

45/0431

CONF-9606116 --18

DRYING TESTS CONDUCTED ON THREE MILE ISLAND FUEL CANISTERS CONTAINING SIMULATED DEBRIS

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APR 17 1996

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A. Joseph Palmer
Lockheed Martin Idaho Technologies
P.O. Box 1625
Idaho Falls, ID 83415-3765
(208)526-8700

ABSTRACT

Drying tests were conducted on Three Mile Island Unit 2 (TMI-2) fuel canisters filled with simulated core debris. During these tests, canisters were dried by heating externally with a heating blanket while simultaneously purging the canisters' interior with hot, dry nitrogen. The canister drying characteristics were found to be dominated by the moisture retention properties of a concrete filler material called LICON used for geometry control. The presence of this material extends the drying process 10 days or more beyond what would be required were it not there. The LICON resides in a nonpurgeable chamber separate from the core debris, and because of this configuration, dew point measurements on the exhaust stream do not provide a good indication of the dew point in the canisters. If the canisters are not dried, but rather just dewatered, 140-240 lb of water (not including the LICON water of hydration) will remain in each canister, approximately 50-110 lb of which is pore water in the LICON and the remainder unbound water.

I. INTRODUCTION

As a consequence of the TMI-2 loss of coolant accident in March 1979, an extensive cleanup action was conducted, during which the damaged core was loaded into stainless steel canisters and transported to the Department of Energy's (DOE) Idaho National Engineering Laboratory (INEL) from July 1986 through April 1990. These canisters are currently stored fully flooded in the Test Area North (TAN) 607 fuel storage pool. The DOE has elected to remove these canisters and place them in dry storage.

The cleanup operations utilized three types of storage canisters: fuel, knockout, and filter. The fuel canisters make up approximately 80% of the 343-canister inventory and were the focus of the drying tests

summarized in this paper. The TMI-2 fuel canisters are 14 inches in diameter by 150 inches tall and incorporate a 9-inch-square internal fuel basket held in position by a special low density concrete called LICON.

In 1989, a study was undertaken to determine the most practical approach for drying the storage canisters. External heating coupled with gas purging and heat-assisted vacuum drying were identified as the most promising options. A short series of tests conducted on a small mockup canister indicated that vacuum drying offered no decrease in drying time over heating and purging. It was recognized that a vacuum drying system would be more complicated than a purging system because of the large amount of contaminated water to be handled by a pump, and so heat-assisted purging was selected as the preferred alternative.

The proposed storage facility is configured such that the canisters are not required to be completely dry. Preliminary analyses have shown that this facility can accommodate even fully flooded canisters; however, by drying the canisters prior to storage, hydrogen generation due to radiolysis will be minimized, and facility costs may be reduced. To help determine an appropriate degree of dryness for the storage facility, these tests investigated: (1) the length of time required to fully dry a fuel canister and means for verifying dryness, (2) the length of time required to remove liquid water from a fuel canister, and (3) the amount of water remaining in a typical fuel canister after dewatering without drying.

II. DRYING PROCESSES AND MEASUREMENTS

A. Summary of Drying Processes

Drying is the result of heat transferred to a material and the accompanying transfer of moisture out. In a

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In the constant-rate period, the material remains at the wet-bulb temperature. The rate of surface evaporation is determined by the rate of diffusion of water vapor through the stationary film surrounding the material, which is proportional to the difference in partial pressure of the water vapor at the surface of the material and that in the drying air. The rate of diffusion increases with increasing air velocity, as the thickness of the stationary film decreases.

governed by the rate of water vapor diffusion through the media. In drying to low moisture contents, this period usually dominates the over-all drying time.^{1,2}

Practical means are very limited for determining the amount of water remaining in a TMI debris canister during drying. Since the canisters were loaded wet, there are no dry weights for comparison. Pulling and holding a hard vacuum was determined to be infeasible for the same reasons vacuum drying was rejected as a drying process. (Hindsight has also shown that the continuous evolution of small amounts of water would have prevented effective use of holding a vacuum as a means of verification.)

1/2" COPPER TUBE

N₂ SUPPLY

PI-1

CV-1

SV-1

HTR-1

TE-3

V-1

V-2

SV-2

TE-1

HEAT TRANSFER PIPE

1" PIPE

PRV-1

LC-1

HEATING BLANKET

FE - FLOW ELEMENT
 GE - GYROMETER
 HTR - LINE HEATER
 P - AIR PUMP
 SV - SOLENOID VALVE
 TE - TEMPERATURE ELEMENT
 V - MANUAL VALVE
 PI - PRESSURE INDICATOR
 PRV - PRESS RELIEF VALVE
 FI - FLOW INDICATOR
 CV - CHECK VALVE
 LC - LOAD CELL

1/4" TUBE, 2X

P-1

P-2

V-3

V-4

V-5

V-6

V-7

FE-1

FE-2

FE-3

GE-1

GE-2

GE-3

FI-4

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III. EXPERIMENTAL

A schematic of the test apparatus is shown in Figure 1. The primary features of the apparatus were as follows. A fuel canister with a heating blanket clamped around it was suspended from a load cell so that a continuous weight measurement could be recorded. The canister was dried by purging with preheated nitrogen while being heated externally with the blanket. Temperature measurements from the canister internals, canister skin, and purge gas were continuously recorded. Hot-wire-type mass flow transducers measured the purge-gas flowrate. Three types of hygrometer probes were employed to measure the exhaust gas dew point: (1) an aluminum oxide capacitance type (GE-1), (2) a thermoset polymer capacitance type (GE-2), and (3) a chilled mirror unit (GE-3).

In these tests, three parameters were under the control of the experimenters: the heating blanket temperature, the purge gas temperature, and the purge gas flow rate. The following logic was employed in setting these parameters.

Each TMI-2 fuel canister is equipped with EPDM seals in the removable head. These seals begin to degrade when temperatures in excess of 300°F are reached. With this constraint in mind, the purge gas temperature was limited to 250°F and the heating blanket set point was set at either 325°F or 375°F, which yielded a canister skin temperature (at midplane) of 265°F and 300°F respectively. In determining the purge gas flow rate, it was recognized that a higher velocity through the debris bed would increase the removal of water due to pressure gradients, and evaporation rate during both the constant and falling rate drying period. However, it was also apparent that very high flow rates would result in an elevated pressure in the canister which would decrease the evaporation rate. A purge gas flow rate of 6–8 SCFM yields a canister pressure increase of 1.1–2.0 psi, which appeared to be a good compromise.

A. Drying of An Empty Canister

To differentiate the drying characteristics of the LICON from the simulated core debris, an empty canister was dried. Figure 2 shows the canister interior temperature, and the canister weight throughout the drying period.

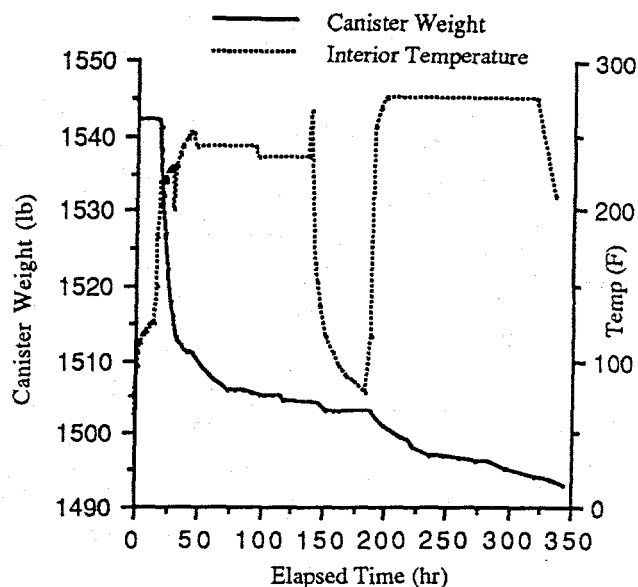


Figure 2. Empty Canister Drying.

For the first 16 hours of the test, the canister was heated at a blanket setpoint temperature of 160°F to determine whether any moisture would evolve. As can be seen from Figure 2, the weight remained constant during this time period. The hygrometer logs (not shown) also indicate that no water was removed at this temperature. Once the blanket setpoint temperature was increased to 325°F, water began evolving rapidly. Over the next 100 hours the water removal rate gradually diminished. For approximately 20 hours the can was allowed to cool, followed by an increased blanket temperature of 375°F, and an increase in the water removal rate was seen. As can be seen in the figure, water continued to evolve from the canister until the test was terminated, at which time the canister had been at temperature for approximately 10 days. During the drying process, 50 lb of water was removed. The great amount of water removed from the LICON, and the long time required to do so, indicates that the presence of this material provides a great hindrance to completely drying the fuel canisters.

During the initial bakeout period, the two capacitance-based hygrometers behaved very erratically as soon as water began evolving from the canister. It was hypothesized that something accompanied the evolution of moisture and caused them to decalibrate. Throughout the remainder of the testing program, these probes behaved erratically and provided only a general indication

of wet and dry. The chilled mirror probe appeared to be unaffected.

B. Drying of a Canister Filled with Sand

1. Canister configuration. A canister was filled with approximately 500 lb of 100 mesh sand to simulate a fuel canister filled with fine debris. Fuel canisters are typically expected to contain debris 800 microns (20 mesh) and larger. Since diffusion through a packed bed is a strong function of particle size,³ this load of fine sand was used to create a "worst case" condition for moisture migration during the falling-rate period.

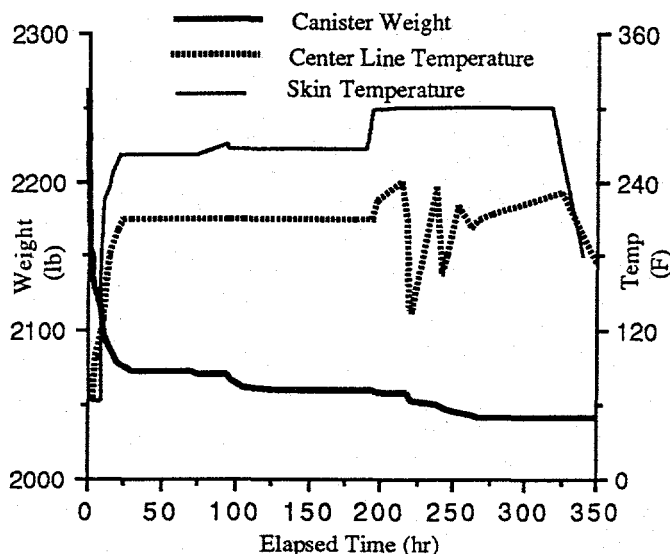


Figure 3. Drying of Canister Filled with Sand.

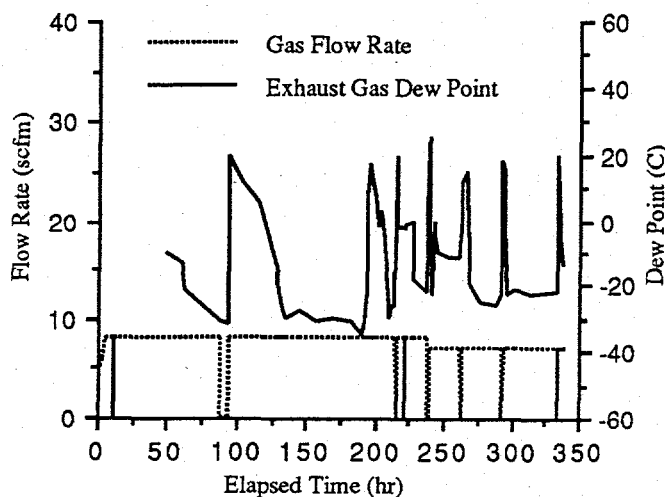


Figure 4. Exhaust Gas Dew Point and Flow Rate.

2. Test results and discussion. Figure 3 shows the canister weight throughout the drying process as well as the temperature measured on the canister skin surface at the canister midplane, and internal center-line temperature of the sand bed, again at canister midplane. Figure 4 shows the purge gas flow rate and the dew point of the exhaust stream as read by the chilled mirror hygrometer.

The very rapid drop in canister weight over the first few hours is a result of the dewatering process. After dewatering, the canister appears to go through a brief constant-rate drying period followed by a falling-rate period until approximately hour 90. At this time, the canister was isolated and a small sample stream recirculated by use of pump P-1. This was done in an attempt to determine if the dew point of the exhausting purge gas was indicative of the dew point of the canister contents. The rapid rise in dew point shows that this was not the case. Throughout the drying process, each time the canister was isolated and a small sample stream recirculated, this sample stream would become extremely wet. In fact, liquid water was found in the recirculation lines the first few times this was attempted. Another phenomenon associated with isolating the canister and then restarting the flow was that an increase in water removal rate occurred immediately afterward.

After approximately 180 hours of drying, the heating blanket setpoint temperature was increased to 375°F. An increase in water removal rate was observed to take place afterwards. Some of this increase was also due to isolating the canister and then restarting the flow.

The canister filled with sand required only a little more time to dry than did the empty canister, indicating that the extended time period required for drying is due to the unusual configuration and properties of the LICON.

3. Reason for lack of dew point correlation. A TMI fuel canister consists of two chambers. An inner chamber, which contains the debris and is directly piped to the inlet and exhaust ports, and an outer chamber containing approximately 4 ft³ of LICON (see Figure 5). The only place the two chambers communicate is at the top of the canister through a relatively narrow passageway.

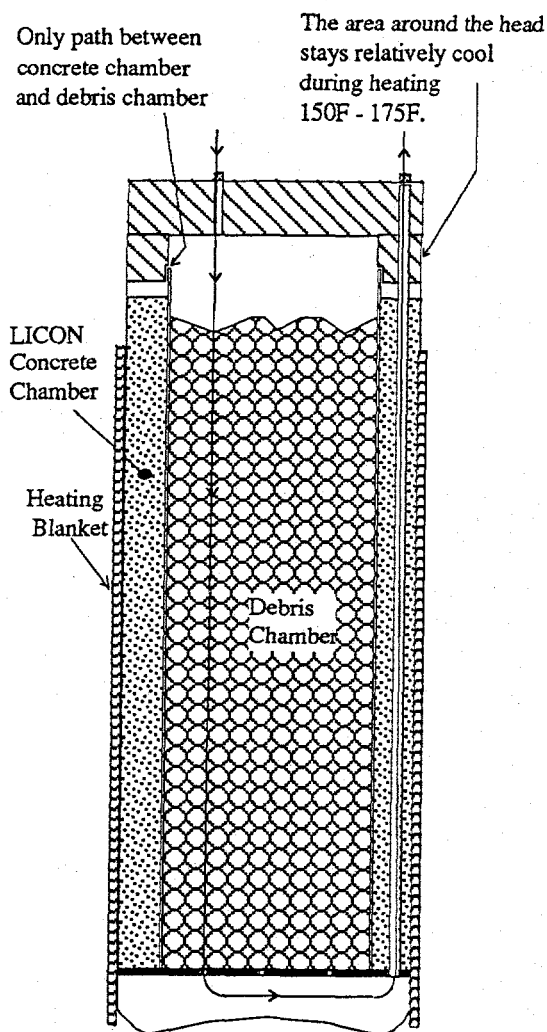


Figure 5. Two Separate Chambers in Fuel Canister.

In the early stages of the drying process, the external heat supplied increases the vapor pressure in the concrete chamber sufficiently that much of it is pushed out into the debris chamber, where it can be flushed out. Eventually, the vapor pressure in the LICON chamber is not sufficient to drive a significant amount of water vapor into the debris chamber. This may be due in part to a heat pipe effect where water is evaporated from hotter parts of the concrete near the canister midplane, which then rises up and condenses in the cooler part near the head. The water may then drip down into hotter regions again and be re-evaporated, creating a closed loop that never generates sufficient pressure to drive the remaining water from the concrete chamber. When flow through the canister is terminated, the pressure in the headspace of the debris chamber drops, and water vapor and even bulk

water is drawn from the concrete chamber to the debris chamber.

It is likely that this problem could be partially avoided by increasing the height of the heating blanket and arranging the heaters on the blanket so that the entire canister is heated uniformly.

4. Hygrometer performance. As mentioned earlier, the chilled mirror type hygrometer was found to be immune to process contamination in this application. However, it was not found to be robust or trouble free. On several occasions when the system was isolated and recirculation started, bulk water entered the sensing unit and it gave no indication that this had occurred. On two occasions, when the hygrometer indicated extremely low dew points, the sensing unit was opened and the mirror was found covered with a thick layer of ice, which resulted in erroneous dew point measurements.

These failures of the chilled mirror hygrometer point to significant risks to its use in a production drying campaign. Although some of the wet conditions created in these tests could probably be avoided in the production campaign, complete reliability of the data from a chilled mirror type instrument is very much in doubt. Furthermore, opening the sensor unit and cleaning or drying the mirror (which was required several times during these tests) would be extremely expensive and time consuming in a radioactively contaminated system.

With the failure of the capacitance-based hygrometers and the delicate nature of the chilled mirror unit, no appropriate instrument type was identified for the production drying campaign.

C. Time Required to Remove all Liquid Water

1. Canister configuration. The purpose of this test was to determine how long it would take to remove all liquid water from a fuel canister with a typical loading and determine how much pore water remained in the LICON once a canister had been dried to this level.

A new canister was loaded with pre-dried lava rock and a small quantity of sand. The canister was then filled with water as before, except in this case a small stream of water was allowed to course through the canister overnight. This was done to ensure that the LICON chamber was completely full of water as would be the case with the canisters that are underwater.

2. Test results and discussion. Figure 6 shows the canister weight and temperatures through the test period. In this test, the canister was allowed to purge overnight to evaluate the water removal rate from simple purging. This rate falls to nearly zero after the first hour or so.

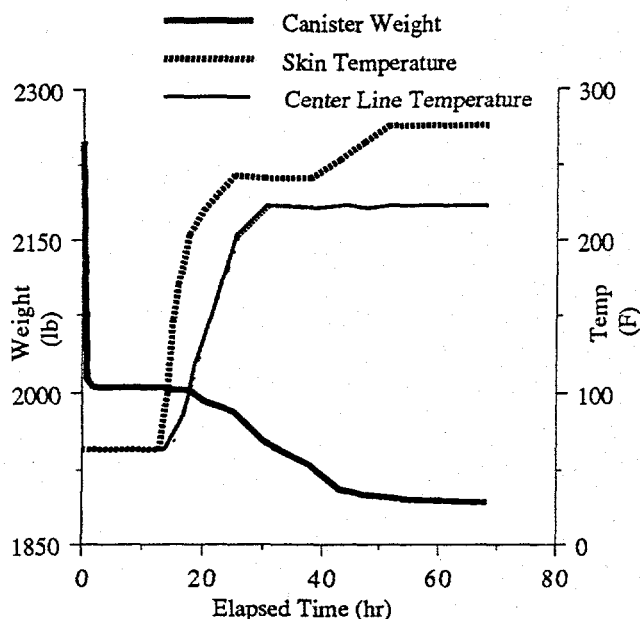


Figure 6. Removal of Liquid Water Test.

After being purged and heated at a blanket temperature of 325°F for 50 hours, the canister was allowed to cool and the contents removed and examined for visible moisture and none was found. The canister was then hung upside down for several minutes to determine whether any free liquid water was present in the LICON chamber, and none was evident. It therefore appears likely that all liquid water can be removed from a fuel canister by heating for 50 hours at a blanket temperature of 325°F while purging.

The advantage of drying for a specific length of time and temperature as compared with drying until some criteria like exit stream dew point is reached is that no extra instrumentation is needed to indicate when the drying process should be terminated.

After being hung upside down, the empty canister was reheated at a blanket temperature of 375°F (not shown in the figure) and an additional 29 lb was removed during this process, indicating that a canister can be free of liquid water while a considerable amount of pore water remains in the LICON.

An unexpected result from this test is the amount of water lost from the LICON. The final weight of 1893 lb was 79 lb less than the beginning empty weight of 1972 lb (not shown in the figure). The earlier test with an empty canister indicated that only about 40 lb of water could be removed from the LICON at 325°F. With the additional 29 lb lost during the second heating, this canister lost 108 lb from its original empty weight.

D. Amount of Water Remaining in a Canister After Dewatering

If the canisters are stored without drying, but rather after dewatering only, a substantial amount of water will remain.

After dewatering, a fuel canister contains water in three distinct regions: (1) a pool of water left standing in the lower head below the fuel basket, (2) water entrained with the debris, and (3) water in the LICON chamber.

The amount of water left standing in the lower head was previously determined at TMI to be 13 lb.⁴

The water entrained with the debris was estimated by TMI to be 3%, or approximately 30 lb for an average 1000 lb fuel canister payload.⁴ As part of these tests, a canister was loaded with lava rock, filled with water, and dewatered. After dewatering, 27 lb of water was left with the lava rock, which correlates pretty well with the TMI estimate. Since the lava rock was in rather large chunks (softball size or greater), the 30 lb TMI estimate is probably about the least amount of entrained water that could be expected. A canister filled with 100 mesh sand retained about 70 lbs of water after dewatering (not counting that in the lower head) and this likely represents the upper bound for entrained water.

The water in the LICON chamber is of three types: (1) "pore" water in the concrete, (2) water of hydration from the concrete curing process, and (3) liquid water that flooded into vacant spaces in the LICON chamber when the canisters were submerged.

Pore water is that water which is hygroscopically bound in small capillary spaces in the concrete. This water exerts a vapor pressure less than that of the pure liquid at a given temperature and is removed by elevated temperatures. Oak Ridge National Laboratory has found that pore water can be effectively removed from portland

based concretes by heating to 480°F for 24 hours while under a rough vacuum, illustrating that complete removal of water bound in this fashion requires a significantly elevated temperature.⁵

The water of hydration used in the curing process becomes part of the crystalline structure of the cement and may also be termed "bound water". As with pore water, water of hydration is removed by heating. If cured at a temperature above 95°F, calcium aluminate cement will not give up water of hydration until temperatures in excess of 400°F are reached.⁶ Since the curing temperature of the LICON may not have been well controlled, some of the water given up in these tests by the LICON upon heating to 300°F could be due to the dehydration of $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ to $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ and finally to $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$.⁶ It is therefore possible that some of the water removed from the LICON during these tests is water of hydration rather than pore water; however, for the purposes of this discussion it is assumed to be pore water. It probably makes little difference which, since in either case, the water is "bound" in that it cannot be removed in the absence of elevated temperatures.

Calcium aluminate cements do not give up their water of hydration completely until a temperature of 1050°F is reached.⁶ No effort was made to quantify the water of hydration in the LICON based on chemical formula because the formulation depends on curing temperature and hydration is frequently incomplete.

The empty canister drying test and the drying of a canister filled with sand test gave an indication of the amount of pore water in a canister. As discussed in the following section, it is possible that considerably more water could be removed at higher temperatures.

To determine the amount of water that floods into the LICON chamber upon submerging, a new canister was weighed, then filled with water and a small stream was allowed to course through the canister for 72 hours. (It was found that over time the canister continued to absorb water and increase in weight.) The canister was then dewatered. A comparison with the empty weight, less the 13 lb left in the lower head, determined the amount of water that entered the LICON chamber.

Table 1 summarizes the estimates for water retained after dewatering for a "typical" fuel canister.

TABLE 1. Water Remaining After Dewatering a Typical Fuel Canister

Location/Type of Water	Min (lb)	Max (lb)
Standing in the lower head	13	13
Entrained in debris	30	70
LICON pore water	50	110
Water that floods into LICON chamber upon immersion	50*	50*
Water of Hydration	Not Incl	Not Incl
Total Water	143	243
Total Liquid Water	93	133

*Max and mins not known, only one test performed.

In Table 1, the term "liquid water" is not the same as the term "free water" frequently used in radioactive waste storage acceptance criteria. Free water is the amount of water that would run out if the canister were cut open. The "liquid water" in Table 1 includes the free water plus all the water that is not hygroscopically bound, which is assumed to be essentially all of the water entrained with the debris.

E. Drying A Sample of LICON

A small cube of LICON (approximately 1 inch on a side) left over from the shipping campaign was subjected to the following procedure. The sample was weighed, soaked 24 hours in demineralized water, and reweighed. The sample was then heated in a low humidity oven for 24 hours at 200°F and reweighed, and then heated to 700°F in 100°F increments for a minimum of 24 hours at each temperature. The sample was reweighed before each temperature increase.

Figure 7 is a plot of the weight lost per cm^3 of sample cube volume. An interesting point of note is that the sample cube lost more weight between 300°F and 400°F than between 200°F and 300°F. During the drying tests described above, the fuel canisters never achieved a temperature above 300°F. This indicates that there could have been a substantial amount of pore water remaining in the LICON after the tests were completed. The canisters were heated for longer than the sample cube (2 weeks vs. 24 hours) and so it is not clear how valid this conclusion might be.

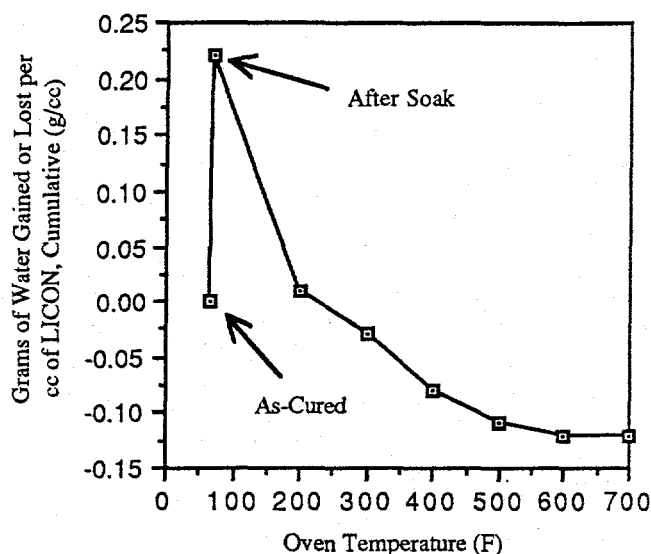


Figure 7. Weight Gained/Lost per cm^3 of LICON as a Function of Temperature.

III. APPLICATION TO FUTURE FUEL CANISTER DESIGNS

Most degraded fuel in the DOE complex is stored wet and the trend is toward packaging it in canisters and drying prior to above-ground storage. Although in hindsight some of the features of TMI-2 fuel canisters that should be avoided in future designs are rather obvious, there may be some value in reviewing them here.

1. Elastomeric seals should be avoided so that the drying temperature is not unduly limited.
2. Pockets that could collect water are to be avoided and the canister drain system should be designed such that no standing water is left in the lower head after dewatering.
3. Hygroscopic filler materials such as LICON must not be a part of the canister design.

IV. CONCLUSIONS

The conclusions reached from this series of tests are as follows.

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1. The TMI-2 fuel canisters cannot be completely dried at temperatures less than 300°F by means of heating and purging.
2. Neither capacitance based nor chilled mirror hygrometers would be effective instruments for a production drying campaign.
3. Liquid water may be removed from the fuel canisters by heating for 50 hours at a blanket temperature of 325°F or greater while purging.
4. After dewatering, a fuel canister can retain as much as 240 lb of water not counting water of hydration.

ACKNOWLEDGMENTS

This work was performed under DOE Contract No. DE-AC07-94ID13223.

REFERENCES

1. M. Fortes and M. R. Okos, "Drying Theories: Their Bases and Limitations as Applied to Foods and Grains", *Advances in Drying*, A. S. Mujumdar Ed., pp. 119-135, Hemisphere Publishing Corp., New York, New York (1984).
2. H. P. Perry and C. H. Chilton, Eds., *Chemical Engineers Handbook*, 5th Ed., Chp. 20, McGraw Hill Book Co., New York, New York (1973).
3. W. C. Krumbein and G. D. Monk, "Permeability as a Function of the Size Parameters of Unconsolidated Sand", *American Institute of Mining Metallurgical and Petroleum Engineers*, 151, pp. 153-163 (1943).
4. TMI-2 Technical Bulletin, "Dewatering Canisters in Preparation for Offsite Shipment", TB 86-33 Rev. 2 (1986).
5. L. R. Dole, et al., "Cement-Based Radioactive Waste Hosts Formed Under Elevated Temperatures and Pressures . . .", ORNL/TM-8579, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1983).
6. G. MacZura, et al., "Refractory Cements", *Ceramic Engineering and Science Proceedings*, 4, 1-2, pp. 46-67 (1983).