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CATALYST TESTS FOR HYDROGEN CONTROL IN CANISTERS OF WET RADIOACTIVE WASTES

J.O. Henrie
B.D. Bullough
D.J. Flesher
Rockwell Hanford Operations

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EG&G Idaho, Inc.
Idaho Falls, Idaho 83415

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ABSTRACT

Catalyst beds are used in the Three Mile Island Unit-2 (TMI-2) core debris canisters to recombine radiolytic hydrogen and oxygen and prevent the buildup of flammable mixtures. This document describes a unique test system for determining the effectiveness of catalyst beds in chemically combining hydrogen and oxygen gases in closed containers and without forced convection. The test system was used to determine the effects of catalyst type, catalyst bed size and shape, cover gas type and pressure, and various additives and contaminants on catalyst performance.

The test program demonstrated that a mixture of specific Engelhard and Atomic Energy of Canada Limited (AECL) catalysts performed better than either catalyst performed separately. When the Engelhard catalyst is dry and well-exposed to the reactive gases, its effectiveness is a factor of approximately 100 greater than when it is dripping wet. The AECL wet-proof catalyst is not as effective as the Engelhard catalyst, but it is not as sensitive to the presence of water. The various additives and contaminants to which the catalyst might be exposed during its life cycle had little effect on catalyst performance; contaminants appear to be effectively removed by the rinsing processes which occur.

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NOMENCLATURE

AECL	Atomic Energy of Canada Limited
atm	atmosphere
°C	degree Celsius
°F	degree Fahrenheit
DOE	U.S. Department of Energy
g	gram
h	hour
in^2	square inch
kg	kilogram
kPa	kilopascal
L/h	standard liters per hour (0 °C, 1 atm)
lb/in^2	pounds per square inch
LICON	light concrete
M	molar
p/m	parts per million
RCS	Reactor Cooling System
TMI-2	Three Mile Island Unit-2
yr	year

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1.0 PURPOSE AND OBJECTIVES

The catalyst test program was conducted under the direction of the U.S. Department of Energy (DOE) to provide a substantive basis for the design of passive catalyst beds in containers of wet radioactive materials. The objective was to select the catalyst types, quantities, arrangements, and environments that would reliably prevent the buildup of flammable mixtures of radiolytic hydrogen and oxygen gases in the Three Mile Island Unit-2 (TMI-2) core debris canisters under normal, offnormal, and accident conditions.

2.0 SUMMARY AND CONCLUSIONS

The test system developed for this program has proven to be ideal for accurately determining the effectiveness of various catalyst types and bed arrangements. An electrolysis (electrodialysis) method was used to generate hydrogen/oxygen gas (in the stoichiometric ratio) at rates which can be accurately determined by measuring and controlling the electric current supplied to the generator. These gases were injected into a test vessel and recombined into water by the catalyst bed being tested in the vessel. The net buildup of hydrogen/oxygen gas in the vessel was determined by very accurate continuous temperature and pressure monitoring, and occasionally verified by chemical analysis. The bed effectiveness is directly proportional to the hydrogen/oxygen gas injection rate and inversely proportional to the equilibrium hydrogen/oxygen gas concentration.

The Engelhard-D catalyst is very active when warm and dry and well-exposed to the active gases. Its effectivity decreases by a factor of approximately 100 when dripping wet, and further decreases to almost zero when submerged. The Atomic Energy of Canada Limited (AECL) silicone-coated catalyst is not as effective as the Engelhard-D catalyst, but it is not as adversely effected by water. A mixture of 20% AECL silicone-coated catalyst and 80% Engelhard-D catalyst performs considerably better than either of the two catalysts alone. Also, since their resistance to various additives and contaminants is different, the mixed catalyst bed was selected and thoroughly tested.

During the fabrication, filling, testing, and storage life cycle of the core debris canisters, the catalyst is exposed to a number of contaminants and additives. These materials have the potential of decreasing catalyst effectiveness by (1) temporarily filling the catalyst sites on a molecular basis, (2) coating the catalyst (like paint) to decrease diffusion of the reactive gases and water vapor to and from the catalyst sites, and (3) chemically reacting with the catalyst materials. The effects of essentially all of the contaminants and additives appeared to be in the first two categories. In each case, they were water-soluble and were readily diluted and removed from the catalyst by rinsing and soaking methods similar to those which would occur in core debris canister filling, dewatering, and storing. The net effect of these potential poisons was therefore less than had been anticipated. However, the effect of hot nitric acid was to chemically attack the catalyst material and separate it from its alumina substrate. This effect is not recoverable, and therefore precludes the use of hot nitric acid in contact with the catalyst.

The final tests included one catalyst bed that had been removed from a fabricated canister, and another bed which had been exposed to contaminants and additives potentially encountered during canister fabrication, filling, testing, and storing. Both of these catalyst beds show a remaining effectiveness factor (for 100 g of catalyst) of 1.0 L/h. For a core debris canister containing 800 kg of core debris, this represents a catalyst bed factor of safety of 9.

Toward the end of the testing program, a new wet-proof (hydrophobic) platinum-on-silica catalyst fabricated by AECL was tested and found to be more effective than the AECL silicone-coated catalyst used in the TMI-2 core debris canisters. Its use in a 50-50 mixture with Engelhard-D catalyst is recommended for future hydrogen control applications.

All of the objectives of this catalyst bed effectiveness testing program were met. The testing program has provided a better and more quantitative understanding of passive catalyst bed performance, particularly under wet conditions, and has resulted in a safe and reliable method of controlling hydrogen in canisters of wet radioactive waste.

3.0 TEST METHOD

Catalyst performance was determined by monitoring temperature-corrected pressure changes in a closed system as the hydrogen and oxygen gases were injected in a 2-to-1 ratio. Concentrations of added gases are proportional to the change in pressure and, therefore, can be accurately calculated. Test apparatus and procedures are discussed in the following sections.

3.1 PHYSICAL DESCRIPTION OF THE TEST SYSTEM

The major items of equipment used in the catalyst performance test system include a hydrogen-oxygen gas generator (operating on the principle of electrodialysis) and a small pressure vessel that models the upper end of the TMI-2 core debris canisters. The test vessel has a volume of approximately 16.8 L and was pressure tested at 500 lb/in^2 (3,435 kPa). Incorporated in the vessel are two thermocouples for measuring the gas and catalyst temperatures, a gas inlet nozzle, and a manifold with pressure relief, gas sampling, and pressure sensing capabilities.

An overall schematic diagram of the test system is shown in figure 3-1.

3.2 GENERAL TEST PROCEDURE

After installing the desired type, amount, and configuration of catalyst into the test vessel, testing proceeded in the following manner:

- The vessel was sealed and purged with argon to displace atmospheric oxygen (and other components of air) and the argon pressure was increased to approximately 2 atm absolute.
- After allowing the pressure and temperature to stabilize, a stoichiometric mixture of hydrogen and oxygen was continuously metered into the test vessel. Generally, a flow rate equivalent to 0.2 L/h of hydrogen and 0.1 L/h of oxygen at standard (0 °C, 1 atm) conditions was used.
- The temperature and pressure of the gas in the vessel and the temperature of the catalyst were monitored and continuously recorded. Changes in temperature and pressure as low as 0.1 °C and 0.01 lb/in^2 (0.07 kPa) could be monitored.
- Normally, testing was judged to be complete when the temperature-corrected pressure began to drop, or at least stabilize, or the pressure exceeded a nominal value of 33.8 lb/in^2* absolute (232 kPa).

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*Represents gas concentration limits of approximately 5% oxygen and 10% hydrogen.

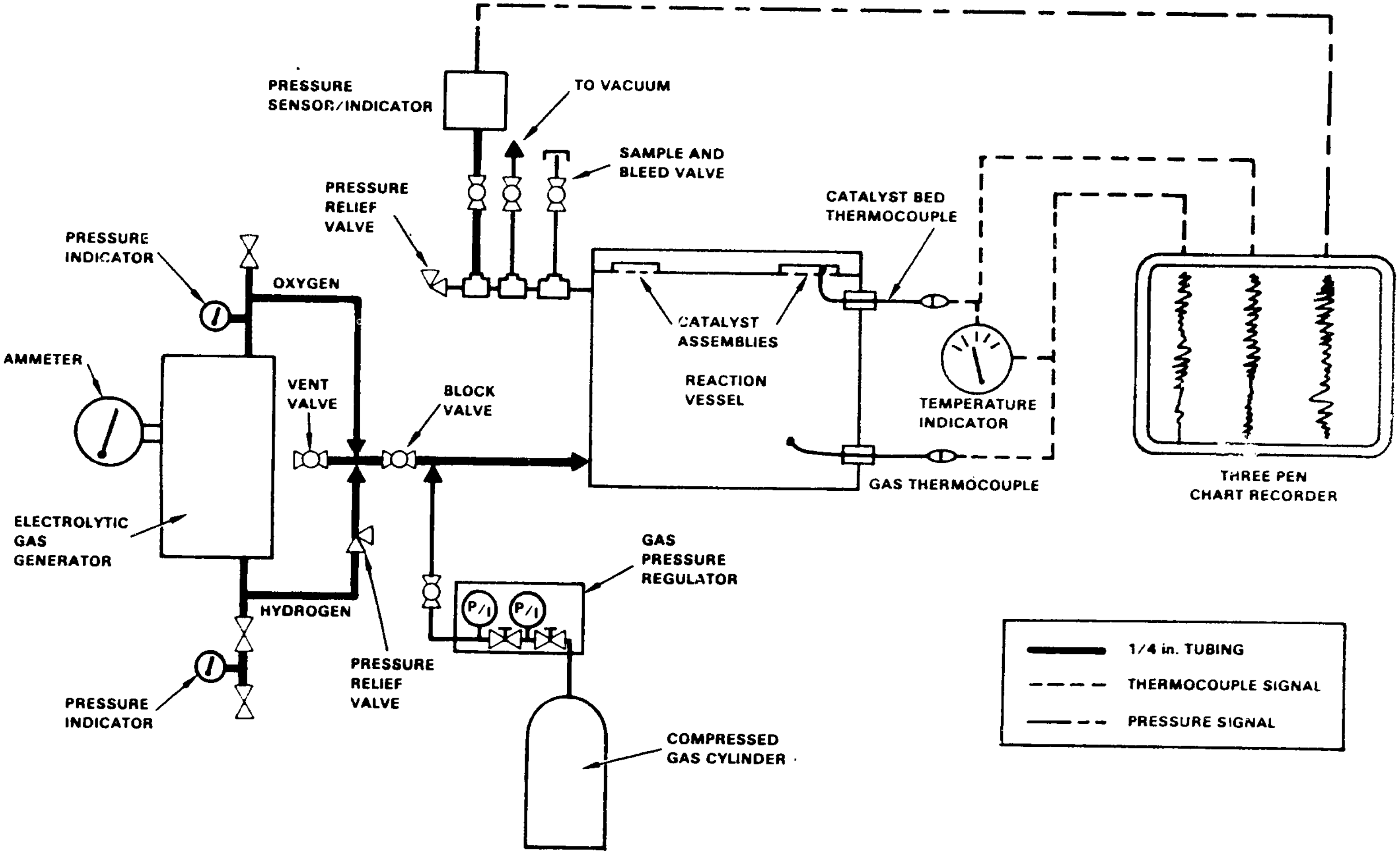

Figure 3-1. Test System Schematic.

- The hydrogen-oxygen gas generator was turned off and valved out. Monitoring continued, usually until the temperature and pressure stabilized at or near original conditions.

A determination of catalyst performance (under the particular pretreatment and test conditions) was made based on the rate of recombination and the percentage of oxygen (or hydrogen) present in the test vessel. When the test parameters have stabilized (with the generator on), the gas recombination rate is equal to the measured gas-injection rate. The oxygen concentration can be calculated using simplified methods based on the ideal gas equation:

1. The corrected pressure (P_2) is determined for any time of interest by compensating for temperature changes (in gas and water vapor) from the original pressure (P_1) conditions.

2. The net added-gas fraction is equal to $(P_2 - P_1)/P_2$.

3. Assuming that stoichiometric conditions are maintained, the oxygen gas fraction is one-third of the net added-gas fraction.

The accuracy of this mathematical calculation of oxygen levels was periodically verified by analyzing gas samples taken at the end of selected tests.

4.0 TEST RESULTS

4.1 OVERVIEW

A method of displaying test results for direct comparison with regulatory requirements (limits) was needed. The regulations, as reported in Henrie et al. (1986a,b, Appendix A), require that either the hydrogen concentration or the oxygen concentration be maintained below 5 vol%. The TMI-2 core debris canisters are inerted with argon after filling, and since radiolysis of water produces hydrogen at twice the rate it produces oxygen, controlling to the oxygen limit is appropriate. Therefore, the test results are presented as graphic displays of oxygen concentration (vol%) versus time, for any specific, constant, hydrogen-oxygen-gas-injection rate. Typically, each successful test is continued until a stable condition is reached, i.e., when the gas recombination rate is equal to the gas generation rate. The time required for the system to stabilize, and the general shape of the curve before and after the hydrogen-oxygen gas source has been shut off, are also useful for test interpretation. Therefore, the display of oxygen concentration versus time appears to be ideal.

A catalyst bed effectiveness factor has been established to provide a simplified numerical comparison for the various catalyst bed sizes, arrangements, and effects of additives and contaminants. The effectiveness factor is defined as the hydrogen-oxygen gas recombination rate (in standard liters per hour) that will be produced by 100 g of a selected catalyst under specific conditions when the oxygen concentration in the gas mixture is normalized to the 5% regulatory limit. Therefore, for a stable hydrogen-oxygen recombination rate of 0.3 L/h, the effectiveness factor for a 100-g catalyst bed would be 1.0 L/h if the steady state oxygen concentration was 1.5 vol%.*

The effectiveness factor can be readily converted to a factor of safety by simply dividing the effectiveness factor by the measured or conservatively calculated hydrogen-oxygen gas generation rate in a closed container of wet radioactive waste. If the resulting factor of safety is judged to be too low, it can be increased linearly by increasing the size of the catalyst bed. Conversely, if the factor of safety is judged to be too high, the bed size could be proportionally decreased.

Design scoping tests (1 through 105) were conducted in 1984 to determine the effects of variations in catalyst design configuration (bed shape and size), type, condition (physical and radiation damage), wetness (deionized water and simulated reactor cooling system water), hydrogen-oxygen gas injection rate, cover gas type, and gas pressure. A conservative design for the catalyst beds for the core debris canisters was based on the results of those tests. In this design, the catalyst is located in two recesses in the underside of the upper head. Each recess is 3.50 in. (8.9 cm) in dia. and 0.375 in. (1.0 cm) deep. Each recess is covered by an 8-mesh stainless steel screen (eight 0.035-in. (.89-mm) dia. stainless steel

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*0.3 L/h x 5 vol% / 1.5 vol% = 1.0 L/h effectiveness factor.

wires per inch in each direction). Test no. 98 and all subsequent tests used this recessed, screened-bottom configuration shown in figure 4-1. The use of a catalyst mixture of 80 g of Engelhard D catalyst and 20 g of AECL silicone-coated catalyst (Henrie et al. 1986a) in this recessed configuration constitutes the final design basis for the TMI-2 core debris canisters. Test no. 106 and subsequent tests were conducted to measure any negative effects of various potential additives, contaminants, and other environmental changes on the performance of the mixed-bed catalyst in the TMI-2 core debris canisters (Henrie and Appel 1985).

A general index of the tests is shown in table 4-1. Test results as they relate to specific catalyst bed parameters and performance of the final catalyst bed design are discussed in sections 4.2 through 4.9.

4.2 CATALYST BED WETTING/DRYING

A key factor in the operation of a catalyst bed is the effect of water on recombination rates. The catalyst bed operates best when dry and does not function when submerged. Submerging the catalyst in water or any liquid cuts off the diffusion of reaction gases to the catalyst, essentially stopping all recombination. Conversely, some catalysts are very effective when dry; tests indicate that 1 g of dry Engelhard Deoxo-D catalyst would maintain safe levels of hydrogen and oxygen in a TMI-2 core debris canister. Between these extremes is a range of wetness conditions that can greatly alter catalyst effectiveness.

To determine the effects of catalyst wetting, the catalysts were tested in the ambient-air-dry condition and in a "dripping-wet" condition. The effectiveness factor of a 100 g bed of air-dry Engelhard-D catalyst was found to be approximately 10. As the bed size was reduced, the effectiveness factor increased, as shown in table 4-2. The smaller beds were more effective for the following reasons:

1. The catalyst pellets in the smaller beds were more effectively exposed to the reactive gases than in the larger beds.

2. The recombination rates were the same (0.3 L/h) and the exothermic energy release heated the smaller beds to higher temperatures.

3. Even though the beds were initially ambient-air-dry, the smaller beds became dryer because of higher temperatures.

A qualitative evaluation indicates that Reason no. 3 is much more significant than Reasons no. 1 or no. 2 in increasing effectiveness factors. The removal of small amounts of water at the near-saturated end of the wetness spectrum also significantly increased the effectiveness factor. When water was added to the bottom of the test vessel and vacuum pumping was minimized during process of replacing the air in the vessel with argon, essentially no drying occurred, and the effectiveness factor was the same as when the air was replaced by purging with 10 volumes of argon. However, when no water was added to the bottom of the test vessel and/or when the

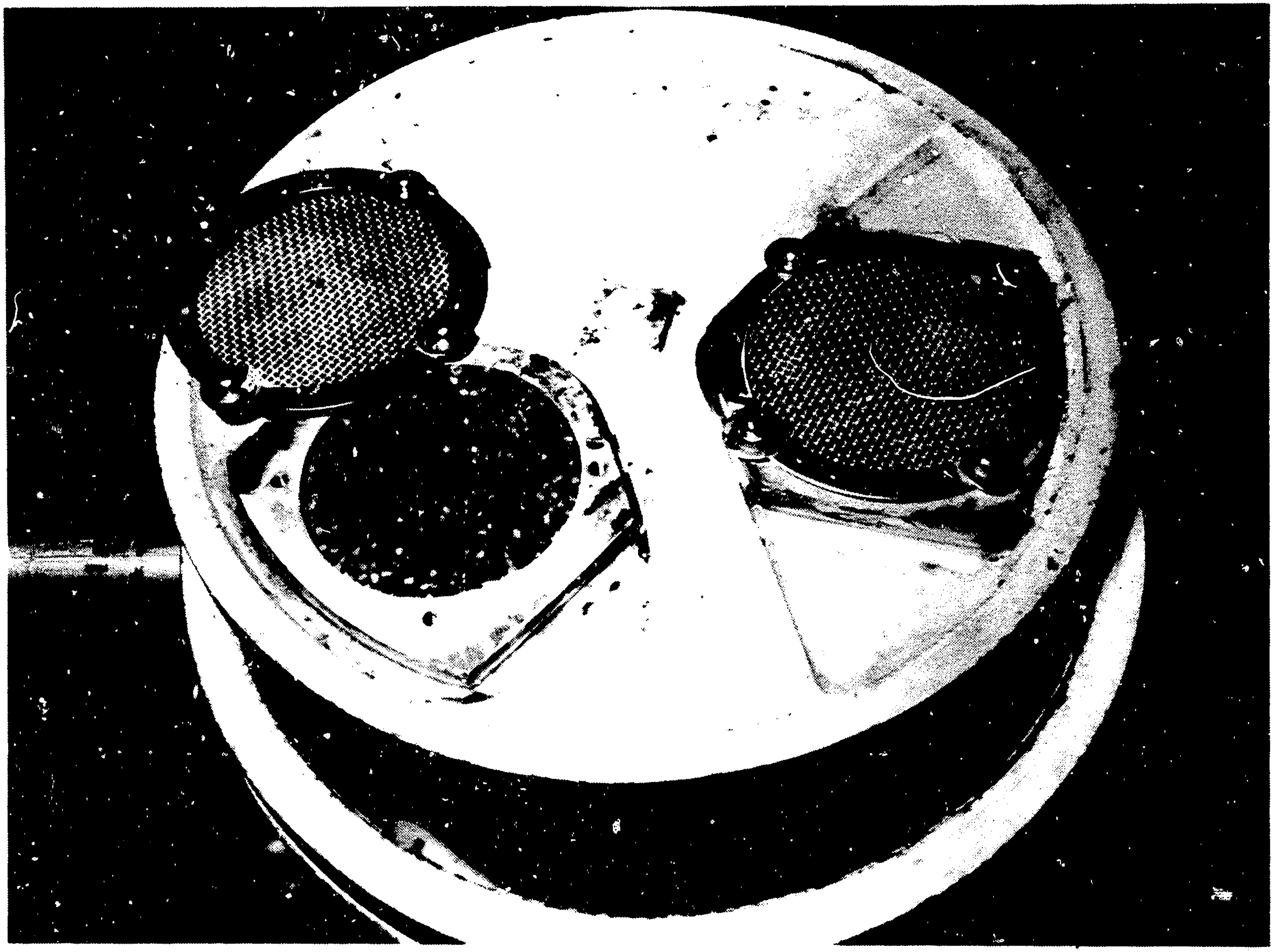

Figure 4-1. Final Catalyst Bed Design as Incorporated into the Upper Head of the Test Vessel.

Table 4-1. General Index and Chronology of Catalyst Bed Test.

FY[a] 1984 Development Testing	Test number
Catalyst bed type, size, and shape; radiation and physical damage; deionized and simulated Reactor Cooling System water; gas injection rate; and cover gas type and pressure.	1-105
FY 1985 Compatibility Tests	
Freezing Conditions.	106-107
Hydraulic fluids -	
UCON, Houghto-Safe, Borate Ester, and Borate Ester/UCON Mixtures.	108-115 117-119
LICON[b] cement slurry.	116
New AECL catalyst.	120-121
Okite 59 cutting fluid.	122-123
FY 1986 Compatibility Tests	
Boric acid.	124
Dye penetrants -	
Magnaflux and Uresco.	125-127
Microbiocides -	
Biosperse 250 and nitric acid.	128-129
Hydrogen peroxide.	130,133,135,136, 138-142
Methanol.	131
Sodium cyanide.	132
Sodium azide.	134
Potential poisons combined.	137
FY 1987 Compatibility Tests	
Quintolubric 807-SN hydraulic fluid.	143,144,146
Betz 1192 coagulant.	145
Betz 1182 coagulant and potential poison combinations.	147-161

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[a] FY-fiscal year.

[b] LICON-light concrete.

Table 4-2. Effects of Catalyst Wetness, Openness, and Bed Size.

Catalyst	Wetness	Bed configuration	Effectiveness factor[a]
● Engelhard	Dry[b]	Open[c], small (4.5 g)	120
● "	"	" " (10 g)	90
● "	"	" " (45 g)	20
● "	"	" (100 g)	10
● AECL	"	" " (10 g)	8
● "	"	" (100 g)	2.5
● Mixed[d]	Wet[e]	" "	1.5
● "	"	Cavity[f] "	1.2
● Engelhard	"	Open "	1.1
● Engelhard	"	Cavity "	1.0
● AECL	"	Open "	0.3
● "	"	Cavity "	0.3

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[a] Effectiveness factor--recombination rate in L/h, per 100 g of catalyst, and normalized to 5% oxygen.

[b] Ambient air dry.

[c] A screened enclosure that allows water vapor to move up and away from the catalyst.

[d] A mixture of 80% Engelhard Deoxo-D catalyst and 20% AECL silicone-coated catalyst.

[e] Dripping wet with water.

[f] Catalyst in a machined recess in the underneath side of the upper head of the canister or test vessel, which prevents the upward escape of water vapor.

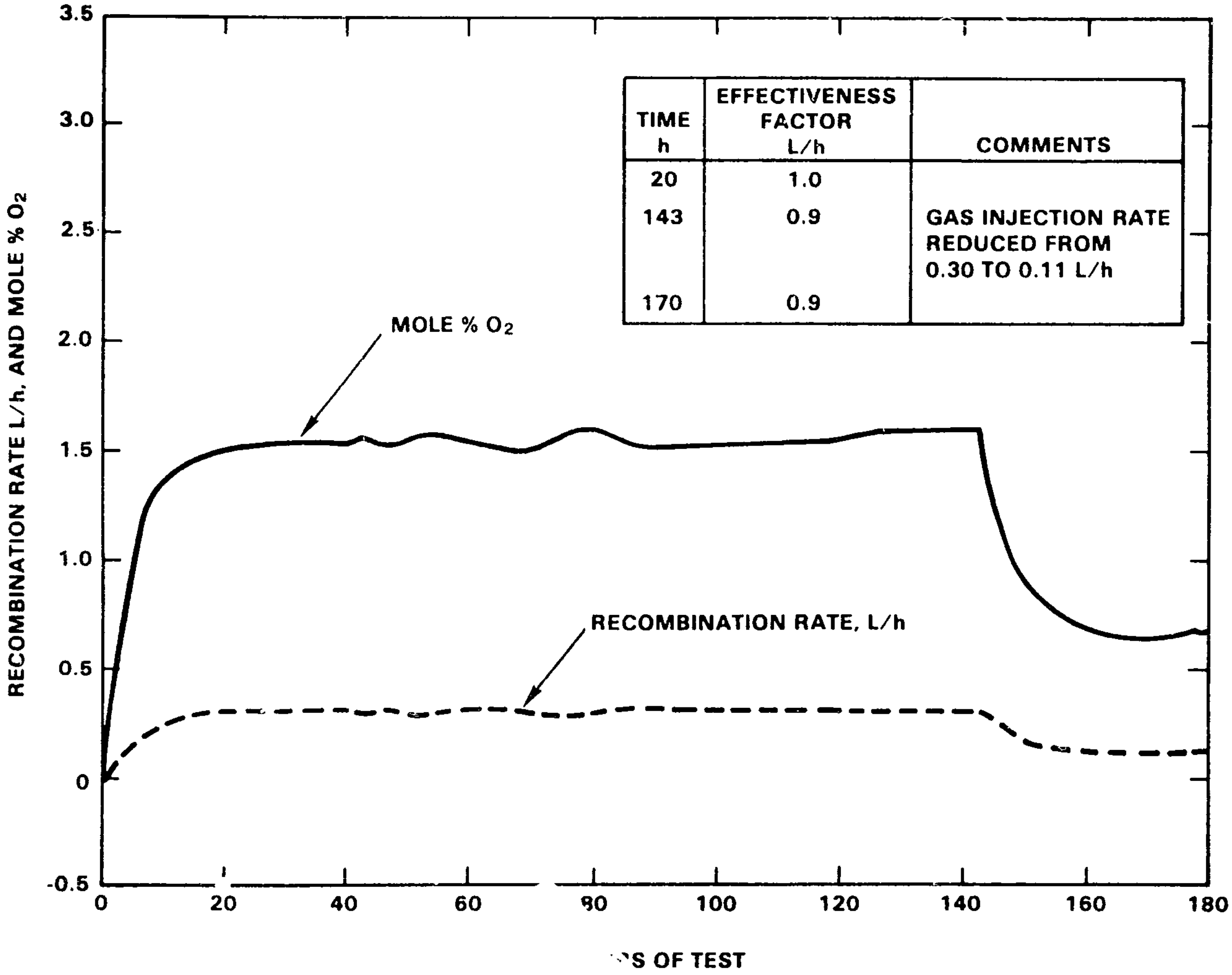
vacuum pumping significantly decreased the catalyst temperature (due to evaporative cooling), the catalyst was partially dried (even though it still had a very wet, glossy appearance) and catalyst performance increased. The effectiveness factor for the final design configuration would increase in some cases from a base-case value of 1.2 to as much as 2.5.

Other indications of the effect of moisture on various catalyst beds were observed in extended-duration tests. When the bed design was relatively open and water vapor could readily diffuse from the bed, catalyst effectiveness was observed to improve with time. However, in the final design, in which the catalyst was located in recesses in the upper head, performance did not improve with time. This condition was caused by the trapping of water vapor, which is much lighter than argon, moving upward in the cavity and condensing there rather than being swept away by convective currents. To test this hypothesis, the test vessel was rotated from its vertical position to a horizontal position during test no. 152. Test results are shown in figures 4-2a and 4-2b. Immediately after rotating the test vessel, the effectiveness factor improved from 0.9, where it had been for almost 200 h, to 1.8 in the next 20 h, and 2.8 in the following 60 h. This improvement was due entirely to the catalyst drying effect allowed by the movement of water vapor up and away from the rotated catalyst bed, where it would then condense on colder surfaces. A similar effect was noted during test no. 157, when one of the catalyst beds dislodged and dropped from the upper head to the bottom of the test vessel. This allowed the water vapor to diffuse up and away from the catalyst and improved catalyst performance by a factor of 2 within five hours.

The AECL silicone-coated catalyst recovered from wetting much faster than the Engelhard-D catalyst; however, the overall recombination rate of the AECL catalyst was relatively low, even when dry. A possible synergism between the AECL silicone-coated and Engelhard-D catalysts was proposed, tested, and demonstrated. Test results presented in figure 4-3 show that the mixed catalyst bed base-case design significantly outperforms either of the two catalysts alone. The synergistic mechanism has not been proven, but the following is proposed: As the wetted, drained catalysts are initially exposed to reaction gases, recombination occurs primarily on the AECL silicone-coated catalyst. At conjunctive points between adjacent AECL and Engelhard pellets, the exothermic reaction on the AECL pellet begins to warm the Engelhard pellet. The reaction promotes rapid, localized drying of a small portion of the Engelhard pellets, which further accelerates the reaction. As noted previously, the effectiveness of the dry Engelhard catalyst is very high; therefore, drying only a small fraction of the Engelhard catalyst greatly improves the overall effectiveness of the bed.

4.3 CATALYST BED GEOMETRY

Several catalyst bed geometries (shapes and volumes) were used in the early screening tests to determine the best configuration. Tests with beds of varying thickness indicated that thin beds were considerably more effective. Diffusion is the primary gas dynamic in this passive system.



TIME h	EFFECTIVENESS FACTOR L/h	COMMENTS
20	1.0	
143	0.9	GAS INJECTION RATE REDUCED FROM 0.30 TO 0.11 L/h
170	0.9	

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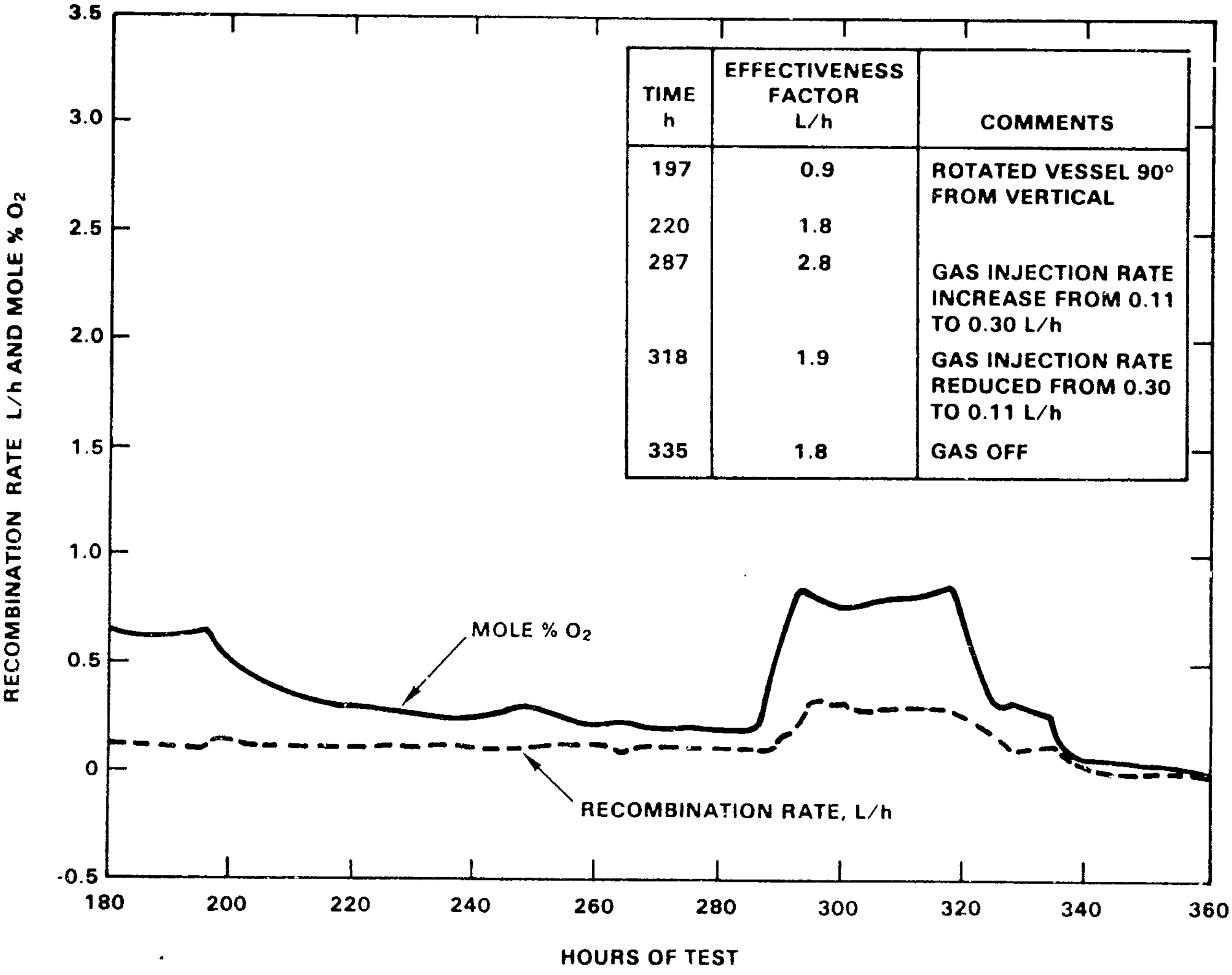
Figure 4-2a. Test No. 152 Showing Effect of Trapped Water Vapor and Extended Operating Period.



TIME h	EFFECTIVENESS FACTOR L/h	COMMENTS
197	0.9	ROTATED VESSEL 90° FROM VERTICAL
220	1.8	
287	2.8	GAS INJECTION RATE INCREASE FROM 0.11 TO 0.30 L/h
318	1.9	GAS INJECTION RATE REDUCED FROM 0.30 TO 0.11 L/h
335	1.8	GAS OFF

2PS8706-5

Figure 4-2b. Test No. 152 Continued, Showing the Effect of Rotating the Test Vessel to Allow Water Vapor to Escape from the Catalyst Bed.

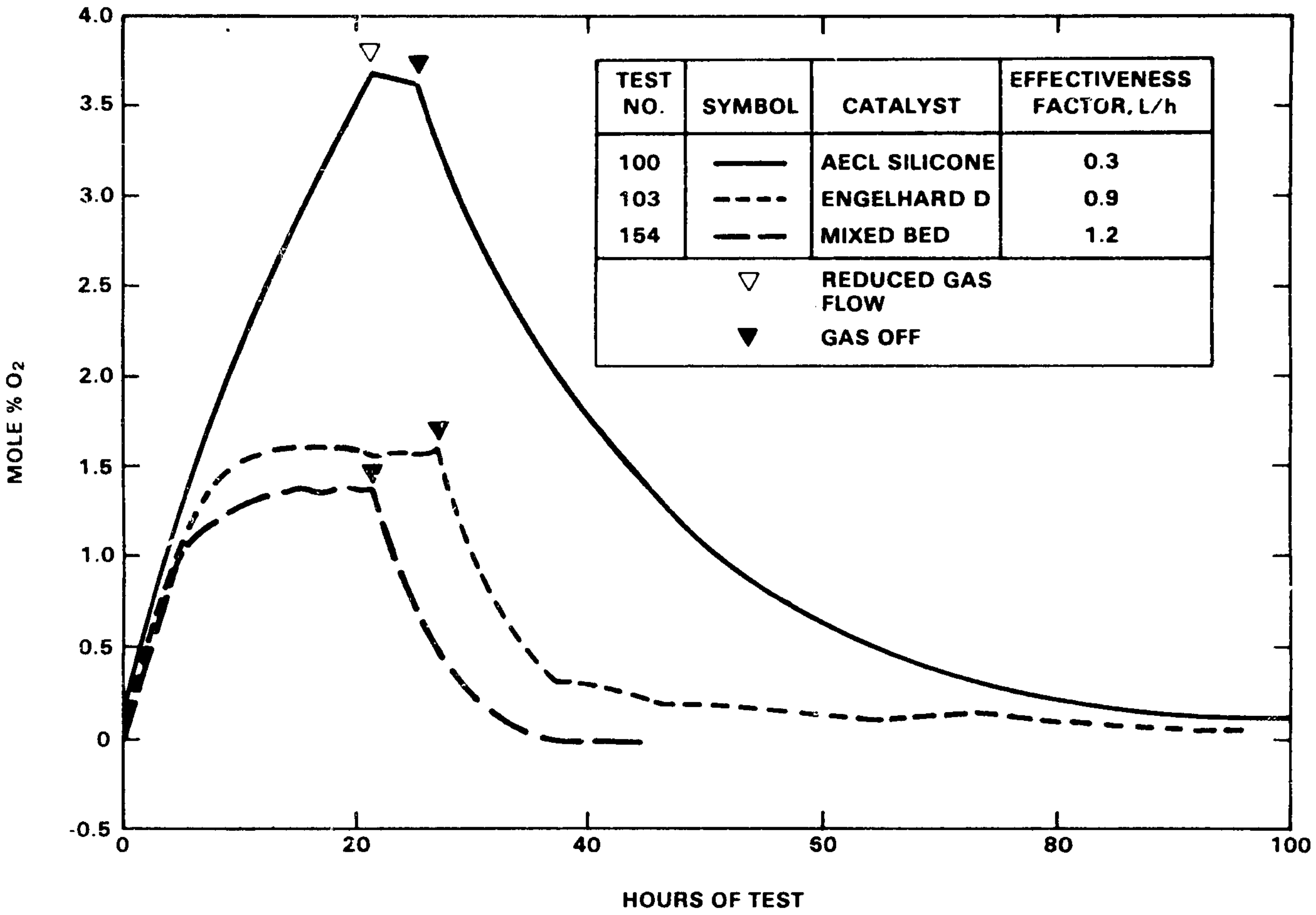


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Figure 4-3. Catalyst Effectiveness Comparison in the Final Design Configuration.

The tests included flat and cylindrical beds ranging from 3/8- to 1-in. thick and containing quantities of catalyst up to 1,000 g. The first layers of catalyst pellets effectively removed a very high fraction of the reactant gases, and subsequent layers had little net effect. The most effective arrangement of the catalyst would be a single layer, to maximize the area available for gas diffusion. A minimum bed thickness of 3/8 in. (1.0 cm) was selected, which allows up to three layers of the 1/8-in. (0.32-cm) cylindrical Engelhard pellets, but only one full layer of the 1/4-in. (0.64-cm) dia. AECL pellets.

Final canister design and fabrication considerations resulted in three slightly different catalyst bed arrangements. The most restrictive of these consists of 3/8-in. (1.0-cm) deep circular recesses machined into the underneath side of the upper head of some of the canisters (knockout and filter). The required 100 g of catalyst was retained in these recesses by stainless steel screens that covered the recesses. This same design (see fig. 4-1) was built into the test vessel and catalyst test no. 98 and all subsequent tests used this design arrangement. The catalyst bed in the upper head of the fuel canisters has 40% more open area and contains more catalyst than the upper heads of the other canisters. The catalyst bed arrangement in the lower head of all canisters is identical, has the same open area and volume as the recessed upper head design, but is better vented and therefore more effective.

4.4 CATALYST TYPES AND MIXTURES

It was initially determined that at least two types of catalyst should be tested for use in the TMI-2 core debris canisters. The catalyst with the longest successful history in highly radioactive environments was believed to be Engelhard Deoxo Type 18467, a palladium-on-alumina catalyst, previously designated as Engelhard Deoxo-D, Nuclear-Grade A16430. A platinum-on-alumina catalyst manufactured by Houdrey was also successfully tested; however, since this catalyst has a less-stable substrate, and has not been as extensively used in nuclear applications as the Engelhard Deoxo Type 18467, it was not fully evaluated.

The second catalyst type to be tested was a wet-proof, silicone-coated, platinum-on-alumina catalyst manufactured by AECL. Two other AECL wet-proof catalysts received limited testing. One catalyst was Teflon-coated and was found to perform as well as or better than the silicone-coated catalyst. The Teflon-coated catalyst was not fully evaluated because of the potential for coating instability and the release of corrosive gases from the radiolytic decomposition of the Teflon. A new AECL wet-proof (hydrophobic) platinum-on-silica catalyst also received limited testing and proved highly successful; however, this product was not used in the TMI-2 core debris canisters because it had not been developed by AECL when the silicone-coated catalyst was procured.

A mixture of 80% Engelhard Deoxo-D catalyst and 20% AECL silicone-coated catalyst was also thoroughly tested. As shown in table 4-2, this mixture proved to be considerably more effective under wet conditions than either the Engelhard Deoxo-D or the AECL silicone-coated catalyst alone.

Another advantage of using mixed-catalyst types is that they are likely to respond differently to various contaminants and additives which they might contact during various fabrication and operational phases of their life cycle. For these reasons, the 80-20 catalyst mixture was recommended and used.

4.5 CATALYST BED SIZE

As indicated in section 4.2, some catalysts were found to be effective in very small quantities; 1 g of dry Engelhard Deoxo-D catalyst is capable of safely recombining the hydrogen produced in a TMI-2 core debris canister.

Larger bed sizes are desirable for two primary safety reasons: (1) a dry catalyst cannot be ensured in wet environments. A small quantity of wet catalyst could allow the buildup of flammable gas mixtures, and as the catalyst dried, it could become an ignition source; (2) a factor of safety must be provided to allow for potential performance reduction caused by catalyst poisoning. To meet regulatory requirements and ensure fully safe conditions, a catalyst bed must be provided which is large enough to exceed design requirements even when wet and after exposure to the degrading (poisoning) effects of contaminants and additives. Since potential poisoning effects may not be fully evaluated at the time during the design phase when the catalyst bed size must be established, it may be necessary to provide a factor of safety of 10 or more. As shown in figure 4-3 (test no. 154) and in table 4-2, 100 g of mixed catalyst in the upper-head-cavity configuration has an effectiveness factor of 1.2 L/h, which is 11 times higher than the established design requirement of 0.11 L/h (Henrie and Appel 1985) for the TMI-2 core debris canisters. Therefore, for that application, the catalyst bed design has a factor of safety of 11 in its dripping wet but otherwise uncontaminated condition.

4.6 CATALYST BED LOCATIONS

As noted in section 4.2, catalysts are ineffective when submerged in liquid because of the restriction of gas diffusion. If the vessel contains free liquid, some method must be provided to ensure that at least one catalyst bed is always exposed to the gas in the container. The installation and appropriate location of two beds in a container will usually provide full assurance that at least one bed is exposed to the gas at all times. Therefore, full capacity catalyst beds were located in both ends of the TMI-2 core debris canisters.

4.7 CATALYST BED TEMPERATURES AND PRESSURES

Temperatures ranged from approximately -10 °C to 30 °C in the testing program. Pressures ranged from a partial vacuum to 2-atm absolute.

Recombination rates are not greatly affected by temperatures in the range of 0 °C to 30 °C. However, temperature differences that cause catalyst drying do result in significantly improved catalyst performance.

The effect of below-freezing temperatures is significant. The formation of water from the recombination of hydrogen and oxygen causes snow-like ice crystals to form on the catalyst. This buildup results in an increased resistance to the diffusion of reactive gases to the catalyst and, therefore, the recombination process becomes less effective with time. The test program did not fully quantify these effects, but it did provide assurance that the catalyst in TMI-2 core debris canisters would function within design limits for a few weeks after freezing.

At temperatures above a few hundred degrees Celsius, catalytic reaction rates become very high for the Engelhard catalyst. These high temperatures would damage the silicone-coated AECL catalyst and would likely decrease its effectiveness.

Consistent with diffusion theory, the tests indicate that pressure changes have no significant effect on recombination rates. The presence of gases such as nitrogen or argon tend to impede the diffusion of hydrogen and oxygen to the catalyst. However, if the hydrogen and oxygen fractions in the gas mixture are held constant as the total pressure increases, the increased numbers of hydrogen and oxygen molecules exactly offset the impedance effect and diffusion remains constant. The principle advantages of the addition of an inert diluent and the resulting higher pressure are (1) more hydrogen and oxygen can be stored before flammable limits are reached, and (2) the intrusion of the water or air surrounding the container can be prevented.

4.8 CATALYST DAMAGE

Catalyst pellets can sustain damage from both physical handling and a limited number of chemical environments. Tests performed to quantify the effects of these types of damage are discussed in the following sections.

4.8.1 Physical Damage

Both types of catalyst pellets are composed primarily of a porous alumina structure or substrate, which is subject to some chipping or other breakage during normal handling. This breakage does not affect the ability of the catalyst material to recombine the hydrogen and oxygen gases, therefore, no reduction in recombination efficiency would be observed. A test was run to determine any effects on the wetting resistance of the AECL catalyst when the wet-proof coating is removed from a small area of each catalyst pellet. No reduction in recombiner effectiveness was detected after notching an entire bed (100 g) of catalyst and submerging it in water, under 2 atm of pressure, for 24 h.

4.8.2 Chemical Damage

Chemical damage can occur in at least two different ways: chemical attack can remove the wet-proof coating from the AECL catalyst, or remove the catalytically active compounds from the pellet. These mechanisms caused the catalyst failure in one test. A mixed bed of catalyst (80% Deoxo-D, 20% AECL) was contacted with a 14% nitric acid solution at 150 °F (66 °C) for one hour, drained, and rinsed with deionized water prior to the test. After being immersed in the hot acid solution, the gray metallic coating of the Engelhard catalyst was removed (clean white pellets remained), and the coating of the AECL catalyst was softened and easily scraped from the hard substrate. As shown in figure 4-4, the recombination rate was very low, and the resulting effectiveness factor was 0.1 L/h.

4.9 CATALYST POISONING

The mixed-bed catalyst was subjected to a matrix of chemicals and compounds to evaluate the effects, if any, on catalyst performance. This list of potential poisons was composed of substances the catalyst might encounter during the processes of fabricating and loading the fuel canisters. Poisoning can be caused by the following:

- Chemical reaction with the catalytic material or the coating
- Sorption to reaction sites on the catalyst surface (molecular bonding and blocking)
- A physical barrier restricting or blocking diffusion of gases and/or water vapor to and from the catalyst.

A considerable reduction in catalyst performance is caused by coating the pellets with water (see section 4.2), although the use of mixed-bed catalyst minimizes the effect of wetting. No further reduction in performance was noted when the catalyst was wetted in simulated Reactor Cooling System (RCS) water instead of deionized water. Other chemicals and materials had varying effects on catalyst performance.

4.9.1 Cutting Fluids

Soaking the catalyst for 1 1/2 h in a 4% emulsion of Okite Formula 59 cutting oil in water had little effect (relative to RCS). After immersing the catalyst in the emulsion for 72 h, catalyst performance may have been reduced slightly.

4.9.2 Dye Penetrants

As a result of canister weld inspections, residual dye penetrants, penetrant developers, and cleaners may contact the catalyst material. Two systems, Uresco and Magnaflux, were evaluated for the effects on catalyst performance. After lightly applying the penetrant, then the developer, the catalyst beds were thoroughly wetted with water and tested. The Uresco system had no detectable effect on recombination rate. Catalyst effectiveness was reduced up to 30% by application of the Magnaflux system, but this material may have been applied too heavily, biasing test results.

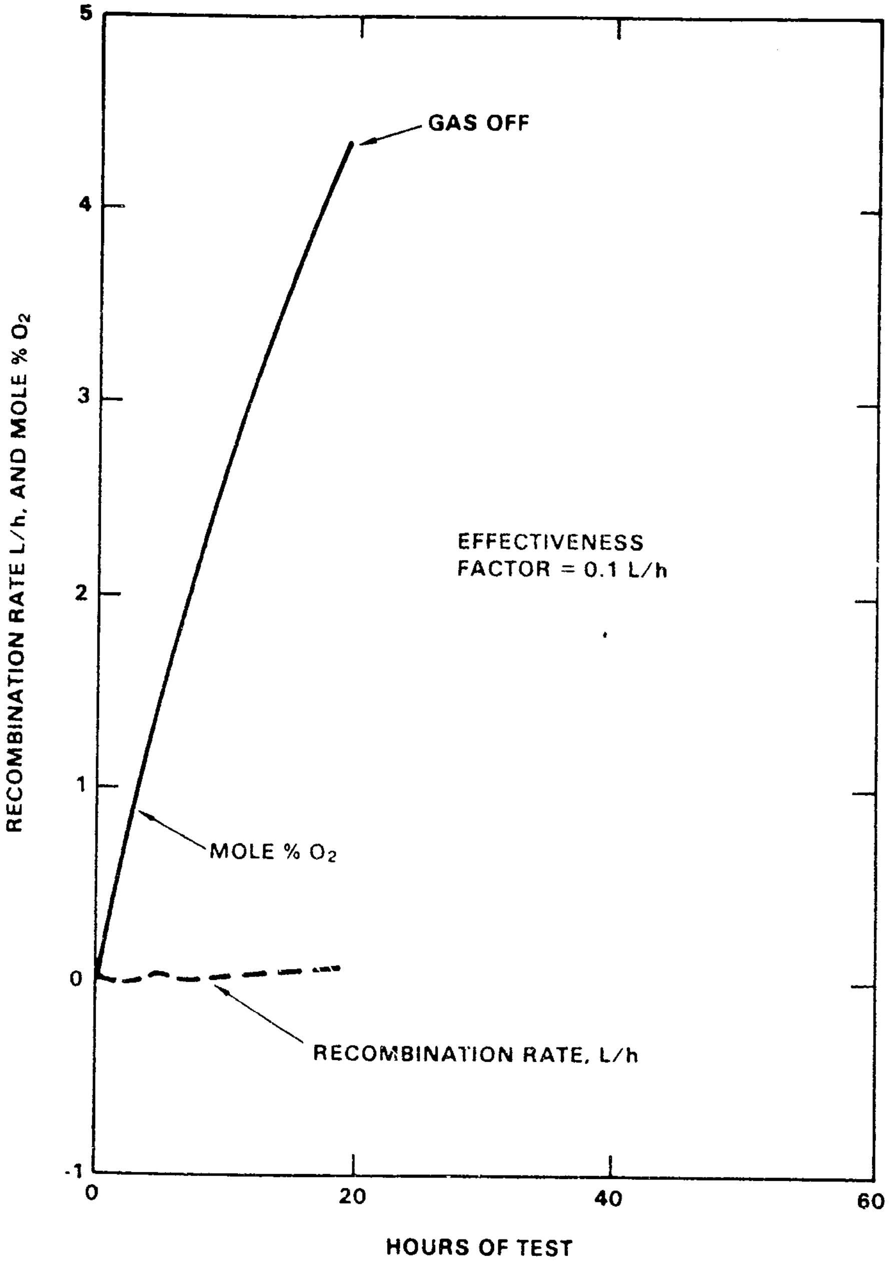

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Figure 4-4. Effect of 14% Nitric Acid Solution at 150 °F (66 °C) for One Hour on Catalyst Bed Effectiveness.

4.9.3 LICON Cement

Light concrete (LICON) is used as a support medium in some of the debris canisters. The material has low solubility in the RCS, but small amounts of the solid could erode from the structure. The resulting light slurry could then coat the catalyst or otherwise affect catalyst operation. A thick slurry was applied to the catalyst bed before testing, providing a physical barrier to diffusion to the catalyst, resulting in somewhat reduced recombination rates. After testing, the slurry easily rinsed away and would, therefore, have no significant effect on the catalyst.

4.9.4 Carbon Monoxide

Carbon monoxide gas, which can result from radiolytic degradation of organic materials, has a temporary effect on the catalyst. Each of the three catalyst types was tested independently under otherwise ideal conditions for catalytic recombination (dry, fresh catalyst). Testing proceeded as follows:

- Fresh, dry catalyst was installed in the test assembly and gas was injected into the reactor
- When recombination was well established, carbon monoxide gas was added to a concentration of 0.92%
- Conditions were monitored as in a normal test.

The uncoated catalysts apparently recovered from the effects of carbon monoxide addition within about 4 h, with a maximum oxygen concentration level of about 0.7%. The AECL catalyst suffered more long-term effects: after about 6 h, the catalyst was only beginning to recover, and oxygen level had reached 2.4%.

4.9.5 Hydraulic Fluids

Several candidate hydraulic fluids (glycol complexes) were identified for potential use in core debris removal operations and were evaluated for the effects on the performance of recombiner catalysts. Three solutions were used in the testing, in both 100% and 2% concentrations:

- 1:3 mixture of Borate Ester in UCON-WS-34
- Borated UCON-WS-34
- Houghto-Safe-620.

No significant change was evident in catalyst performance characteristics after thoroughly wetting in 2% fluid concentrations. Each of the concentrated solutions, however, had dramatic negative effects on the catalyst, with effectiveness factors dropping to between 0.26 and 0.33 L/h.

Since these solutions are highly water-soluble, they would be rinsed in the normal canister-filling processes and result in no significant effect on catalyst performance.

An additional series of qualitative tests was run to evaluate the effects, if any, of the catalysts on the hydraulic fluids. No evidence was obtained that the fluids were being decomposed to their basic components (water, hydrogen, carbon dioxide, or light gaseous organics).

4.9.6 Boric Acid Solutions

A solution of boric acid saturated in water at room temperature (nominally 20 °C) reduced catalyst performance by a factor of approximately 2. The catalyst was submerged in the concentrated solution (approximately 3.3M) for about 90 h prior to installing, dripping wet, in the test apparatus. Reactor coolant solution has a boric acid concentration of approximately 5,000 p/m, or 0.27M, which had no measurable effect on catalyst performance.

4.9.7 Microbiocides

Most closed-water systems are plagued with microbial activity, and some system of control must be used to prevent buildup of organic material and fouling of various equipment in the system (filters, heat exchangers, etc.) The TMI-2 cleanup operation is no exception. Filters used in the cleanup operation began to clog with these materials as microbial activity developed in the RCS water. The high radioactive doses present did little to control this activity. Bacterial control agents, microbiocides, would be required.

During February through April 1986, a series of tests were run to check the effect of these agents on catalyst efficiency. The biocides tested included Biosperse 250, hydrogen peroxide, methanol, sodium cyanide, and sodium azide. These biocides caused only minor poisoning effects. A 1,000 p/m solution of Biosperse 250 caused the most significant poisoning; the resulting effectiveness factor was 0.5 L/h. However, since this material was not used at TMI-2, washing/rinsing methods to test recovery were not pursued. The tests using methanol, sodium cyanide, and sodium azide did not conclusively indicate significant poisoning. The effects of hydrogen peroxide on catalyst performance were difficult to establish since the catalyst decomposes hydrogen peroxide and releases oxygen. After performing 10 tests, it was conclusively determined that all observed hydrogen peroxide effects on catalyst performance were temporary.

4.9.8 Coagulants

Coagulants are used to assist in the removal of very fine particulates from the RCS water and the water in the spent fuel storage basins. To ensure that these coagulants would have no significant adverse effects on catalyst performance, two candidate coagulants, Betz 1192 and Betz 1182 were tested. The tests showed that the dilute solution of Betz 1192 had no measurable effect on catalyst performance. However, after the catalyst had been immersed in a 50 p/m solution of Betz 1182, catalyst performance decreased by approximately 20% to an effectiveness factor of 1.0.

4.9.9 All Poisons Combined and Base Cases

The first all-poisons test to be conducted was test no. 137. The catalyst was subjected (by GPU Nuclear Corporation) to the contaminants additives and microorganisms in the order in which they might be encountered during fabrication and operation. The poisoning reduced the catalyst effectiveness factor to 0.7, resulting in a margin of safety of 6 for core debris canisters.

The same catalyst used in test no. 137 was immersed in a solution of Betz 1192 coagulant and again tested. In this test, the effectiveness factor was 0.8. The improvement is attributed to the rinsing effect of the dilute coagulant in removing contaminants from the catalyst.

A new base case was established in test no. 150. For this test, the air in the test vessel was replaced by purging with 10 volumes of argon, without vacuum pumping. The effectiveness factor was 1.25.

The effectiveness of catalysts that had gone through the actual manufacturing process, then removed from the upper head of the canister (canister no. 130), was established in test no. 152. After extended operation, the effectiveness factor was 0.9, as shown in figure 4-2a.

A final set of base-case and all-poisons tests was conducted near the end of the testing program. The results are shown in table 4-3. For these tests, the treated catalysts were shipped from TMI-2 to the Hanford Site in 1/2-L bottles filled with simulated RCS water. The relatively low poisoning effect and high effectiveness factors are attributed to the rinsing effect of the simulated RCS water in removing the poisons from the catalyst.

The results indicate that after the poisoning and rinsing processes which are expected to occur in the life cycle of the catalyst in TMI-2 core debris canisters, the remaining catalyst factor of safety will be 9 (1.0/0.11 = 9).

Table 4-3. Effect of Mixed Contaminants and Additives on Catalyst Bed Performance.

Test run	Catalyst designation	Catalyst treatment	Effectiveness factor
154	Blank	RCS water	1.2
160[a]	Blank	RCS water	1.1
155C	A	Contaminants plus 50 p/m coagulant	1.2
156	B	A[b]	1.1
158	C	Contaminants plus 10% coagulant	1.0
161	D	C[b]	1.0

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[a] The air in the test vessel was replaced by a 10-volume purge (170 L) with argon (no vacuum pumping).

[b] Same as the indicated treatment with contaminants and Betz no. 1182 coagulant, except that a pretreatment with hot boric acid and a post-treatment with hydrogen peroxide were also included.

5.0 OTHER APPLICATIONS

One of the best ways to control hydrogen in containers of radioactive wastes is to remove essentially all water and organic materials from the container. However, removal of the water from the TMI-2 core debris canisters was judged to be impractical (Henrie and Appel 1985). Removal of the water and organic materials from a wide variety of other containers of radioactive materials also appears to be impractical, and the addition of catalysts and vents has proven to be effective (Henrie et al. 1986a).

This area of potential use includes several categories of nuclear waste from a variety of sources. Any radioactive material that is used or stored in the presence of water or other hydrogenous materials (such as organics) is subject to radiolysis and potential hydrogen gas buildup. Thus, any of the following could be considered as potential applications:

- Transuranic wastes
- Nuclear laboratory or hospital wastes
- Decontamination and laundry wastes including:
  - Cleaning solutions
  - Solvents
  - Wiping cloths, papers, etc.

While the use of catalyst beds may seem an exotic solution to radiolysis, simple catalyst systems have been proven effective. Small quantities of catalyst have proven to be effective for control of gases in storage drums at the Hanford Site. Thousands of these units have been used effectively over the past 10 yr at minimum cost.

One recent application of catalyst beds for hydrogen control is in the disposal by land burial of U.S. Navy submarine reactor compartments. To accommodate these burials without venting or drying, a 50/50 mixture of Engelhard D catalyst and an improved platinum on a silica base, wet-proof catalyst was used (Henrie et al. 1986b). This improved catalyst was tested under the program reported in this document, but the development came too late for use in the TMI-2 core debris canisters.

Another improvement that materialized as a result of this catalyst testing program is the catalytic vent (DOE patent applied for), which consists of a catalyst bed with porous metal filters at each end to prevent the escape of particles, but to allow gases to flow/diffuse to and through the catalyst. When installed in a port in a container of wet radioactive waste, the catalytic vent offers the following advantages:

- Venting of the container to prevent overpressure or underpressure
- High-quality filtration of gases to prevent particulate escape

- Control of radiolysis products produced within the vessel
- Prevention of excess hydrogen (resulting from radiolysis and oxygen scavenging) loss by reaction with external (ambient air) oxygen.

This device permits the storage of vessels or waste containers within a building or other confined area without the problem of either container overpressure, or hydrogen buildup within the container or within the facility.

6.0 REFERENCES

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