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SUBTASK

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SUBJECT Summary of Studies on Stability of Ion Exchange Resins in Radiation Environments

ABSTRACT

A summary of state-of-the-art work performed on the subject of resin stability has been prepared. This summary touches upon the Brookhaven literature survey incorporating work from Sandia, Penn State, and Georgia Tech. Those portions specific or judged as applicable to the known technical nature of the TMI-2 EPICOR II resins are given. In addition NRC and GPU reviews are stated. The conclusion is that actual sampling and analysis of the EPICOR resins would be desirable to positively evaluate the liner and resin status.

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SUMMARY OF STUDIES ON STABILITY OF ION EXCHANGE RESINS IN RADIATION ENVIRONMENTS

Brookhaven National Laboratory (BNL) conducted a literature search of the state-of-the-art of knowledge on radiation effects on ion exchange organic resins in 1977.[1] A number of generalizations were stated in that study, several of which are believed applicable to EPICOR resins. These are:

1. Radiation chemical changes in ion exchange resins are a direct function of the total dose absorbed by the resin.
2. Most anion exchange resins show considerable degradation when the total absorbed dose increases above 10^7 to 10^8 rads, while most cation exchangers show significant attrition only above 10^8 rads.
3. In most ion exchange resins, an absorbed dose of 10^9 rads or higher results in sufficient damage to make the material unserviceable.
4. There are two well recognized forms of radiation effects on ion exchange systems - one is the direct action of radiation on the ion exchanger matrix while the other is the indirect action of radiolytic decomposition products of the materials in the environment of the resin.
5. The primary effects of radiation on ion exchange resins are degradation and cross-linking of the macromolecular structure along with the scission of ion exchange functional groups.
8. The free radical concentration in ion exchange resins being irradiated increases steadily and tends to reach a limiting concentration. This limiting concentration of free radicals is reached at integral doses of 10^8 to 10^9 rads in most resins.
9. The exchange capacity of ion exchange resins, in general, decreases with increasing radiation dose.

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[1] T.E. Gangwer, M. Goldstein, K.K.S. Pillay, "Radiation Effects on Ion Exchange Materials", BNL-50781, November, 1977.

10. Under identical conditions, when radiation sources of low Liner Energy Transfer values (γ-rays, x-rays, fast electrons and β-particles) are used, there are no apparent differences between the radiation effects on resins, whether the source is external or internal.

11. Radiation effects on organic ion exchangers result in color changes of the resin matrix. The resins change from their original shades to amber, brown, dark red and black with increased doses.

12. As a consequence of radiation damage, the particles of resins (beads) become gouged, pitted, cracked and at times solubilized when the integral dose exceeds $10^8 - 10^9$ rads.

13. Irradiated resins are less resistant to degradiation by thermal effects. (SIC-Heat degrades resins in addition to ionizing radiation)

14. Gaseous products resulting from the action of ionizing radiation on ion exchange resins primarily consists of hydrogen. Other gaseous products of resin decomposition include CO_2, CO, N_2O, NO and SO_2."

Discussions with Sandia National Laboratories on liner integrity raised bacterial degradation as an area of concern which had not previously been raised; however, radiation dose levels of about 10^5 R would pasteurize and about 10^6 R would sterilize the resin matrix.

Ferguson of ORNL has stated that phenolic resin coatings similar to those used for treating the interior surfaces of the EPICOR II liners have radiation stabilities analogous to the resins themselves. Therefore if the resin stability is in question, so should the integrity of the liner coating stability be questioned.

NRC Review

NRC's position on the resin wastes was initially presented in the May 15, 1980 letter, J.T. Collins, NRC to R.C. Arnold, GPU, which formally asked for information on the EPICOR II wastes. This letter transmitted a BNL letter report on the status of initial studies on the leachability, structural integrity and radiation stability of organic ion exchange resins. In the area of radiation stability of ion exchange resins, BNL stated that the fundamental processes of radiation damage were not well understood. However at Cesium-137 activities of $40 Ci/ft^3$ significant decomposition of the resins could occur with loss of the ability to retain radionuclides. As a result of the radiolysis of the resins, gaseous products would be evolved mainly hydrogen and carbon dioxide. Other gases such as CO, O_2, CH_4, N_2 and oxides of nitrogen and sulfur have been identified. At integral doses of 10^9 rad, pressures of 1.5 to 15 atmospheres could be produced from gas evolution in the 4 x 4 EPICOR II liner

Unofficially, NRC has irradiated resins at Penn State University and at BNL to determine radiation stability. At Penn State, resins typical of those used in normal reactor plant radwaste operations were irradiated and yielded pH in the range of 1-3 at equivalent integral doses of 5×10^7 R in one year (based upon $125 Ci/ft^3$ due to non-uniform distribution of activity on resins).

BNL irradiated resins obtained from Hittman as typical of those used in EPICOR II for cement solidification purposes at integral doses of - 7×10^7 R (corresponding to one year's irradiation) pH ranged from 1.5 to 3; at 10^8 to 10^9 R pH reached 1.1 to 1.2. These studies at Penn State and BNL confirm NRC's concerns on gas generation and acid production that could adversely affect the liner integrity if imperfections exist in the protective coatings of the carbon steel EPICOR II liner internals.

More recently, in support of the BNL on resin degradation, Robert McFarland at Georgia Tech has been subcontracted to perform post mortem examinations of a number of resin capsules irradiated under a Chem Nuclear-GPU study of ion exhange materials to be used in the SDS waste treatment system. The resin samples evaluated for gas production under CO-60 gamma irradiation to 10^9 R resulted in substantial (200 psi) gas generation; predominantly hydrogen due to void water and aliphatic (straight-chain) hydrocarbons at lower concentrations as reported in a February 1980 report. The more recent work by McFarland for BNL is as yet unreported, however, preliminary results support greater physical damage to anionic resins than with cationic resins; reaching pH ranges of 2.5 to 3 for 10^{8} R integral doses.

GPU Review

GPU has stated in meetings with the NRC that EPICOR II liners were fabricated and tested to withstand 6 psi internal pressure. Leaks occurred at 19 to 20 psi during hydrotesting of three liners. Liners were sandblasted to white metal on the interior surfaces prior to coating with plascite two-coat finish resin materials to prevent corrosion. The pH should not go below 5.5 because buffering agents were used, and evaluations indicate less than 3 psi pressure generation for infinite integrated dose.

Summary

While identity of the specific EPICOR II resins is unknown, a review of the literature of radiation effects on ion exchange resins indicates that both cationic and anionic resins substantially lose their ion exchange capacity as a function of increased irridiation in the range of 10^{8} to 10^{9} R. Anionic resins have measurable gas generation at doses of 5 x 10^{7} R while cationic resins retain their physical character to higher levels, but also generate gases beginning at 10^{8} R. Gas generated is primarily hydrogen, with aliphatic hydrocarbons secondarily generated. Hydrogen is present due to radiolyses and combustible or explosive mixtures may result during handling and care should be exercised.

Liner integrity has been questioned due to the radiolytic decomposition products which exert pH levels in the range of 1-3. Corrosion rates of carbon steel in these environments are rapid. Liners may not be protected thoroughly to prevent corrosion. In the absence of greater confidence than the above information provides, characterization of the EPICOR II ion exchange resins and integrity of the liners is considered an urgent priority.