APPENDIX 4

HAZARDS RESEARCH
CORPORATION
Fire and Explosion Hazards Evaluation

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INVESTIGATION OF INCIDENT IN ION EXCHANGE RESIN

HRC Report 3719

- to -

Atlantic Richfield Hanford Company
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pipe was 36 inches long, and was closed on the top with a 1/8 inch thick flat plate and on the bottom with a 1/4 inch thick flat plate. A 1/2 inch inlet nozzle and a 1/2 inch pressure relief valve nozzle were in the top closure, and a 1/2 inch outlet nozzle was in the bottom. Two 3/4 inch nozzles were attached to the side wall, one near the top for resin addition and one near the bottom for resin removal. Rings were welded in near the top and bottom to support perforated plates and filters to support the resin column. The internal volume of the column was approximately 19 liters (0.67 cubic feet).

B. The Ion Exchange Resin

The resin used in the column is a cation exchange resin, Dowex 50. Dowex 50 is a sulfonated polystyrene which is about 4 percent cross-linked with divinyl benzene. It has a relatively high capacity, 5.3 meq/g of dry resin.

C. Description of Normal Operation

Under the design operating conditions, the column is filled with 13 liters of Dowex 50 resin and conditioned with 0.3$\underline{M}$ HNO_3. The column is then loaded by passage of the americium ion solution in 0.2$\underline{M}$ HNO_3 through it. Americium is subsequently removed by elution with 7$\underline{M}$ HNO_3. The operation is pipe was 36 inches long, and was closed on the top with a 1/8 inch thick flat plate and on the bottom with a 1/4 inch thick flat plate. A 1/2 inch inlet nozzle and a 1/2 inch pressure relief valve nozzle were in the top closure, and a 1/2 inch outlet nozzle was in the bottom. Two 3/4 inch nozzles were attached to the side wall, one near the top for resin addition and one near the bottom for resin removal. Rings were welded in near the top and bottom to support perforated plates and filters to support the resin column. The internal volume of the column was approximately 19 liters (0.67 cubic feet).

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III. DESCRIPTION OF EVENTS LEADING TO INCIDENT

A. History of Column W-14 A

Column W-14A was a relatively new component. It was installed in December of 1975 and conditioned with 0.3M HNO_3. It was first loaded with americium in March of 1976. This loading was not yet removed in August when additional americium solution was added to the column. The outflow was observed to be abnormal in appearance, and so the loading was stopped. The outflow was a dark orange color, suggesting resin degradation.

On August 29, the resin was prewashed with 0.3M HNO_3. The effluent was very dark. Subsequent analysis showed it to contain 1.56 grams of americium per liter of solution, indicating that the column had lost a significant amount of its retention capability.

On the same day, at approximately 11:45 PM, 7M HNO_3 elution was started, and was complete at about 2:00 AM.

B. Events Immediately Preceding the Incident

After the completion of the elution, the column was left with 7M HNO_3. At approximately 2:30 AM, an operator heard a hissing sound described as like a steam leak. He then observed a dark vapor, like iodine, coming from the vent nozzle of the W-14A column. He reached into the glove box to check the vent valve to make sure it was open. At that point, he observed a second leak described as originating near the bottom of the vessel. He then left the glove box and was preparing to leave when the explosion occurred.

IV. DESCRIPTION OF DAMAGE EFFECTS

A. Description of Damage

Post-incident investigation revealed that the W-14A column had failed in hoop stress. The failure appeared to originate near the bottom of the column, where significant pitting is observed in the photographs, and proceeded upward to about 60 to 70 percent of the total length. The bottom section was pulled away from the side wall at the bottom weld. The retaining ring and perforated plate were still attached to the bottom plate. The bottom section was displaced from the rest of the column and was accelerated, causing significant damage to attached and adjacent piping. The inside of the upper section of the column appeared clean, and did not seem to suffer very much erosion, nor did the perforated plate appear to be distorted.

Glass closures on the glove box were shattered, and some of the gloves also failed. Others were blown out but did not seem otherwise damaged.

Nitric acid and resin beads were accelerated from the column, and the effects of their impact could be seen in the area.

B. Failure Pressure

The yield stress for stainless steel is about 33,000 psi. The minimum tensile strength is about 75,000 psi. It is difficult to accurately calculate the pressure at which rupture failure will occur because the condition of the pipe changes between the time that it starts to yield and the time that it ruptures. In addition, in this case, there is some evidence that the wall thickness may have been partially eroded. However, it is safe to say that if the sidewall was in good condition, the pressure required for hoop stress failure would be about 2500 psi.

The flat end plates should fail at a lower pressure. The calculated failure pressure for the top closure is about 110 psi, the bottom 435 psi. Since these plates did not appear to be damaged it is unlikely that the internal pressure was significantly higher than 100 psi.

Since the side wall failed and the top end plate did not, it is apparent that the side wall must have been weakened by local heating, a poor weld at the bottom or chemical corrosion.

C. Energy Equivalence

The energy dissipated on the shock wave when a pressure vessel fails is estimated by the work done by the expanding gases against the environment. For this case computations were made on the basis of a vessel half full of vapor and half full of 40% HNO_3, at the time of failure. For failure at 100 psi and 2500 psi respectively, the energy output is given below.

	100 psi	2500 psi
Output from gas (kcal)	4	204
Output from vapor (kcal)	55	440
Total (kcal)	59	644

The standard energy for TNT is taken as 500 kcal per pound. Thus failure at 100 psi is equivalent to 0. 12 pounds of TNT, failure at 2500 psi is equivalent to 1. 3 pounds of TNT.

D. Blast Effects

Ideal blast overpressures as a function of distance for 0.12 and 1.3 pounds of TNT equivalence are given below:

Pressure (psi)	Distance (ft.)	
	0.12 lbs. TNT	1.3 lbs. TNT
1	25	55
3	8	17.6
5	5.5	12
10	3.25	7.2

It can be seen that the distance at which a given overpressure occurs is not very sensitive to explosive yield. (The distance at which a given pressure occurs is related to explosive yield as a cubic function, thus it requires eight times the explosive yield to double the distance at which equivalent pressures occur.) Nevertheless it appears that the damage to the steel glove box is more consistent with the lower yield. The front panel of the box is strengthened by the frames of the entrance and view ports. The side panel, which has a larger flat area, is weaker and will probably begin to yield at about 3 psi. Some bulging was observed in the side panel, but it is not immediately apparent whether that was caused by overpressure or by impact of the vessel fragments.

Because of the complex geometries involved, an analysis of blast pressures outside the glove box is difficult. However, from a consideration of the physiological effects of blast waves (1 psi overpressure can knock a man down and 5 psi ruptures eardrums), there is no indication that the operator suffered ear drum damage, and he may have been accelerated by the blast so that would put the overpressure at between 1 and 5 psi at that point. This is more consistent with the lower explosive yield.

V. TYPE OF EXPLOSION

In order to establish the cause of the incident, it is necessary to identify the type of explosion that occurred. Three types of reactions which lead to explosion were considered.

A. Detonation in Condensed Phase

A detonation is a propagating reaction which proceeds at supersonic velocities. In the condensed phase, the peak pressure in the detonation wave will be of the order of 100 to 300 thousand atmospheres. Such overpressure shrapnelizes containers which are confining. The current explosion produced only two or three fragments, indicating a failure at a lower pressurization rate.

A condensed phase detonation is probably further ruled out by theoretical thermochemical considerations. The energy density of a 7M HNO_3 slurry with polystyrene beads is not great enough to support a steady-state detonation.

B. Detonation in Vapor Phase

Brown nitrogen dioxide fumes were observed venting from the vessel. Nitrogen dioxide is a powerful oxidizing gas and can form detonable mixtures with hydrogen or other organic vapors. The maximum pressures developed by such reactions would be between 20 and 40 times the initial pressure of the vessel, or about 600 psi in the extreme. Such pressure could cause the column to fail. However, a vapor phase detonation would cause failure of the 1/2 inch steel transfer lines due to pressure piling in such elements. However, a careful examination of the photos does not reveal any damage to the lines due to an internal vapor phase detonation. In addition, a vapor phase detonation or deflagration would produce a fireball having a volume at least ten times the original volume of the explosive vapor mixture. Careful examination of the photographs failed to show any indication of such a fireball. Very fine threads of hemp rope in the vicinity of the reactor were not at all scorched. Thus, a detonation in the vapor phase must also be ruled out.

C. Thermal Explosion

A thermal explosion is an explosion which is caused by an exothermic reaction that proceeds under conditions of confinement, with inadequate provisions for dissipating the heat of reaction. Under these conditions, the heat of reaction manifests itself as sensible heat increasing the temperature of the reaction mixture. The increased temperature aggravates the situation, since it causes an increase in the reaction rate, which further increases the temperature. Ultimately, the rate of temperature rise (accompanied by an increased rate of pressure rise) becomes rapid enough to cause the container to fail if it is not adequately vented.

The observations in this particular incident are completely consistent with a thermal explosion. They include the condition of the container fragments and the exponential rise in the pressurization rate, observed first by rapid venting through the vent valve, and finally by failure of the vessel.

D. Thermal Explosion of HNO_3 Resin Systems

1. Chemical Potential

Nitric acid is a good oxidizer. In stoichiometric compositions with organic substances, it can produce carbon dioxide and water, which are very stable products. The chemical potential of the 40 percent nitric acid system with organics is significant. A specific calculation for this mixture has not been made, but it is estimated that the adiabatic constant volume reaction temperature would be well over 1000°C. There is no question that an adiabatic reaction of 7M nitric acid with polystyrene can produce the kind of effect observed. The Dowex resin is routinely handled with 7M HNO_3, so the question arises as to what occurred in this instance to accelerate the rate.

2. Action of Radiation on Stability of Resin

It has been established that radiation results in degradation of the polymer. At least one interpretation of the data on the radiation degradation of Dowex resins is that the initial degradation process involves only the cleavage of active sulfonate groups from the resin. These groups dissolve and are partially converted to sulfate ion in the aqueous phase

The resin, which was exposed to americium for several months, had indeed been observed to be degraded. The high concentration of americium in the 0.3<u>M</u> HNO_3 wash indicated that significant amounts of the active sulfonate groups had been cleaved from the resin.

3. Presence of Catalytic Impurities

The exact nature of the degraded polymer and the degradation products is not known. It appears that at least sulfate ions were present. The common nitration acid is a mixture of nitric and sulfuric acids. The sulfuric acid acts as a catalyst in this case. In the presence of sulfuric acid, and perhaps some other catalysts such as Fe^{+++}, it is possible to nitrate the aromatic ring. The nitration of the aromatic ring is an exothermic reaction, and while it may proceed very slowly at first, the overall heat transfer characteristics of the ion exchange resin column are poor; and so it would allow the temperature of the column to increase, gradually at first, and then rapidly as the reaction changed from nitration to oxidation with increasing temperature.

VI. CONCLUSIONS AND DISCUSSION

On the basis of the observed effects, it is concluded that the explosion was a thermal explosion caused by a run-away exothermic reaction. Detonations in the condensed or vapor phases are ruled out as possible causes of the explosion on the basis of theoretical grounds and on the basis of observed damage effects.

The pressure at which the reactor failed was probably of the order of 100 psi. The computed explosive yield is about 0. 1 pound of TNT equivalence, which is consistent with the blast wave effects.

While it is not possible to specify exactly which reactions were responsible for initiating the nitric acid oxidation of the polymer, it is clear that the combination does contain the chemical potential to produce the observed effect. The long incubation period in the presence of americium caused degradation of the resin, and it is likely that at least some of the degradation products could be catalysts for the nitration reaction. Having initiated in a stagnant vessel with poor heat transfer, the exothermic reaction increased exponentially until the rate of pressure generation exceeded the capacity of the relief valve.

Examination of the photographs seems to show the vent valve in the closed position. This is not consistent with the report that vapors were escaping through this line. It is possible that, in the excitement of the moment, the operator had inadvertently closed the valve when checking to see if it were open. If the column were properly vented, the explosion would not have occurred. The fact that a second leak had developed near the bottom of the vessel some time before the explosion occurred, and this combined venting was not capable of preventing catastrophic pressure failure, may indicate that the 1/2 inch vent line may not have been sufficient in any event.

VII. RECOMMENDATIONS

On the basis of the above analysis, certain operating modifications suggest themselves. Some recommendations are outlined below. It should be pointed out that these recommendations are made on the basis of the potential hazard associated with the ion exchange column only. Their impact on other steps of the process were not necessarily considered, and implementation may be precluded if they affect the rest of the process adversely.

1. The use of an alternate source of protons, other than the oxidizing acid HNO_3, should be considered. HCl or H_2SO_4 come to mind.

2. If the process requires the formation of the nitrate salt, then the lowest concentration of HNO_3 consistent with an acceptable elution rate should be used.

3. The temperature of the column should be monitored and provision made for rapid dumping or water flushing in the event of an observed temperature increase.

4. The contact time of the strong acid in the column should be limited and never held stagnant; because exothermic run-away reactions proceed exponentially and it takes some time to develop explosive violence.

5. Adequate vents should be provided. The sizing of appropriate vents may be a problem, since the reaction rate may be variable depending on the exact concentration of degradation products, catalysts, etc. Nevertheless, vents can be designed to protect against all reasonable occurrences.

6 The exposure of the resin to radioactive nuclides should be minimized. It would be appropriate to establish the exact dose tolerable.

7. In view of the corrosion observed in the column involved in the incident, it seems wise to section the column still in use to determine whether corrosion is a common problem or only occurred at the high temperature of the run-away reaction.