm)-THICK
CATALYST BEDS

(OR, AN EQUIVALENT SINGLE,
LARGE-DIAMETER FLAT BED)

VENT HOLES

TWO 1/16-L, 3/8-in (1-cm)-THICK
CATALYST BEDS

VERTICAL SECTION
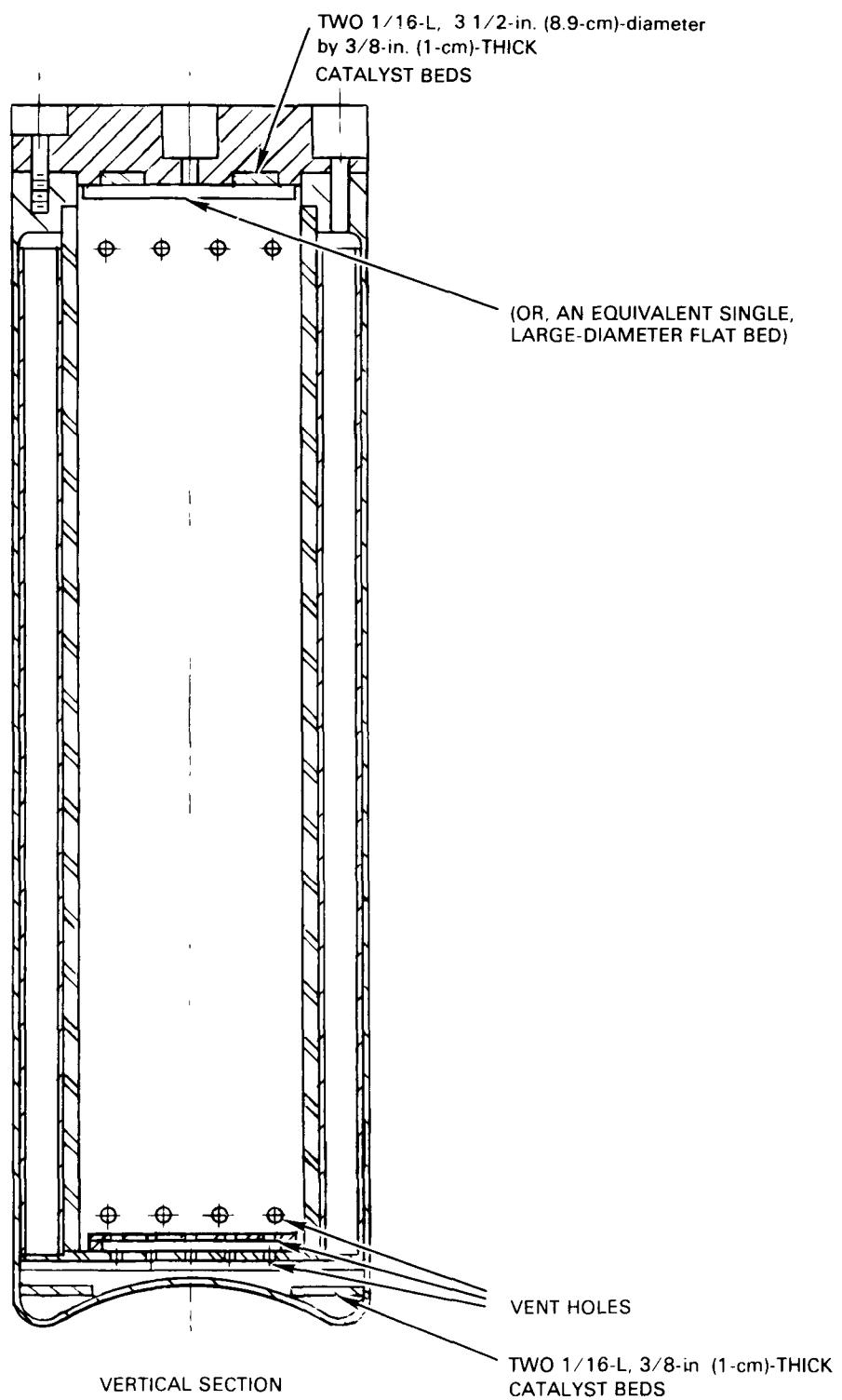
Figure 12. Canister Catalyst Bed Size and Location.

12.0 VENTING

There are three conditions for which venting has been considered. The first is to allow venting from the canister to the cask under high-pressure conditions that could prevail during the unlikely event of an "extended" fire. A rupture disk, pressure-relief valve, or simply an overpressure rupture should be acceptable since the cask as planned provides the two required levels of containment. The advantage of providing a rupture disk or pressure-relief valve is that a canister overpressure condition would be relieved slowly through a specific pathway. The advantages of not providing a pressure-relief device, which would allow a canister to rupture if its ultimate pressure is reached as a result of an "extended" fire, are as follows:

1. Pressure-relief devices would require installation on a temporary basis only and would have to be removed after shipping and prior to long-term (30-yr) storage to avoid potential corrosion and subsequent failure during the storage period. The cost and contamination risks involved during installation and removal of the devices may be significant.

2. The risk and consequential result of premature failure of the pressure-relief devices during handling and shipping would be significant.

3. When its ultimate pressure is reached, the canister failure would be in the form of a longitudinal tear in its cylindrical wall. Venting into the 15 1/4-in. (38.7-cm) outside diameter by 3/8-in. (1-cm) wall inner cask enclosure would be rapid, but would not be expected to damage the cask. Therefore, the extremely unlikely event of a canister rupture due to overpressure would be tolerated without catastrophic results.

Therefore, the addition of pressure-relief devices to the canisters is acceptable but not recommended. Apparently, the most acceptable way to prevent overpressurization is to design the cask (or cask and canisters) to withstand the standard hypothetical accident. A venting system such as rupture disks or melt plugs is recommended to prevent overpressurization of the shipping cask (both levels of containment) in the unlikely event of an "extended" hypothetical fire.

Another condition for venting considers the possibility of recombiner failure. Under this abnormal condition, oxygen and hydrogen would build up inside the canister. However, the Engelhard catalyst (80% of the mixed bed) has an excellent history of performing satisfactorily for extended periods in high radiation environments, and both catalysts tested perform satisfactorily under very wet (non-submerged) conditions. Further, a pressure check of each canister just prior to shipment will provide full assurance that the catalyst is functioning adequately. Therefore, venting during shipping should not be required and is not recommended.

A third condition considered for venting is that of long-term wet storage. Based on the assumption that oxygen scavengers may be present in the core debris, hydrogen could build up inside the canister. Since a long-term hydrogen buildup potential exists, provisions for venting are recommended during long-term storage.

13.0 RECOMMENDATIONS

Hydrogen/Oxygen Recombination

Two or more hydrogen/oxygen recombiner catalyst beds should be installed in each core debris canister during fabrication, one at the top and one at the bottom. Each bed (or an equivalent set of smaller beds) should contain a minimum of 100 g of a combination of 80% Engelhard Deoxo-D and 20% AECL silicone-coated catalyst. The beds should be located such that not more than half of the catalyst will be submerged, regardless of canister orientation, at any time after dewatering and closure.

Water Removal

Water should be removed from each canister by gas displacement (drip drying) as described in section 6, method 1. This can probably be accomplished in most instances by one or two drip-dry operations.

Debris/Water Weight and Gas/Vapor Volume in Each Canister

The loaded canister weight after dewatering and the gas/vapor volume in each canister should be measured and controlled to predetermined limits by weighing each loaded canister before and after dewatering (see appendixes B and C). For a loaded canister after dewatering, the recommended maximum weight is 2,940 lb (1,336 kg) (for up to 5% of the canisters) and the recommended minimum gas/vapor volume is half of the inside void volume of the empty canister (see appendix B).

Cover Gas

Two atmospheres (25 to 30 lb/in^2 (absolute))of argon cover gas (including water vapor) should be added to each canister after dewatering.

Catalyst Bed Operation and Monitoring Prior to Shipment

The weight of each canister should be measured just prior to shipment to detect any water intrusion. The pressure of each canister should be monitored (see appendix D) sometime prior to shipment to detect any lack of recombiner operation. If temperature and pressure changes are measured to a precision of 1.0 °C and 0.10 lb/in^2 (0.68 kPa), a 1-week observation period would be adequate. However, in that case, any net temperature-corrected pressure increase observed for a canister for the 1-week period would require an extension of the observation period for that canister (see appendix D).

Containment During the Hypothetical Accident

The shipping cask should be designed to limit the temperature of the canister contents such that the pressure in the inner containment of the cask will remain below its design pressure during the standard hypothetical accident.

Venting

Venting of the canisters during shipping is not recommended. The rupture of canisters in the cask inner containment in the unlikely event of a fire extending far beyond that defined by the standard hypothetical accident is considered to be acceptable and provides more overall safety than the addition of venting devices to each canister. Venting of the cask inner containment to the outer containment and to the atmosphere by the use of rupture disks or melt plugs in the unlikely event of an "extended" fire is recommended. Provision for venting of canisters during long-term storage is recommended.

Pyrophoricity Onsite Testing During Defueling

Some pyrophoricity testing should be conducted during defueling to assure that adequate safety-related information will be available during canister opening.

14.0 REFERENCES

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APPENDIX A

HYDROGEN GENERATION RATE CALCULATIONS

The rate at which hydrogen and oxygen will be generated in a canister of fuel debris can be only approximated by calculations since there are so many variables involved. These variables include the following:

1) The amount of fuel debris in each canister

2) The amount and type of ionizing radiation (alpha, beta, gamma, and neutron) emanating (decreasing with time) from the fuel debris

3) The amount of water in the canister (which is not well known) and its proximity to the radiation source (which changes with heat and hydrogen/oxygen generation)

4) The fraction, F, of the ionizing radiation absorbed by the water (which is a function of the first three variables and the geometry and position of the canister)

5) The net number of molecules of gas generated, G, per unit amount of ionizing radiation absorbed (100 eV). The G value varies with the type of radiation and with the extent to which back-reactions occur to produce water. The extent of back-reactions is a complex function of the amount and type of impurities and dissolved hydrogen present.

Therefore, it is practical to attempt to calculate only probable-maximum generation rates (see section 3). On this basis, the following estimates appear to be appropriate:

1) Ionizing radiation per canister
    containing 800 kg of core debris
    (8.6 kW total (see fig. A-1)
    x 800 kg/127,000 kg)   54.2 W

2) Fraction, F, of the gamma and beta energy
    absorbed in water (Turner 1968)   0.2

3) Hydrogen gas generation value, G, in
    molecules of H_2 per 100 eV absorbed
    (Turner 1968)   0.44

4) Ratio of the peak energy from the fuel
    debris in a canister to the energy in
    the same quantity of average debris
    (peak-to-average).   1.9

A-1
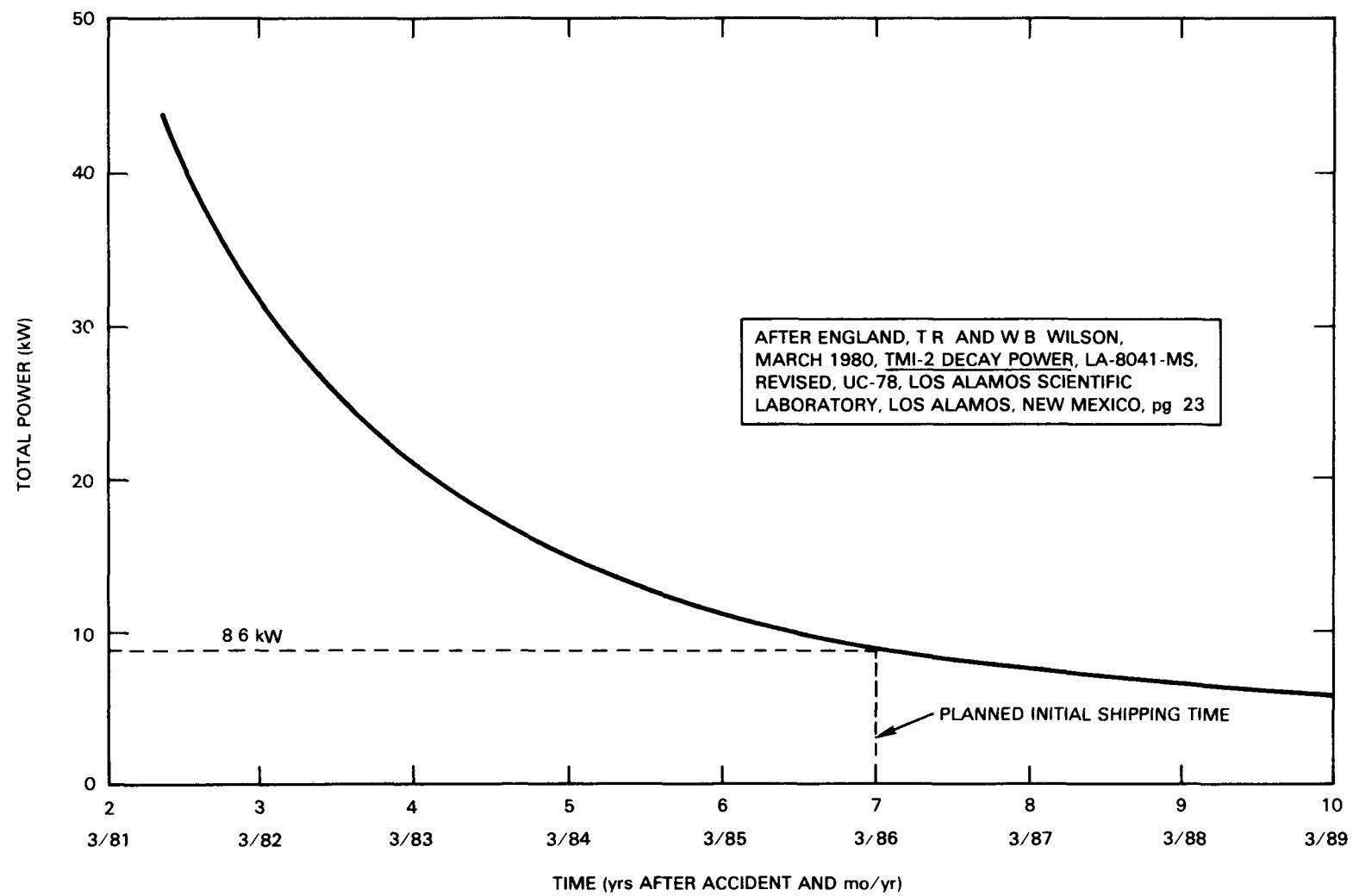
Figure A-1. Three Mile Island Unit 2 Reactor Core Power Decay Curve.

On this basis, the probable-maximum hydrogen generation rate is as follows:

$$54.2 \text{ W} \times 1.9 \times 0.2 \times \frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ W-s}} \times \frac{0.44 \text{ molecules}}{100 \text{ eV}} \times$$

$$\frac{22.4 \text{ L}}{6 \times 10^{23} \text{ molecules}} \times \frac{3600 \text{ s}}{h} = .076 \text{ L/h}$$

Therefore, the probable-maximum oxygen generation rate is 0.038 L/h, and the total probable-maximum gas generation rate is 0.11 L/h.

It is of interest to note that using calculational methods identical to those described herein, a gas generation rate of 0.83 L/h was calculated for a highly loaded TMI-2 submerged demineralizer system vessel. Values of 0.5 and 0.44 for F and G respectively were used. The zeolite particles are not as fine as the core debris expected in the filter canisters, but they are less dense and more porous. The resulting calculated gas generation rate was later confirmed by measurement (Quinn et al. 1984).

APPENDIX B

CANISTER LOADING CHARACTERISTICS

Table B-1. Canister-Loading Characteristics for the
Weight- and Volume-Limited Condition.

	Units	Canister type			
		Fuel		Filter	Knockout
1. Maximum loaded weight, dewatered[a]	lbs	2,940	2,800	2,800	2,800
2. Empty canister:					
Weight in air[b]	lbs	1,230	1,230	1,440	1,046
Displacement[b]	lbs	806	806	816	816
Weight in water[b]	lbs	424	424	624	230
3. Inside free volume, empty[b]	ft^3	6.75	6.75	9.94	10.73
	L	191	191	281	304
4. Maximum wet debris weight (W_t)	lbs	1,710	1,570	1,360	1,754
	kg	777	714	618	797
5. Minimum gas/vapor volume after dewatering[c]	L	96	96	141	152
6. Maximum wet debris volume (V_t)[c]	L	96	96	141	152
7. Maximum debris volume (V_d)[d]	L	92	84	64	87
8. Maximum water volume (V_w) at maximum debris volume[d]	L	4	12	77	65
9. Maximum debris weight (4-8)	kg	773	702	541	732
10. Water volume/debris volume (8/7)	%	4	14	120	75

[a]Up to 5% of the loaded, dewatered canisters may weigh 2,940 lb. All other canisters are limited to 2,800 lb. Characteristics at higher limits are shown only for the fuel canisters because they are the most restrictive. The limits were set by Idaho National Engineering Laboratory based on storage facility floor-loading limits.

[b]From Jacks (1984)(the Babcock and Wilcox design report). Actual weights and volumes are to be measured and corrected for possible error bands to assure conservatism under actual conditions.

[c]To positively assure that at least 50% (100 g) of the catalyst in each canister is not submerged at any one time after dewatering, at least 50% of the inside free volume of each canister should be void of water and debris.

[d]Simultaneous solution of two equations:

$$W_t = \rho_d V_d + 1 V_w; \quad V_t = V_d + V_w$$

$$V_w = \frac{\rho_d V_t - W_t}{\rho_d - 1}$$

where ρ_d = density of debris. The average density of the debris in the entire core is calculated to be 8.4 (see Henrie 1983 and appendix C).

APPENDIX C

CALCULATED VAPOR, WATER, AND DEBRIS VOLUMES AND WEIGHTS AND THEIR SENSITIVITY TO ERRORS IN DEBRIS DENSITY ESTIMATES

- Known, measured data.

  W_c = Weight of empty canister, in air

  V_{c_1} = Internal free volume of empty canister

  V_{c_e} = External volume of canister (displacement)

  W_b = Buoyant weight of loaded canister before dewatering

  W_a = Buoyant weight of loaded canister after dewatering

- Calculation of weight and volume of loaded canister contents from known data.

  Let V_d = Volume of debris W_d = Weight of debris

  V_w = Volume of water W_w = Weight of water

  V_t = $V_d + V_w$ = Volume of wet debris W_t = $W_d + W_w$

  V_v = Volume of vapor/gas W_t = $(W_a + \rho_w V_{c_e}) - W_c$

  V_v = $\dfrac{W_b - W_a}{\rho_w}$ ρ_w = W_w/V_w = Density of water

  V_t = $V_{c_1} - V_v$ ρ_d = W_d/V_d = Density of debris

● Calculation of weight and volume of water and debris in a loaded canister as functions of known data and estimated debris density.

Let α = Water volume ratio = V_w/V_t

1) W_d = $W_t - W_w = W_t - \rho_w V_w = \underline{\underline{W_t - \rho_w \alpha V_t}}$

2) V_d = $V_t - V_w$

$\dfrac{W_d}{\rho_d}$ = $V_t - \alpha V_t$ $\qquad\qquad W_d = \underline{\underline{\rho_d (V_t - \alpha V_t)}}$

combining 1) and 2) by equating

3) $W_t - \rho_w \alpha V_t = \rho_d (V_t - \alpha V_t)$ $\qquad\qquad \alpha = \underline{\underline{\dfrac{\rho_d V_t - W_t}{V_t (\rho_d - \rho_w)}}}$

Therefore, from known, measured data, and any estimated ρ_d, α can be determined. Then, $V_w = \alpha V_t$ and $W_d = W_t - \rho_w V_w$.

- Tabulation of various characteristics for a measured V_t and W_t, with various estimates of ρ_d.

  As a typical example, assume the following:

  $W_t = 830$ kg, and $\qquad\qquad V_t = 125$ L

  Then for ρ_d between 8.0 and 9.0:

ρ_d	α	V_w (L)	W_d (kg)	Decrease in W_d	
				kg	%
8.0	.194	24.3	805.7	0.0	0.00
8.1	.206	25.7	804.3	1.4	0.17
8.2	.217	27.1	802.9	2.8	0.35
8.3	.227	28.4	801.6	4.1	0.51
8.4	.238	29.7	800.3	5.4	0.67
8.5	.248	31.0	799.0	6.7	0.83
8.6	.258	32.2	797.8	7.9	0.98
8.7	.268	33.4	796.6	9.1	1.13
8.8	.277	34.6	795.4	10.3	1.28
8.9	.286	35.8	794.2	11.5	1.43
9.0	.295	36.9	793.1	12.6	1.56

Conclusion: Assuming no weight or volume measurement errors, a 10% increase in actual ρ_d over estimated ρ_d would result in an increase of 10 kg of water and a decrease of 10 kg (1.3%) of debris from that calculated.

APPENDIX D

MINIMUM OBSERVATION PERIODS OF CANISTER TEMPERATURES AND PRESSURES PRIOR TO SHIPMENT

- Lowest recommended initial wet argon pressure: 25 lb/in^2 absolute.

- Highest flammable gas concentration allowable in twice the shipping time (88 days): 5% hydrogen plus 5% oxygen = 10%.

- Maximum allowable temperature-corrected pressure starting at 25 lb/in^2 absolute: $25 \div 0.9 = 27.8$ lb/in^2 absolute.

- Maximum allowable pressure rise in 88 days: $27.8 - 25 = 2.8$ lb/in^2.

- Gas volume loss resulting from an undetected, underwater leak rate of one 4 mm-dia. bubble (or eight 2 mm-dia. bubbles, etc.) every 5 min: $4/3 \pi (2)^3 \div 5$ min x conversion factor = 67.5 cc/wk.

- Maximum gas pressure loss due to undetected leak: 67.5 cc/wk $\div$ 96,000 cc x 25 lb/in^2 absolute = 0.02 lb/in^2.

- Maximum allowable pressure rise in 1 wk: $2.8 \times 7/88 - 0.02 = 0.20$ lb/in^2.

- Pressure change resulting from a 1 °C temperature rise: $25 \times 294 \div 293 - 25 = 0.09$ lb/in^2.

Table D-1. Maximum Allowable Temperature-Corrected Pressure Rise for Various Measurement Precisions and Observation Periods.

Measurement precision (error)		Observation period			
ΔT (°C)	ΔP (lb/in^2)	1 wk (lb/in^2)	2 wk (lb/in^2)	3 wk (lb/in^2)	4 wk (lb/in^2)
0	0	0.20	0.40	0.60	0.80
0.1	0.01	0.18	0.38	0.58	0.78
0.5	0.05	0.10	0.30	0.50	0.70
1.0	0.10	0.01	0.21	0.41	0.61
1.0	0.20	--	0.11	0.31	0.51
2.0	0.20	--	0.02	0.22	0.42
1.0	0.50	--	--	0.01	0.21