RADIATION EFFECTS ON RESINS AND ZEOLITES AT THREE MILE ISLAND UNIT II

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Introduction

During normal nuclear power plant operations, contaminated water is routinely processed through ion exchange media systems. Processing of liquid wastes by this method does not normally result in waste forms that pose handling or disposal problems. However, the cleanup operations of the Three Mile Island Unit II created certain waste forms that are not routinely encountered in normal light water reactor plants. The Department of Energy and the Nuclear Regulatory Commission through a Memorandum of Understanding have agreed that Three Mile Island should not become a long term repository for these abnormal wastes. Under the terms of this memorandum the Department of Energy will accept certain special wastes for research and development and for disposition. The waste materials include:

- Highly loaded (up to 2.6 curies of fission products/liter) organic ion exchange resin (EPICOR-II System)

- Highly loaded (up to 500 curies of fission products/liter) inorganic zeolites (Submerged Demineralizer System)

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- o Purification demineralizer system organic ion exchange resins (approximately 20 curies of fission products/liter)

Research work done for safe management of these wastes has identified radiation effects on the zeolite and resin beds containing residual water. These effects include radiolysis of residual water and degradation of organic resins.

EPICOR II System Ion Exchange Resins

Fifty EPICOR II System containers with 850 liters of organic ion exchange resins or a mixture of organic resins with inorganic zeolite were loaded to a maximum level of 2200 curies of fission products (predominantly cesium and strontium plus daughters) during processing over 2,000 cubic meters of contaminated water in tanks located in the fuel handling and auxiliary building. Radiolysis and resin degradation generated a variety of gases including hydrogen, oxygen, CO_2 and trace quantities of CH_4 and CO. Table 1 shows the approximate curie loadings, measured gas generation rates and initial hydrogen and oxygen gas concentrations for selected dewatered EPICOR II system vessels when sampled after two years of storage (Reference 1). Most prefilters were found to be at atmospheric pressure and all were depleted in oxygen. Prefilter 6 had no detectable hydrogen present. Several vessels were found to be pressure tight. The hydrogen gas generation rate in each vessel was found to be directly proportional to curie content.

TABLE 1. EPICOR II SYSTEM ION EXCHANGE LINERS

Prefilter Liner	Approximate cesium + strontium and daughter products, Curies	Gas Generation Rate, 10^{-6} l/hr	Gas Generation Rate, 10^{-6} l/hr-Ci	Gas Concentration* Volume Percent, H_2	Gas Concentration* Volume Percent, O_2
2	1052	8.32	0.0079	4.50	0.5
3	1878	9.90	0.0053	9.90	<0.2
6	166	None	None	<0.01	<0.2
18	2025	9.42	0.0047	26.00	<0.2
44	1845	10.70	0.0058	10.40	<0.2
45	2036	12.00	0.0059	0.70	0.7
50	1600	9.49	0.0059	13.40	<0.2

*CO, CO_2 and CH_4 were also present in small quantities.

EPICOR II system prefilter-16 contained both inorganic zeolite and organic resin and contained 2058 curies of of fission products, predominantly cesium, strontium and daughters. Core samples from this vessel were analyzed by Battelle Columbus Laboratory (Reference 2). The resin beads in the samples were found to be spherical with very little evidence of surface defects. It was concluded that the resin was essentially undamaged. Examination of the prefilter vessel lid indicated the presence of some corrosion, however, after the sluicing of the resins at the Idaho National Engineering Laboratory, further examination of the coating inside the container showed very minimal vessel corrosion damage.

EPICOR II system prefilter-3, which contained only organic resin, was loaded to 1878 curies of of fission products, predominantly cesium, strontium, and their daughters. Again, core samples of the resin were analyzed by Battelle Columbus Laboratory (Reference 3). Visual examination found the material darker at the top of the sample than at the bottom.

Although dose levels were higher at the top, because the identity of the resin material used is proprietary, it is not possible to definitively determine why some of the spherical particles were darker in color than others. From the curie loading, a maximum total absorbed dose of approximately 10^7 rads was estimated. Microscopic examination of the sample indicated the presence of some fragmented beads and spherical beads with surface defects near the bottom of the sample. The top section showed few defects in resin beads. Visual examination of the vessel after sluicing of the resin at the Idaho National Engineering Laboratory showed essentially no vessel corrosion.

Gas sampling of the EPICOR II system vessels and analysis of the samples provided information to determine gas generation rates as a function of curie loading. The average hydrogen gas generation was 6×10^{-6} liters/hour-curie at standard temperature and pressure. As no oxygen was detectable, it was determined that all liners had significant O_2 scavanging. The source of the hydrogen, CO_2 and trace quantities of CH_4 and CO is radiolysis of the residual water and degradation of the organic resin.

Submerged Demineralizer System Zeolites

Approximately 2500 cubic meters of contaminated water from the reactor containment building sump and greater than 1900 cubic meters from the reactor coolant system were processed through inorganic ion absorbers (zeolites) using the Submerged Demineralizer System. Fifteen vessels containing zeolite media have been loaded with radioactive cesium,

strontium, and daughter products up to a level of 113,000 curies. Gas sampling and analysis provided information on gas generation rates as a function of curie loading. From this data, the average gas generation rate per curie was found to be 4×10^{-6} liters/hour-curie (hydrogen and oxygen). Analyses of the gases for SDS vessels after the bulk dewatering are shown in Table 2.

TABLE 2. SDS ZEOLITE VESSELS

Vessel	Approximate Total Activity Curies	Gas Generation Rate $\frac{10^{-6}l}{hr}$	Gas Generation Rate $\frac{10^{-6}l}{hr\text{-}Ci}$	Average Observed Mole Ratio (H_2/O_2)
D10011	88,158	421	0.0048	2.7
D10012	112,635	613	0.0054	5.2
D10013	97,151	418	0.0043	2.9
D10015	12,896	33	0.0026	Infinite
D10016	112,622	476	0.0042	2.8
D20028	86,334	353	0.0041	3.7

The gas generation rates are accurate to ±20 percent. The data indicate an increase in gas generation with increasing curie content. The average observed mole ratios show that the gas mixtures were not stoichiometric with some oxygen being depleted. No oxygen was detected in vessel D10015. A piece of plastic was later found which accounted for oxygen depletion in this vessel.

In a recent report by Battelle Pacific Northwest Laboratory (PNL), the mechanisms by which O_2 and H_2 are produced were described (Reference 4). In particular it is believed that the formation of hydrogen peroxide (H_2O_2) initially limits the production of stoichiometric

proportions of hydrogen and oxygen gas until equilibrium is reached. Also, the presence of dissolved ions and metallic components of the container walls will also influence the rate of oxygen production. While oxygen has been found in less than stoichiometric quantities for zeolites, it is in much higher concentrations than for the organic ion exchange resins.

Makeup and Purification System Resins

During the Three Mile Island Unit II accident, the makeup and purification system demineralizer resins (in both the A and B tanks) at Three Mile Island Unit 2 were highly contaminated by the letdown of reactor coolant through the system. Large amounts of fission products including cesium, strontium and iodine, and fuel debris were trapped by the organic resin resulting in elevated resin bed temperatures estimated to be as high as 800 K from fission product decay heat. Radiation exposure to the resins was estimated to be approximately 10^9 rads. Gamma scans of the A tank estimated about 5,000 curies of cesium. Analysis of a resin sample from the purification demineralizer B-tank by Oak Ridge National Laboratory showed 21,000 micro curies of cesium per gram of resin which resulted in an estimated 17,000 curies of cesium in the purification demineralizer B-tank. The A resin sample showed 4,800 micro curies of cesium per gram of resin for an estimated 4,000 curies of cesium in the purification demineralizer A-tank.

Pacific Northwest Laboratory performed scoping studies using non-radioactive resin tests to determine levels of resin damage from various combinations of temperature and radiation. As shown in Table 3,

these tests predicted that the purification demineralizer resins would be reduced in size, possibly fragmented but potentially still in a sluicable form.

TABLE 3. ORGANIC RESINS

Temp. °F	Radiation	Resin	Effects
395	None	Battelle PNL	reduction in weight and size
535	None	Battelle PNL	reduction in weight and size
670	None	Battelle PNL	reduction in weight and size/black and splitting
810	None	Battelle PNL	reduction in weight and size/black and fragmented
Ambient	1.74×10^9	Battelle PNL	darkened (wet)
455	None	Battelle PNL	sticking to the glass noted
455	1.74×10^9R	PNL	darkened and sticking to the glass
Ambient	10^7R	EPICOR Prefilter-16	undamaged
Ambient	10^7R	EPICOR Prefilter-3	darkened but mostly undamaged
800	10^9R	Purification A-Demineralizer	dry, some beads black and fragmented, others still light in color; cracking
800	10^9R	Purification B-Demineralizer	wet, darkened, some clustering and cracking

The actual purification demineralizer vessels have been assayed for fuel content. Also, gas, liquid and resin samples have been obtained. High transuranic and cesium levels have been found. Hydrogen and organic

gases are being produced through radiolysis and resin degradation. As in the case of EPICOR II system gas studies, oxygen is being absorbed. The purification demineralizer B-tank resin bed is covered by approximately one foot of water while the purification demineralizer A-tank was relatively dry but has been refilled with water and sparged with nitrogen to facilitate sampling. Examination by Oak Ridge National Laboratory of a resin sample from the A purification demineralizer showed many carbonized particles which were black and amorphous, many light colored and intact resin spheres, some cracked spheres, no transparancy of the beads and obvious debris. The examination of the resin sample from the B purification demineralizer showed beads overall darker in color than the A sample, many opaque spherical beads, some transparent (amber) beads, many grape-like clusters of beads and foreign materials. The resins in both tanks are believed to be sluicable for eventual removal.

Table 3 shows a comparison of resin damage to the EPICOR and purification system resins for different radiation and temperature loadings and compares these to the tests performed by Battelle Pacific Northwest Laboratory. The Battelle Pacific Northwest Laboratory tests show reduction in weight and size for organic resins due to temperature with damage increasing with temperature. Damage to the resin from the A-purification demineralizer tank is greater for some resin beads than the B-purification demineralizer tank probably due to the absence of water and the lack of this cooling effect. Darker resins with cracking were observed to a larger degree in the B purification demineralizer resin sample.

Table 4 shows the concentrations of gases found in the purification demineralizer vessels. Hydrogen gas generation rate of 2×10^{-6} liters/hour-curie was found for the B purification demineralizer resin and is similar to that found for the EPICOR II system resin wastes.

TABLE 4. PURIFICATION DEMINERALIZER

	A	B
Estimated curies cesium^{137}	4,000	17,000
Estimated Total Curies	10,000	35,000
Gas generation rate	NA	0.0017 cc/hour/curie
Initial Gas Composition*	(Volume Percent)	
O_2	.02	<.01
H_2**	7.15	81.3

* Other species identified included CO_2, N_2, CH_4, Ar, CO, and Xe.

** Difference in H_2 volume percents are due to sampling methods.

Conclusion

Radiation effects on resin and zeolite used in the waste cleanup at Three Mile Island Unit II have been examined both experimentally and in-situ. Hydrogen and organic gases are generated due to absorbed radiation as a function of resin material, curie loading and residual water content. Significant oxygen scavaging was demonstrated in the organic resin liners. Hydrogen and oxygen gases in near stoichiometric quantities are generated from irradiation of residual water in inorganic zeolites. Gas generation was determined to be directly proportional to curie content but correlates poorly with residual water content in zeolite vessels.

Results of the gas generation analyses of EPICOR II liners show that vessels with less than 166 curies had almost no hydrogen generated during two years of storage and therefore did not require safety measures for shipment or storage.

Experimental measurements done at research laboratories predicted similar results associated with hydrogen gas generation and oxygen depletion. X-ray diffraction examinations and ion exchange capacity measurements indicated no evidence of irradiation effects on the structure or cesium exchange capacity for zeolites exposed to 10^{10} rads.

Darkening and damage of organic resin due to radiation has been identified. Breaking and agglomeration of the purification demineralizer resin is believed to be the result of temperature effects. No damage was identified from radiation effects on zeolite.

Organic and inorganic sorbents used in the processing of contaminated waters at TMI-2 have been shown to be effective in maintaining long term stability under high radiation conditions. The effects of radiolytic degradation have been shown by direct measurements and simulation tests and are of use in their general application throughout the industry.

REFERENCES

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