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IN-SITU ZEOLITE DRYING

G. H. Bryan
L. L. Burger
D. E. Knowlton

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Pacific Northwest Laboratory
Richland, Washington

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INTRODUCTION

The radiolysis of water in the SDS liner zeolite results in the generation of H_2 and O_2. At certain ranges of concentration, mixtures of these gases are explosive. Consequently, shipment of the liners is not permitted unless a way is found to either remove the water from the zeolite or prevent buildup of explosive concentrations.

One method of removing the water is to pass warm, dry air through the zeolite. If the partial pressure of water in the air is less than that of water contained in the zeolite, the driving force is to transfer the water from the zeolite to the dry air. Therefore, very dry air may theoretically be used to dry zeolite to very low levels. The use of a flowing gas has, in other experiments, been shown to be kinetically superior to vacuum pumping in removing volatile components from zeolites. The object of this research was to determine if wet zeolite can be dried by this procedure to a sufficiently low level, ~3%, to reduce the hydrogen and oxygen generation rates from radiolysis so the zeolite can be safely shipped offsite. The time required to adequately dry the zeolite must also be within practical limits for operation at the TMI-2 site.

A further restraint on the drying system requires that it be performed in-place at TMI. As TMI facilities are very limited, it is necessary, for shielding purposes, that the system operate while the liner is sitting near the bottom of the fuel storage pool.

An additional objective of this work was to subject the dried zeolite to high-energy radiation to determine the actual amounts of H_2 and O_2 produced. These numbers may then be used to predict the gas generation while the SDS liners are in shipment.

EXPERIMENTAL

IN-SITU ZEOLITE DRYING

Two approaches were attempted to dry the zeolite with warm, dry air on a laboratory scale. The first approach was to cover a container of zeolite with a bell jar so that a layer of air existed between the container of zeolite and the water container in which it was immersed. The intent was to insulate the zeolite from the water to prevent heat loss. The second approach was to immerse a stainless steel zeolite container directly in the tank containing water, without regard for heat loss. The water in the tank was maintained at ~18°C.

Figure 1 is a photograph of the containers that were used for the two experiments. The containers were constructed to simulate the geometry and conditions that an actual SDS liner would impose. The apparatus used for the testing is shown in Figure 2. Supply air to the apparatus was dried to 6 to 10 ppm water content with a commercial air dryer and then heated to 150°C. The air flow was controlled with a manual flow control valve. The air supply lines were contained within a larger-diameter line to provide air insulation as they passed through the water within the tank. The water removed from the zeolite was collected by a condenser operated at about 5°C, followed by a bed of water-absorbing material. Zeolite 13X and silica gel were employed at various times. The water contents of the inlet and exit air were measured continuously by in-line moisture analyzers.

The vessel used for the first experiment had a diameter of 3 in. and contained 0.5 L (350 g) of zeolite. Zeolite was added to the container, covered with water, and allowed to stand for 30 min. Excess water was removed by blowing air through a dip tube. This procedure reduced the water content to about 40 wt%. The air was injected at the bottom of the container via a center dip tube and allowed to flow up through the zeolite. An air flow rate of 1.0 m^3 (35 ft^3) per hour was used.

The vessel used for the second experiment had a diameter of 15 cm (6 in.) and contained about 3.7 L of zeolite. The zeolite was added to the vessel, covered with water, and allowed to stand for two hours. The excess water was

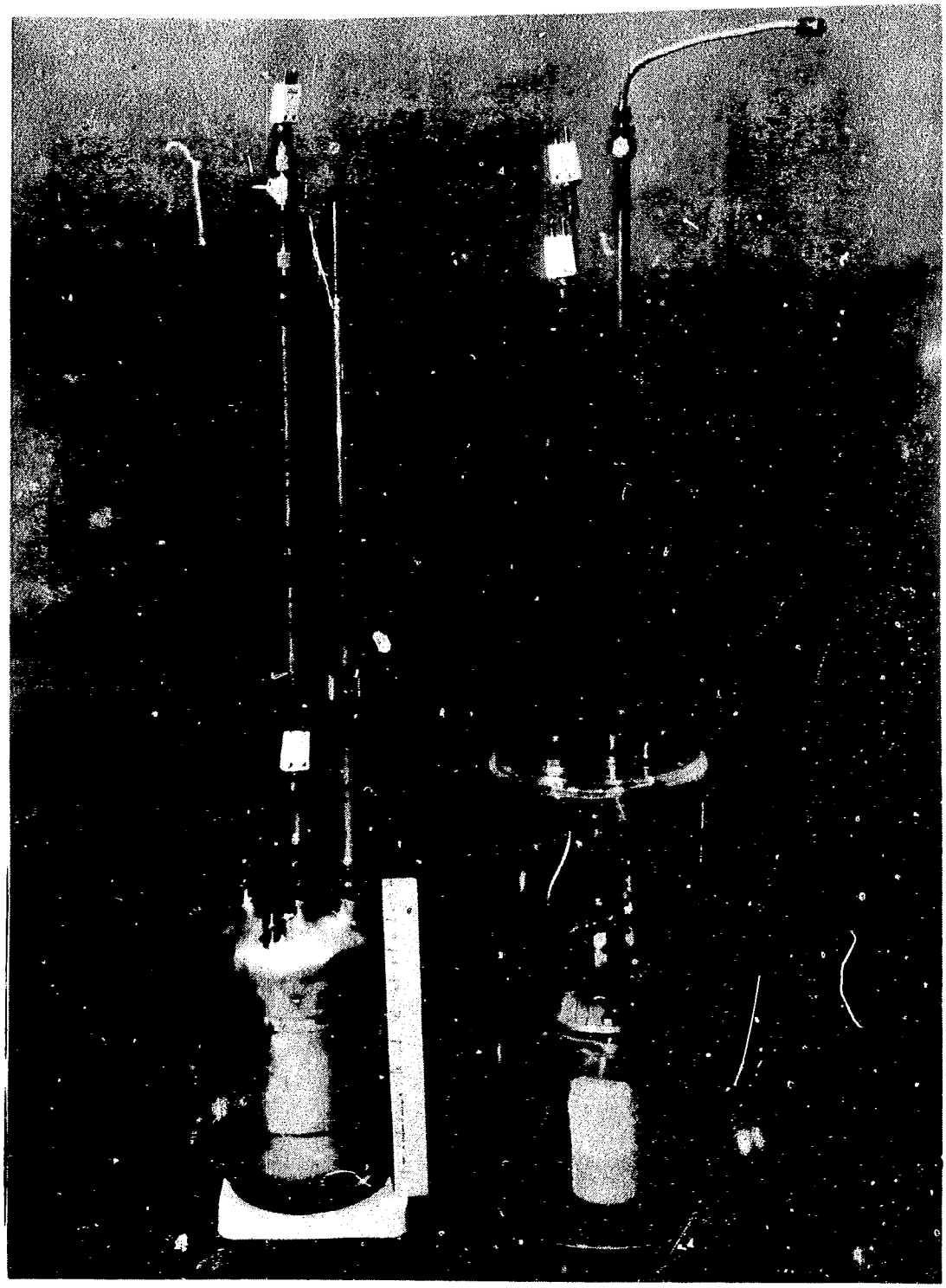

FIGURE 1. Zeolite Drying Containers

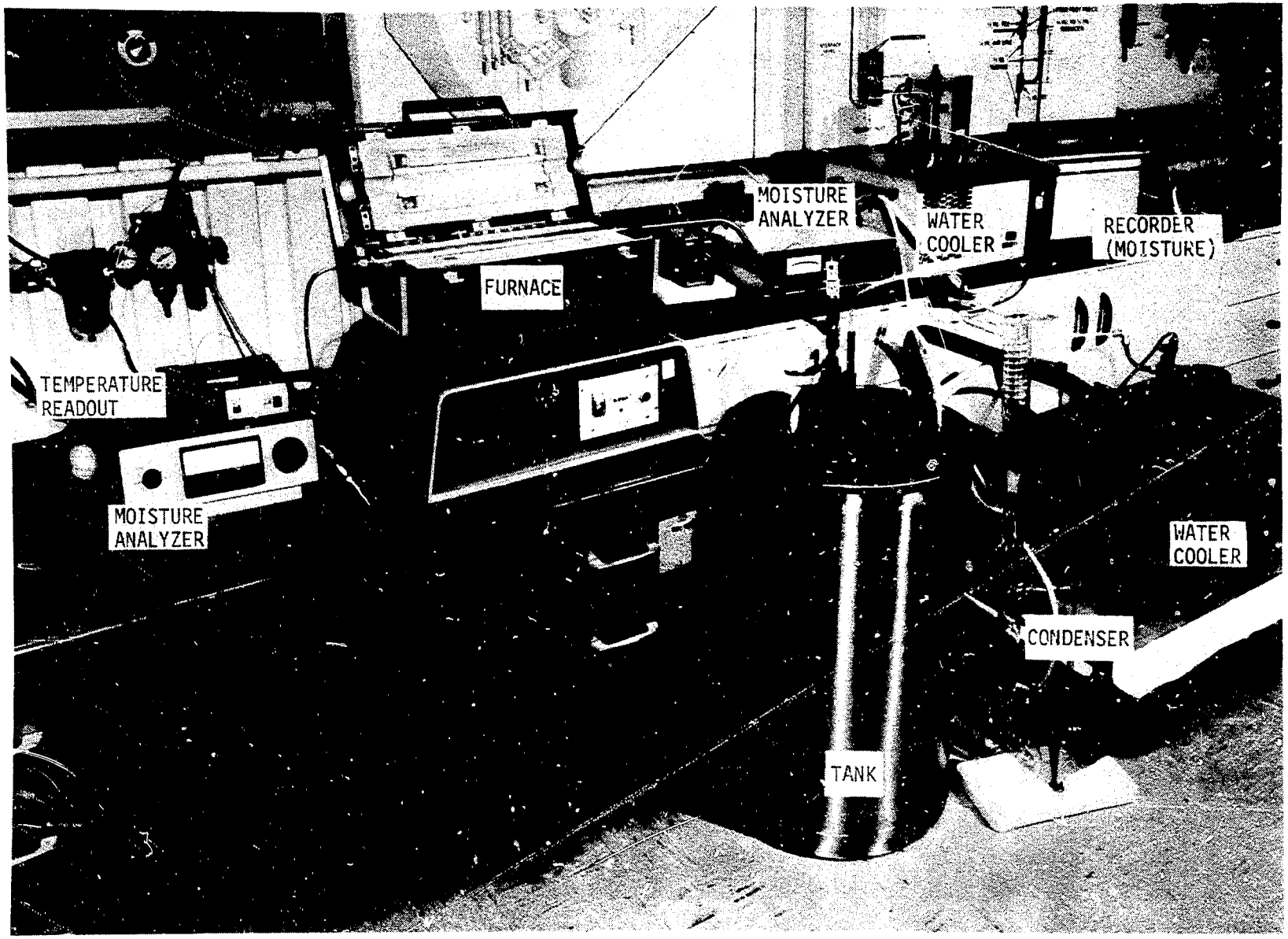

FIGURE 2. Zeolite Drying Apparatus

then removed by purging air through the zeolite. The air flow used for drying was from the bottom to the top by way of a central dip tube. Due to a pressure buildup in the water collection system, the air flow rate was maintained at 2.8 m^3 (100 ft^3) per hour or less until the bulk of the water had been removed from the zeolite. The air flow rate was then increased to 3.5 m^3 (125 ft^3) per hour.

In both experiments, the water content of the zeolite was determined by heating about 50 g of the zeolite to 1000°C for an hour and assuming the entire weight loss was due to water. At a temperature of 1000°C, the zeolite crystal structure broke down, thus releasing any interstitial water within the crystal. It is believed that some of the weight loss was due to other volatiles, thereby biasing the residual water content on the high or conservative side.

IRRADIATION OF DRIED ZEOLITE

The sample canister for the irradiation tests was fabricated from 304L stainless steel and was 5.72-cm (2.25-in.) dia by 30-cm (11.75-in.) long. The canister was connected to a pressure gauge via a 1/8-in. stainless steel tube about 6-m (20-ft) long. Valving allowed the container gas to be evacuated, sampled or isolated. A Type K thermocouple monitored the zeolite temperature.

An accurate measure of the pressure buildup in the canister was not possible, as the ^{60}Co facility provided air flow used to cool the canister could not be regulated (temperature or flow) to a sufficient degree to permit the acquisition of meaningful data.

The ^{60}Co facility supplied a flux of about 8 x 10^6 rad/h. This is about 10 times the average flux zeolite would experience in a SDS liner that is loaded to about 55,000 Ci of Cs and 2,000 Ci of Sr. However, the Cs and Sr are not loaded uniformly, and the zeolite may have areas where the flux is much greater than the average.

The first sample irradiated used zeolite dried to a water content of 3.3 wt% (Run #3). After filling the canister with this material and attaching the connecting tubing, a vacuum (22-in. Hg, 200 torr absolute pressure) was drawn on the canister and then backfilled with argon. This process was repeated

four times. The canister was placed in the ^{60}Co facility and the temperature allowed to equilibrate at about 82°C (180°F), while the pressure within the canister was adjusted to about 1.61 atm (9 psig) by venting. The canister was left in the gamma field for 168 hours. At the end of this time, the canister was removed and the gas sampled for mass spectroscopic analysis.

A second irradiation test was performed using the same apparatus as the first test and containing zeolite with a water content of 3.3 wt% (Run #4). It was felt that the evacuate-backfill sequence may not have removed all the air from the zeolite. Thus, for the second test, the canister was purged with argon for 24 hours prior to being placed in the ^{60}Co facility for irradiation. A sample of the gas within the canister was taken prior to irradiation. The zeolite was irradiated for a total of 168 hours at about 79°C (175°F) before it was withdrawn and a gas sample was taken for analysis.

RESULTS

Two runs were made using the bell jar apparatus, and two were made using the stainless steel container without air insulation. The data in Figure 3 show the rate of water removal for Runs #1 and #2. After 120 hours (~5 days), water contents of 3.2 wt% and 3.3 wt% were achieved for Runs #1 and #2, respectively. Drying curves for all four runs, based on exit air moisture content, are shown in Figure 4. The water content of zeolite from Run #3 was also 3.3 wt% after 250 hours (~11 days), indicating air insulation of the vessel containing the zeolite is not necessary if somewhat longer drying times are acceptable. Run #4 used 170°C inlet air (temperature limit on the liner quick-disconnect seals). The higher temperature and longer drying time (30 days) still resulted in a zeolite water content of 3.3 wt%.

The final face velocity of the air through each of the two vessels was approximately the same for each of the runs. Runs #1 and #2 had an average face velocity of 3.63 m/min, while the average face velocity for Runs #3 and #4 was 3.23 m/min. These values are close to the maximum flow allowable without fluidization of the zeolite.

The water content of the zeolite from Run #3 was also determined to be 1.84 wt% by a commercial water analyzer that heats samples to 400°C. The difference between this result and the method described in the Experimental Section is primarily due to insufficient temperature in the commercial analyzer to drive all the water from the zeolite. At 1000°C, the zeolite cavities are destroyed and water removal is rapid.

The mass spectroscopic analysis of the first zeolite irradiation test gases are shown in Table 1. Although the H_2 value is quite low, the O_2/N_2 ratio cannot be explained other than that some foreign oxidizable material was introduced into the canister (e.g., organics, metals, etc.).

The O_2 and N_2 concentrations suggest that the O_2 resulted from the presence of air. The oxygen could be used to form H_2O from the hydrogen generated. However, the amount of O_2 consumed is in large excess of the maximum calculated amount of H_2 generated using a G_{H_2} value of 0.45 (G_{H_2} for pure water is 0.45) for the water present in the zeolite. The He content of the canister is from that added for a leak test of the apparatus.

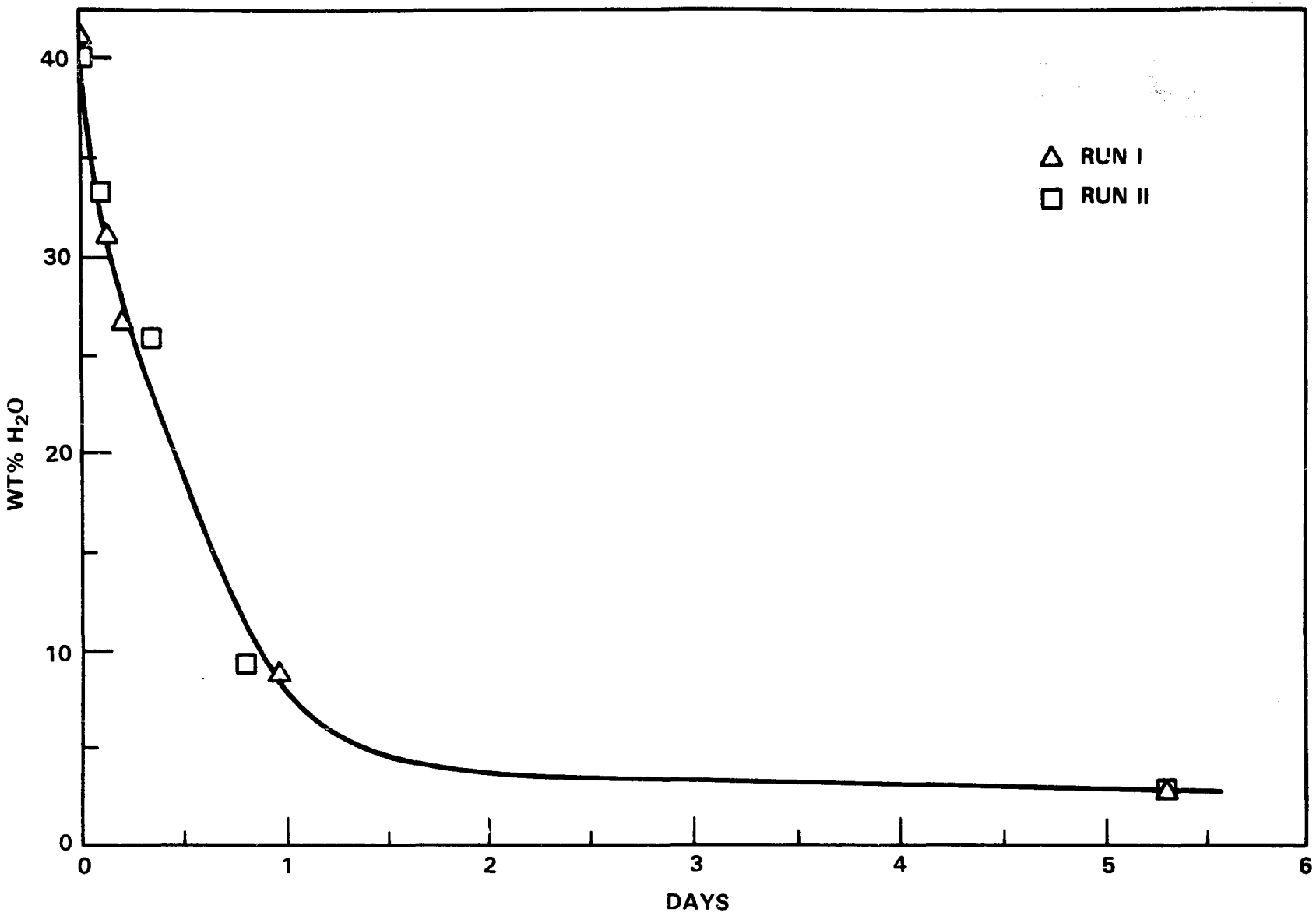

FIGURE 3. Drying Time Versus Weight Percent H_2O in Zeolite

CONCLUSIONS

The use of warm, dry air is a viable method by which SDS liner zeolites may be dried. The method is simple, easily adaptable to storage pool use, and may be used without insulation between the liner and the pool water.

It is signficant that only very small amounts of hydrogen are apparently generated during irradiation of dried zeolites (~3.3 wt% H_2O) in a ^{60}Co source with a dose of 8 x 10^6 rad, an order of magnitude higher than the average flux calculated for a high-activity SDS liner (~60,000 Ci of Cs and Sr). Irradiation with ^{60}Co gamma does not entirely duplicate the exposure of dried zeolite loaded with radioactive Cs and Sr, but only small differences in gas yields would be expected.

An upper limit to the hydrogen produced may be calculated using reported radiolysis hydrogen yields. Using a G_{H_2} value of 0.015[a] for zeolite loaded to 60,000 Ci of Cs and Sr and 3 wt% water, calculations indicate the total H_2 generation in an unvented liner after 14 days (maximum shipping time from TMI to PNL) would be ~13 L. Based on this calculation, the liner may be pressurized to 2 atm (30 psig) with N_2 just prior to shipment, and which at the end of 14 days will yield an H_2 content of 2.1 vol%, well below the 4.1 vol% necessary for combustion.

Based on these data, the system described for the in-situ drying of the zeolite contained in SDS liners is an acceptable method to prepare the zeolite for shipment under existing regulations.

(a) Extrapolated value from N. Bibler, Savannah River Laboratory, March 1982. This also agrees with a calculated value for 3.3% water in the zeolite based on a G_{H_2} for pure water of 0.45.