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# RUSSIAN STUDIES OF THE SAFETY OF ANION EXCHANGE IN NITRIC ACID

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## ABSTRACT

The Russian literature pertinent to the thermal (chemical) and radiolytic degradation of anion-exchange resins has been reviewed, and some of the results are summarized. The review covers strongly basic resins of both the conventional (divinylbenzene–styrene) and the more recently developed pyridinium types. Thermal and radiolytic degradation causes loss of functional groups (primarily in the conventional resins) and induces reactions in the polymeric structure. Experimental data on gas evolution from resin–nitric acid mixtures are presented, including results obtained from studies of radiation effects.

Process incidents involving anion exchange encountered in the Soviet nuclear processing industry are listed. The most serious of these, a column explosion occurring at the Mayak plant in 1993, is described in considerable detail.

* Retired.

## INTRODUCTION

Synthetic ion-exchange resins have long been used in the Russian nuclear industry. These resins, which are similar to those used in the West, include pyridine-based resins, as well as the more conventional polybenzyltrimethylammonium resins. In this paper the latter are represented by AV-17 resin, while the VP-1AP resin is an example of the former.

The sensitivity of these amines to reaction with nitric acid and other oxidants has been a concern in Russia as in the West, and numerous laboratory experiments have been conducted to study the reactions involved. Several incidents involving pressure or temperature excursions have provided incentives for such studies (see Table 1, and the section below on the 1993 incident). This paper briefly summarizes the results obtained. The Russian authors of this paper have provided additional details on that incident in a recent report that has been issued as a U.S. Department of Energy document (1).



The separation of plutonium, neptunium, etc., from other materials by ion exchange requires fairly strong nitric acid (6-8 *M*) (2). In some systems, such as the processing of $^{238}Pu$, intense ionizing radiation may also be present during ion-exchange separation. As a result, it is necessary to consider not only thermal hydrolysis and oxidation and their effects on the resin, but also radiolysis. All of these effects were investigated in the Russian studies.

## THE 1993 INCIDENT

The most recent safety-related incident involving ion exchange occurred in the Mayak plant, located just east of the Ural Mountains in Siberia, in July 1993. A quantity of $^{238}Pu$ was being purified by anion exchange in a remote radiochemical facility. Figure 1 shows schematically the layout of the process equipment. A water-jacketed column, SN-04, was loaded with 374 g of $^{238}Pu$ and washed with 7.0 *M* nitric acid. Because there was a delay in preparing the elutriant solution, the column was left for approximately 3 h without further activity. At this time a loud noise was heard, and the column was found to have ruptured in an explosive manner. Some of the expelled resin was charred.

**TABLE 1**

ION EXCHANGE INCIDENTS IN RUSSIAN FACILITIES

| DATE, PLACE | INCIDENT | CAUSE |
|---|---|---|
| 2/62, Mayak | Column Explosion (Not Loaded) | 7 M Nitric Acid, 55° to 60°, Relief Valve Closed |
| 4/67, Mayak | Temperature Excursion (Not Loaded) | Temperature Control Cut Off |
| 11/67, Tomsk-7 | Column Explosion (Not Loaded) | 7.5 M Nitric Acid, plus Hydrogen Peroxide & Oxalic Acid. Relief Valve Closed |
| 12/73, Mayak | Column Rupture During 238Pu Processing | Column Heated, Relief Valve Closed |
| 7/93, Mayak | Column Exploded During 238Pu Processing | Column Allowed to Stand and Self-Heat While Isolated (Inadequate Cooling) |



Analysis of the incident showed that (i) the radioactive loading exceeded levels previously used, and (ii) cooling calculations had not been made for this loading. A leak in one of the valves in the system (No. 2728) had necessitated manual control of the process, which allowed the column to be isolated from its relief system. The leak in the valve was compensated for via pressurization of the line, but this action required valve 0443 to be closed. This allowed the column to heat up along its top centerline and dry out. Once a region of the loaded column was dry, exothermic reactions caused additional heating and pressurization of the column, which led to the explosion. Differential thermal analysis of resin recovered from the incident showed strong exotherms, as shown in Figure 2; these are the cause of the accelerated heating and pressurization that were experienced in the incident.

Heat transfer calculations have been made to determine the rate of heating to boiling and dryout in the column. They agree well with the actual observations. Combination of the heating calculations with the results of the thermal studies showed that large amounts of gases would be generated, producing internal pressures in excess of 33 atm. At this point, rupture of the column would be expected.

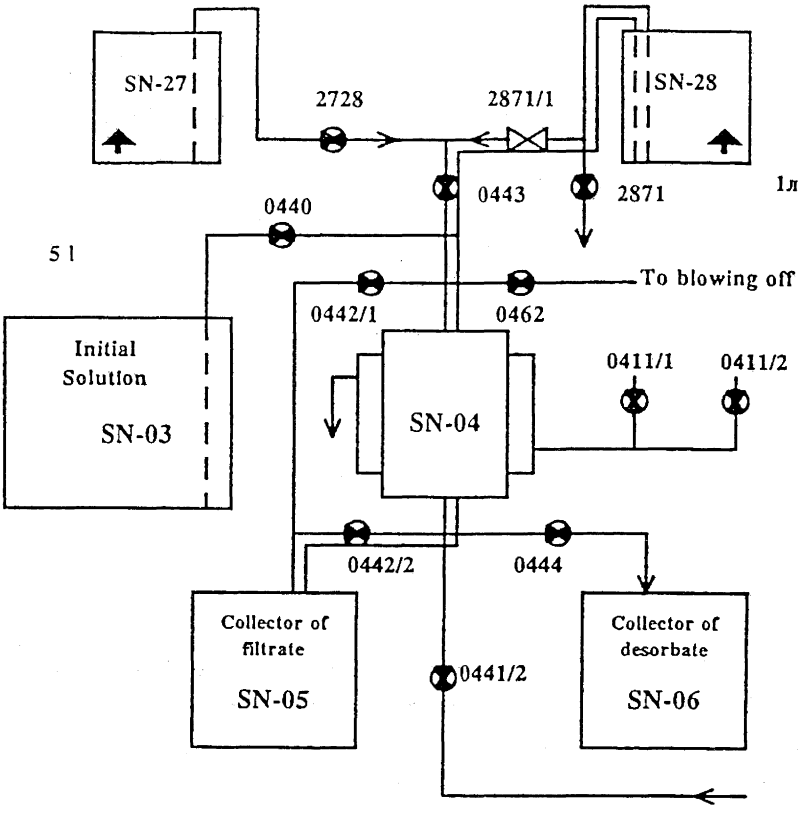


Figure 1:
Equipment Layout
for the Facility 45-03

The apparatus was redesigned and rebuilt to incorporate a rupture disk and thermocouples to detect unacceptable heating. A supply tank containing a desorbent was also added, along with a number of automatic safety systems.

## THERMAL DEGRADATION

Heating can degrade anion-exchange resin, particularly in the presence of oxidants. The first part of Table 2 shows the effects of heating the AV-17 resin in water, in terms

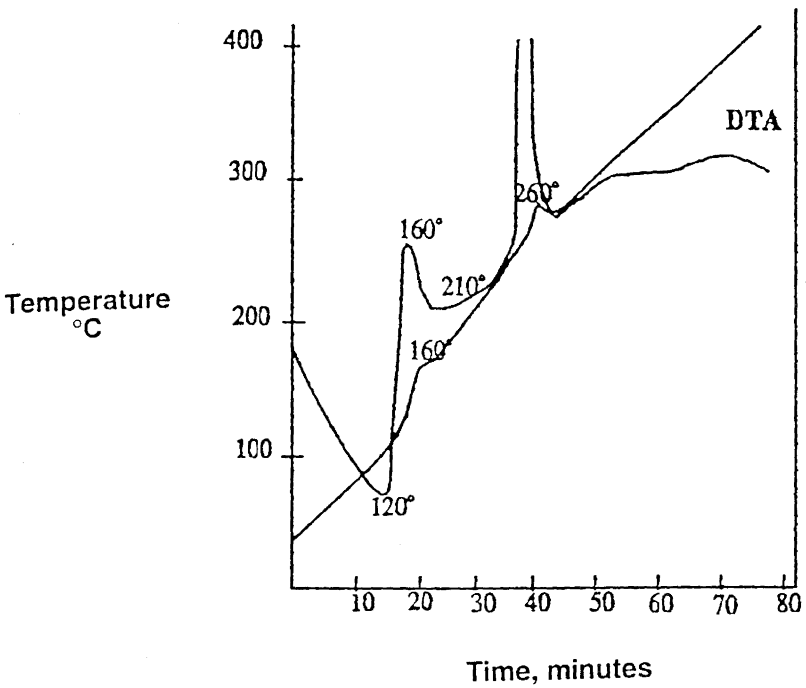


Figure 2:
DTA Scan of VP-1AP Resin
from Column SN-04



of both loss of strong base capacity and formation of methanol (3,4). Methanol is formed by hydrolysis of the amine, leaving behind a weaker base. The second section of the table shows the effect of heating the pyridinium resin (VP-1AP) in water under autoclave conditions (5). This resin is more resistant to hydrolytic damage than AV-17 resin.

## RADIOLYSIS

Ion-exchange resins used for radiochemical separations are generally exposed to ionizing radiation—alpha radiation in particular. The effect of such irradiation on organic resins has been investigated extensively and is reviewed in two articles by Pillay (6,7). The results of some of the Soviet studies are briefly summarized here.

TABLE 2

Thermal Degradation of Anion Exchange Resins

**AV-17 in Water, 100°C**

| Time, Days | Methanol Formed m mol/g | Weak Base Formed meq/g |
|---|---|---|
| 10 | 0.11 | 0.08 |
| 20 | 0.16 | 0.17 |
| 30 | 0.31 | 0.29 |

**VP-1AP in Water**

| T, °C | Heat Time, hr | Capacity, meq/g |
|---|---|---|
| | 0 | 3.9 |
| 230 | 36 | 3.8 |
| 200 | 60 | 23. |



Particular emphasis in these studies was placed on pyridine-based resins, which tend to be more resistant to radiation than conventional substituted benzenes.

Table 3 shows the effect of irradiation on exchange capacity for a conventional ion-exchange resin, the Russian AV-17 (X6), which is similar in structure to Dowex 1 (8). The irradiation was performed on resin in water. After receiving a dose of 3 MGy, the resin had lost more than 75% of its capacity, primarily as the result of the loss of the amine group.

In comparison, Table 4 shows the effect of $^{60}Co$ on the pyridinium resin VP-1AP, which was irradiated in nitric acid solution (9). The loss of exchange capacity, which tracks the loss of resin weight, is much less than the corresponding value for conventional resins. The loss of weight apparently corresponds to loss of fragments of the resin. A study by investigators at the Khlopin Institute followed the weight loss and characterized

**TABLE 3**

LOSS OF EXCHANGE CAPACITY ON GAMMA IRRADIATION ANION RESIN AV-17 (6% CROSSLINKED, $OH^-$ FORM)

| Dose, MGy | Exchange capacity, mol/kg |
|---|---|
| 0 | 4.16 |
| 0.8 | 2.76 |
| 1.0 | 2.44 |
| 1.6 | 1.95 |
| 3.0 | 0.91 |
| 6.0 | 0.19 |
| 8.0 | 0.08 |
| 15.0 | 0.02 |

**TABLE 4**

LOSS OF EXCHANGE CAPACITY ON IRRADIATION ANION RESIN VP-1AP IN 7 *M* NITRIC ACID

| Dose, MGy | Weight Loss, % | Exchange capacity, mol/kg |
|---|---|---|
| 0 | 0 | 3.9 |
| 2 | 3.4 | 3.6 |
| 4 | 14.8 | 3.4 |
| 6 | 28.0 | 3.1 |
| 10 | 35.8 | 2.5 |



the fragments (10). The rapid increase in weight loss above about 3 MGy appears to be associated with large fragments of the polymer matrix breaking away from that matrix (see Figure 3).

The data cited here are consistent with the following interpretations:

1. In the absence of oxidizers, radiation tends to cross-link resins; however, in the presence of oxidizing materials, cross-links are broken and the resin swells.
2. Radiation can introduce new functional groups, such as carboxylic acid groups or (in the presence of nitric acid) nitrated groups, into resins.
3. Vinylpyridine anion resins, particularly those based on 2,5-

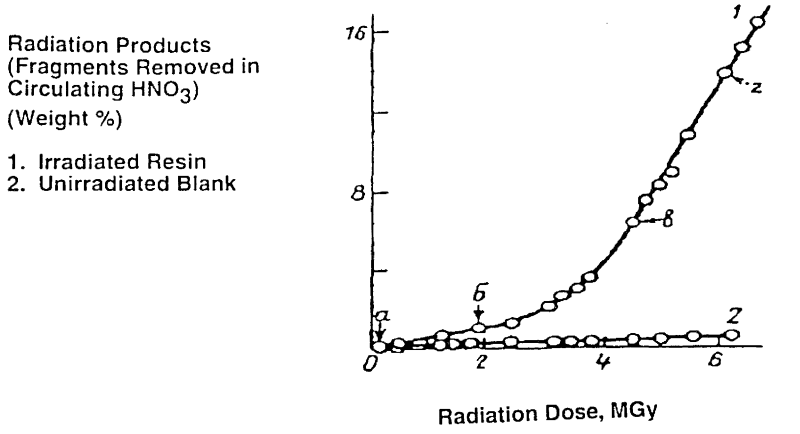


Figure 3:
Radiolytic Decomposition of
VP-1AP Pyridinium Resin
(Ref. 10)



methylvinylpyridine, can withstand radiation doses up to 3 MGy with little damage to functional groups or the resin structure. At higher doses, degradation of the polymer structure causes a loss of material and capacity.

## SAFETY CONSIDERATIONS

Safety concerns in ion exchange are dominated by the release of gases from degraded resins. When caused by an accelerating chemical reaction, such releases can lead to the explosive rupture of equipment. Reaction rates are fastest in resin that has dried.

Gas evolution in VP-1AP resin that has been heated and contacted with nitric acid is shown in Figures 4 and 5. The gas evolution rate is observed to increase with both temperature and acidity. It is noted that these rates in unirradiated resin do not represent an explosive hazard in an open system, even at temperatures up to the boiling point when in contact with 12 *M* nitric acid. In addition, under the conditions normally used for separations (temperature below 75°C, nitric acid concentrations below 8.0 *M*), the solutions are stable and gas evolution rates are low.

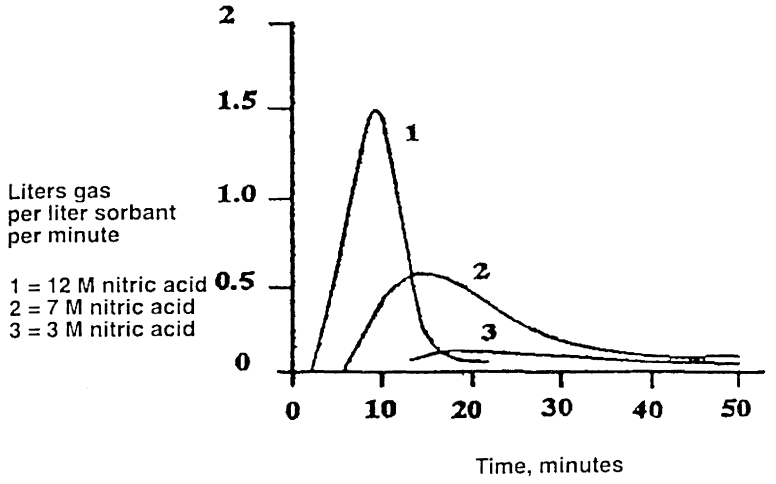


Figure 4:
Evolution of Gas from VP-1AP Pyridinium Resin Heated in Various Nitric Acid Solutions at 100 °C
(Ref. 11)

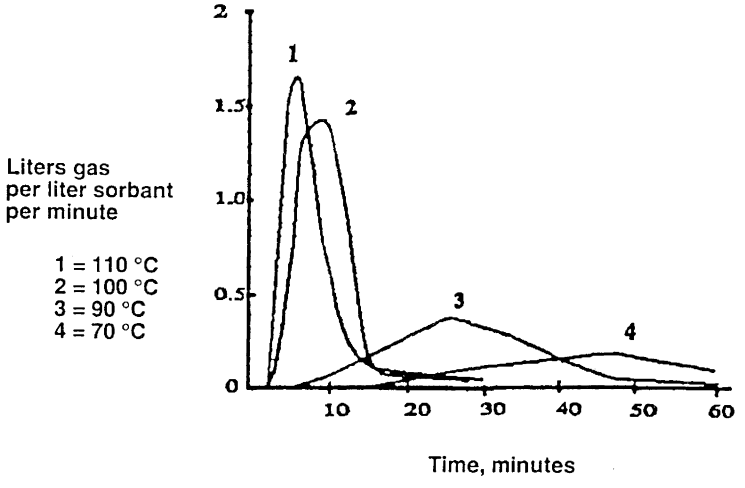


Figure 5:
Evolution of Gas from VP-1AP Pyridinium Resin Heated in 12 *M* Nitric Acid
(Ref. 11)

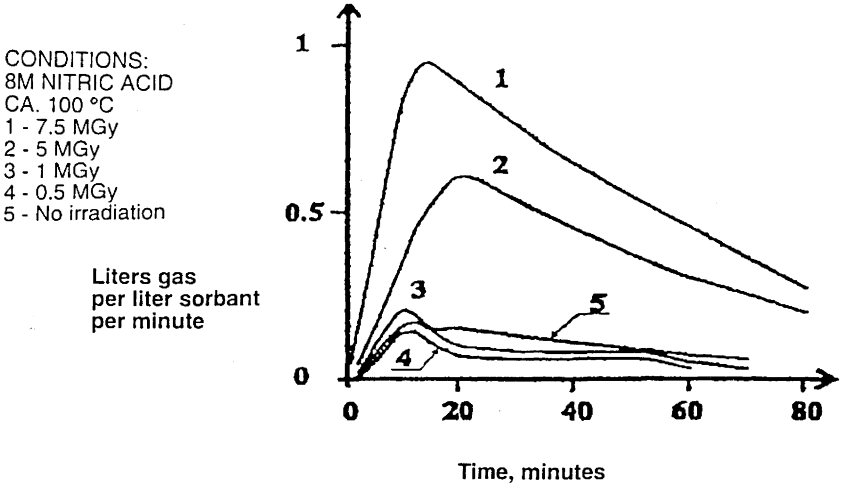


Figure 6:
Gas Evolution in Heated VP-1AP Resin
Following γ-Irradiation
(Ref. 11)

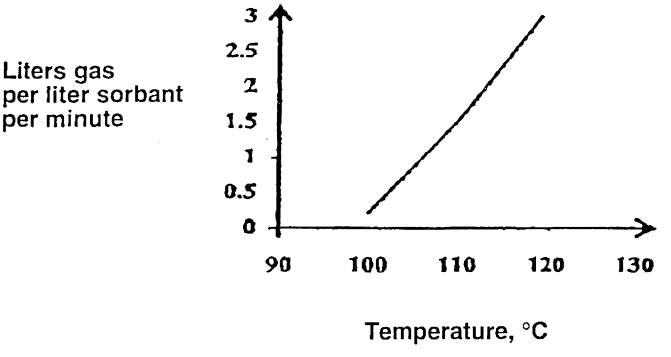


Figure 7:
Maximum Rate of Gas Evolution
On Heating In Closed Vessels
Unirradiated VP-1AP Resin,
Nitrate form in 12 *M* $HNO_3$
(Ref. 11)

The effect of ionizing radiation on thermally induced gas evolution is illustrated in Figure 6, which shows substantial increases in gas evolution for irradiations in the MGy range. Both the gas evolution rate and the total volume of gases involved increase severalfold.

In a closed apparatus, the attainable temperatures are higher and the rate of gas evolution from unirradiated resin increases accordingly (see Figure 7). In combination with radiation effects, very high evolution rates can be observed. Because these reactions are also exothermic, they can self-accelerate in a closed system. In such systems, heat is not removed by evaporating steam.

Because of the concern for self-accelerating reactions in closed systems, an investigation of explosiveness was undertaken (11). The experiments were performed in a bomb apparatus using a high-explosive detonator. The results showed that nitrated resin containing >8 *M* nitric acid could be detonated in the absence of an aqueous phase.



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