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ANALYSIS OF POTENTIAL HAZARDS ASSOCIATED WITH ^{241}Am LOADED RESINS FROM NITRATE MEDIA

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ABSTRACT

LANL has been contacted to provide possible assistance in safe disposition of a number of ^{241}Am-bearing materials associated with local industrial operations. Among the materials are ion exchange resins which have been in contact with ^{241}Am and nitric acid, and which might have potential for exothermic reaction. The purpose of this paper is to analyze and define the resin forms and quantities to the extent possible from available data to allow better bounding of the potential reactivity hazard of the resin materials. An additional purpose is to recommend handling procedures to minimize the probability of an uncontrolled exothermic reaction.

BACKGROUND ON INDUSTRIAL ACCIDENTS INVOLVING RESIN MATERIALS IN HNO_3

Deflagrations/explosions with ion exchange resins and nitric acid have been noted in industry and at DOE sites.[1] The incidents have been observed in both non-rad environments, and in recovery/separations efforts involving radioactive isotopes. One of the more infamous DOE accidents with resins occurred in separation of ^{241}Am at the Hanford site in 1976. A large (6" diameter by 36" length) column of Dowex 50 cation exchange resin (sulfonate functional group) was left loaded with ^{241}Am from nitric acid media for about 6 months. The resin likely had heated itself to dryness in the presence of nitrate media, leading to degradation of the resin. Following the start of elution of this resin material with 7 M HNO_3, a rapidly accelerating decomposition reaction was observed to begin, apparently aided by pressurization within the column. The column was noted by operators to be making a hissing noise from building pressure during the event.[2] The reaction accelerated to a point where the schedule 10, 304L stainless steel column suffered a deflagration, which breached the integrity of the glovebox windows/gloves. An operator was physically injured and also suffered the largest known

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[1] C. Calmon, *"Explosion Hazards of Using Nitric Acid in Ion-Exchange Equipment",* Chemical Engineering, Vol. 87, Issue 23, pp 271-274 , Nov. 17, 1980.

[2] *"Explosion of Cation Exchange Column in Americium Recovery Service, Hanford Plant August 30, 1976"* BNWI—1006 DE91 007084, October 8, 1976.

contamination and uptake with ^{241}Am. Numerous reviews/evaluations of the accident postulated 2 possible mechanisms as causes for the event.[3,4,5,6]

The mechanism of a high temperature, runaway reaction of high concentrations of a strong oxidant (nitric acid) and materials that can be oxidized (the resin) is likely the primary mechanism of reaction. Almost any organic material can be made to decompose with HNO_3 when subjected to adequately high concentrations, pressures, and temperatures. Oxidation of anion or cation exchange materials, containing aromatic or aliphatic groups has been observed. Anion exchange materials having quaternary ammonium groups in nitrate form resemble alkyl-substituted ammonium nitrate materials.

Numerous additional studies on resin stability in HNO_3 have been performed, [7,8,9,10] and notable improvements achieved in designed resin safety over the years. Fred Marsh of LANL and Reilly Industries jointly developed Reillex HPQ polypyridine based anion exchange resin now used extensively in the USA for actinide separations.[11,12] Polypyridine based anion exchange resins offer better resistance to radiolytic and chemical damage than quaternary ammonium functional groups and these resins have become the standard at the LANL Plutonium Facility and many other DOE sites.

Decomposition of a nitro-organics has been inferred as an additional mechanism imparting rapid energy release, as nitrated aromatic organic molecules like trinitrotoluene (TNT) are capable of explosive decomposition. Nitrated aromatics are typically prepared by electrophilic aromatic substitution of aromatic ring compounds (like toluene or styrene) by heating in mixtures of very concentrated nitric and sulfuric acid (very low

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[3] R. C. Thompson, *“1976 Hanford Americium Exposure Incident: Overview and Perspective”,* Health Physics Vol. 45, pp 837-845, 1983.

[4] F. W. Miles, *“Ion-Exchange-Resin System Failures in Processing Actinides”*, Nuclear Safety, Vol. 9, No. 5, pp 394-406 , Sept, 1968.

[5] H. T. Fullam, G. Jansen (Jr), W. J. Van Slyke, *“Thermochemical Instabilities in Anion-Exchange Processing”*, Conference on Ion Exchange in the Process Industries, pp 71-81, 1969.

[6] C. Grelecki, *“Investigation of Incident in Ion Exchange Resin”* Hazards Research Corporation Report 3719 to Atlantic Richfield Hanford Company, Sept 21, 1976.

[7] S. F. Marsh, *"The Effects of In Situ Alpha-Particle Irradiations on Six Strong Base Anion Exchange Resins"*, LA-12055, Los Alamos National Laboratory, Los Alamos, NM (April, 1991).

[8] S. F. Marsh, *"The Effects of Ionizing Radiation on Reillex HPQ, A New Macroporous Polyvinylpyridine Resin and on Four Conventional Polystyrene Anion Exchange Resins"*, LA-11912, Los Alamos National Laboratory, Los Alamos, NM (Nov, 1990).

[9] S. F. Marsh, K. K. S. Pillay, *"Effects of Ionizing Radiation on Modern Ion Exchange Materials"*, LA-12655, Los Alamos National Laboratory, Los Alamos, NM (Oct, 1993).

[10] W. J. Crooks, E. A. Kyser, S. R. Walters, *"Qualification of Reillex HPQ Anion Exchange Resin for Use in SRS Processes"*, WSRC-TR-99-00317, Westinghouse Savannah River Company, Aiken, SC (March 10, 2000).

[11] S. F. Marsh, *"Evaluation of a New, Macroporous Polyvinylpyridine Resin for Processing Plutonium Using Nitrate Anion Exchange"*, LA-11490, Los Alamos National Laboratory, Los Alamos, NM (April 1989).

[12] S. F. Marsh, *"The Effects of Ionizing Radiation on Reillex HPQ, A New Macroporous Polyvinylpyridine Resin and on Four Conventional Polystyrene Anion Exchange Resins"*, LA-11912, Los Alamos National Laboratory, Los Alamos, NM (Nov, 1990).

water content). It is proposed that partial nitration of the styrene based Dowex 50 cation exchange resin occurs over time with the combination of radiation, heat, dehydration, nitric acid, sulfuric/sulfonic acid (from the resin) to produce reaction products capable of rapid decomposition and large energy release when heated. The resin accidents to date have been best characterized as deflagrations rather than explosions implying that while decomposition of nitro-organics can contribute energy, they do not dominate the decomposition reaction.

The oxidative decomposition reaction initiation could be by either mechanism or a combination, but literature examples have been tied to initiation with concentrated HNO_3. The initiation of the exothermic reactions, which self-catalyze to very rapid rates, has been attributed to heat (helped by pressure in some cases). The confinement vessel has ruptured violently in some cases with the evolution of gaseous degradation products (these gases also can be combustible). The initial heat may come directly from chemical reaction with the nitrate (oxidation of alcohols, as radiolysis products, often blamed), heat of mixing of the concentrated HNO_3, or direct from the radioisotope (large columns heavily loaded with ^{238}Pu in some cases).

The alpha decay specific activity of ^{241}Am is significantly greater than typical weapons grade Pu, but less that ^{238}Pu, contributing to a concern that a loaded resin column may heat itself to dryness over a period of time. The calculations for heat loading are in many ways similar to those for resin radiation damage. Parameters reducing the heat loading issues include small column size (which translates to greater column surface area for heat loss, and less potential for insulation by the resin material) and loading capacity.[13]

BACKGROUND INFORMATION ON INDUSTRIAL RESIN MATERIALS

Resin materials are noted to be "stripped" of ^{241}Am by 8 N HNO_3.[14] Elution of ^{241}Am under these conditions would be consistent with the chemistry associated with a cation exchange resin. Use of cation exchange resin would be a reasonable separations method for 1978/1979 recovery operations to win ^{241}Am from industrial solutions.

"Container 2" is listed as containing two resin columns from final ^{241}Am concentrate, and was listed as having been assayed at 0.924 Ci (+/- 30%) of ^{241}Am, which converts to 0.275 g ^{241}Am (specific activity of ^{241}Am is 3.42 Ci/g), or 1.14 mMol Am.

"Container 3" is listed as containing three resin columns, and was listed as having been assayed at 4.2 Ci (+/- 100%, a surprisingly large uncertainty value) of ^{241}Am, which converts to 1.23 g ^{241}Am (specific activity of ^{241}Am is 3.42 Ci/g), or 5.10 mMol Am.

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[13] Recent formulations (since 1997) of Reillex HPQ anion exchange resins have modestly increased Pu loading capacity to 117 g per liter of resin. E. A. Kyser *"Plutonium Loading On to Reillex HPQ Anion Exchange Resin"*, Westinghouse Savannah River Company WSRC-TR-2000-00372.

[14] Memo describing ^{241}Am residues to Mr. Nels R. Johnson from Bruce Coomer, Project Manager, September 19, 2000.

One of the columns in "container 3" is described as containing ~100 mL of a viscous material (possibly having originated from the resin material). It's reasonable to assume that radiolytic degradation of the resin has resulted in some amount of depolymerization of the resin structure.

Use of a series of five ion exchange columns are noted in the source document.[14]Separate notation above shows two resin columns in "container 2" and three resin columns in "container 3". A more detailed description of a single resin column describes the arrangement as consisting of 2 columns joined at the bottom (each of 50 mm diameter and 215 mm length). Looking at the photo of the "joined column" (see Figure below) there is clearly something wrong with the dimensions discussed in the reference document. The photos show columns that are about 1" diameter. The green column caps in the photo are significantly oversized relative to the columns, appearing to be ~2" diameter, and are the probable source of the size discrepancy in the reference document.

Figure Caption. Photograph of a worker handling two items, believed to be ion exchange columns. The side-by-side arrangement would be consistent with the description, which suggests that each column is actually a pair of columns connected in parallel joined at the bottom by a "rigid connection".

Volume for a right circular cylinder may be readily calculated by $V = \pi r^2 h$. Assuming column segments of 25 mm diameter and 215 mm length volume for each column segment is about 106 mL. With five columns total, each consisting of two joined column segments of the specified dimension, a total volume of about 1.06 L is possible in the described columns.

			$V = \pi r^2 h$
	diameter (mm)	height (mm)	volume (L)
"Industry" cation exchange column	25	215	0.106
(photo dimension estimate)	(about 1 inch)	(about 8.5 inch)	
	diameter (in)	height (in)	volume (L)
Hanford cation exchange column	6	36	16.68

The original volume of resin in the columns may have been less in operation as cation exchange resins like DOWEX 50 may swell fairly dramatically (2X) with changing loading conditions. Assuming a summed maximum volume of 106 mL, and a loading capacity of 2 mEq/mL volume of wet resin for DOWEX 50, a typical cation exchange resin of the time, the theoretical capacity of Am^{+3} for an individual column segment full of resin would be about 0.071 moles or 17 g.[15] This theoretical value is far in excess of the practical operational loading of the resin, and serves only to illustrate the amount of Am under discussion could easily be present on the resin material. Residual Am quantities in the mg to gram range remaining on the resin (with incomplete stripping) would not be unreasonable.

HAZARDS ANALYSIS/SUGGESTED SAFE HANDLING PRACTICES

Several parameters are noted below to aid in safe handling practices, should LANL engage in transport, staging, and/or handling of the material discussed in this paper.

Size of columns:

The industrial accidents involving resins and nitric acid have universally occurred in large columns. Smaller columns are inherently safer as regards self-catalyzed exothermic reactions. Among the reasons that column size is relevant: (1) larger columns have a larger material content, and larger associated possible total energy release from an exothermic reaction; (2) a larger column having a greater thickness of (dry)[16] resin can more efficiently insulate hot spots in the column, reducing heat transfer/dissipation; (3) the ratio of column surface area to resin volume is smaller in larger columns, reducing the rate of heat transfer/dissipation to air surrounding the large column.

In the accident at Hanford (see table above) the column volume is calculated at about 16.7 L.[17] This total column volume is about 160 times larger than the column segments in the industry case under discussion. The total amount of chemical energy that might be available in an exothermic reaction is thus 160 times smaller.

In the accident at Hanford (see table above) the column radius of 3” is about 6 times larger than the 0.5” radius industry case under discussion. Radius is a good estimate of the maximum possible thickness of insulating dry resin. The probability of an insulated

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[15] This calculation assumes a single atom of trivalent Am^{+3} will occupy three cation sites on the resin.

[16] Dry resin is important to this mechanism, because if aqueous solution is present it provides a more efficient path to conduct heat.

[17] While the simple volume calculation shows ~ 17 L, some accident reports list the column volume at ~ 19 L.

hot spot which results in initiation of an undesired exothermic reaction within the small column is subsequently much less.

In the accident at Hanford the ratio of column surface area to resin volume is about 6 times smaller in the larger columns, reducing the rate of heat transfer/dissipation to air surrounding the column. The larger surface area per unit volume of the small column transfers heat more efficiently, which reduces the possibility of initiation of an undesired exothermic reaction within the column from internal heat.

Heat:

The industrial accidents involving resins and nitric acid have universally occurred at elevated temperature. The source of heat for initiation of a self catalyzed exothermic reaction with resin may be radiolytic (large amounts of high specific activity isotopes), an external source of heat to improve ion exchange reaction kinetics, chemical (oxidation of alcohols by nitric acid for example), or heat of mixing of concentrated HNO_3 with more dilute solutions. Studies referenced above to reproduce the conditions of initiation of these self catalyzed exothermic reactions have found the lowest initiation temperature to be ~135°C (at ambient pressure).[5]

The handling recommendation is to not expose the resin materials to external sources of heat during shipment and storage to minimize the probability of initiating an exothermic reaction.

Pressure:

Increasing pressure increases reaction kinetics in a manner similar to increasing heat. The industrial accidents involving resins and nitric acid have often occurred at elevated pressure, and noted pressure increase contributing to gradual acceleration of the runaway reaction. The energy associated with the sudden release of pressure (as a column fails) has often been a significant mechanism in damage/injury. The small glass columns containing the resin material (note photo above) equipped with rubber tubing and hose clamps would not contain much pressure to accelerate an undesired reaction. Workers who handle the columns during packaging operations should have a minimum of good eye protection and gloves when handling the glass columns. Additional PPE to protect from glass from a burst column should be considered.

Rapid changes in HNO_3 molarity:

The resin materials should not be exposed to highly concentrated nitric acid. Among the first steps in process handling the resin material if treatment options are considered should be addition of water to act both as a heat sink and to dilute any HNO_3 remaining. The water reduces the probability of initiation of a runaway reaction between nitric acid and organic material.

Explosive sensitivity:

No known cases of impact or friction initiation were associated with triggering the industrial accidents involving resins and nitric acid accidents. Observation of the evidence from the accidents does not indicate a level of violence resulting from the highpower of a detonation event, but it is possible that thermal ignition and resulting deflagration may have occurred. Although impact initiation should not play a role, production of compounds or mixtures with explosives sensitivity cannot be ruled out, and reasonable care should be exercised to not significantly jar or drop the columns. Gentle handling should be a suitable precaution in procedures that directly manipulate the columns. Shipping containers should include material such as sand or vermiculite to protect the glass columns.