

Radiation-Chemical Resistance of Anion Exchangers and Safety of Sorption Processes in Nitric Acid Media: V. Thermochemical Degradation Dynamics of VP-1AP Anion Exchanger

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Abstract—Thermal degradation of VP-1AP anion exchanger and its mixtures with HNO_3 was studied in open vessels at 40 to 260°C. The anion exchanger ignites only after drying and heating to 220–260°C. Heating VP-1AP mixtures with 3–12 M HNO_3 to 100°C is accompanied by gas evolution at a rate of $0.6 \text{ l min}^{-1} (I_{\text{sorb}})^{-1}$. Removal of the aqueous phase from the mixtures at 130–170°C initiates intensive oxidation. It is accompanied by a temperature jump in the sorbent phase and by gas evolution acceleration and can be regarded as thermal explosion. Mixture preheating and irradiation reduce the thermal explosion “onset” temperatures.

Ion-exchange sorption processes are widely used in radiochemistry for spent nuclear fuel processing and radioactive isotope production, water treatment in nuclear installations, as well as at radiochemical enterprises. Ion exchangers typically operate under fairly severe conditions (ionizing radiation, oxidative medium, and high temperatures). These conditions decrease the heat resistance of sorbents when mixed with HNO_3 solutions and eventually initiate oxidation accompanied by heat and gas evolution. The radiochemical production experience suggests that a number of emergency situations are associated with sorption processes. For details on such accidents, as well as for analysis of published data on the heat resistance of sorption systems, see [1, 2]. It turned out that the emergency situations are primarily due to the ion exchanger degradation in a nitric acid medium during processing of actinide solutions, with the heat resistance of the anion exchangers strongly varying with the ion exchanger type.

Russian radiochemical enterprises use primarily VP-1AP anion exchanger. Hence, in this work we studied the heat resistance of VP-1AP anion exchanger in the nitrate form and of VP-1AP– HNO_3 mixtures with the aim to reveal the process conditions at which explosion or fire hazards become real.

EXPERIMENTAL

Experiments on gas evolution under heat treatment of sorption systems up to 100°C were run in a two-necked flask equipped with a reflux condenser and placed on a water bath. The temperature of the mixtures was controlled accurately to within 2°C; the volume of the gases evolved was estimated volumetrically, from the volume of the liquid (concentrated NaCl solution) displaced from the measuring buret. As the zero (reference) point for measuring the volumes of the evolving gases we took the instant when the prepared anion exchanger sample was introduced into the HNO_3 solution heated to the appropriate temperature. The pretreatment of the anion exchanger sample before experiments consisted in its swelling in an HNO_3 solution for several hours. Also, air was removed from the anion exchanger pores immediately before the experiment by heating the swollen anion exchanger samples for 5 min at 100°C in the acid solution of the appropriate concentration.

The heat resistance of the sorption systems above 100°C was studied in stainless steel cells; along with gas evolution, the temperature variation in the sorbent phase was monitored.

Figure 1 shows schematically the setup for study-

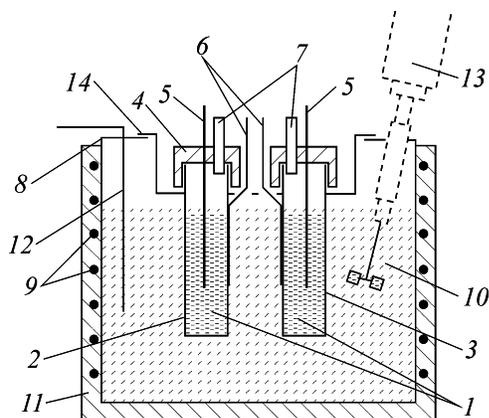


Fig. 1. Diagram of the differential measurement unit of the setup for heat resistance studies: (1) system under study, (2, 3) experimental cells, (4) cell cover, (5) internal thermocouples, (6) external thermocouples, (7) gas outlet tubes, (8) thermostat case, (9) electric heating cells, (10) high-temperature heat carrier, (11) electric and heat insulation, (12) thermocouple of the temperature controller of the thermostat, (13) stirrer, and (14) thermostat cover with a block of experimental cells.

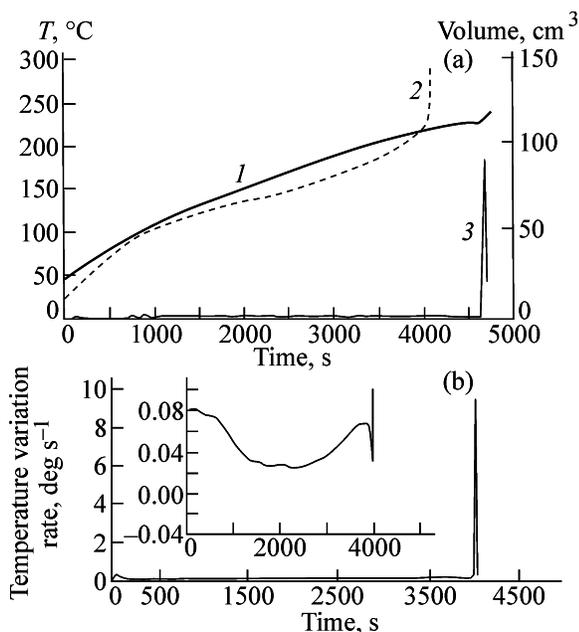


Fig. 2. Time dependences of (a) temperature of the air-dry VP-1AP anion exchanger and of the amount of evolving gases and (b) sorbent temperature variation rate upon heating the VP-1AP sorbent in the NO_3 form in an open vessel. The insert in Fig. 2b shows the scaled plot for the sorbent temperature variation rate in the same coordinates as the main plot. (1) Reaction vessel wall temperature; (2) air-dry VP-1AP sample temperature, and (3) volume of the evolving gases.

ing the heat resistance at elevated temperatures. We used 6 cm^3 cells; control tests on 50 cm^3 sorbent samples were run in a 300 cm^3 open vessel heated in an air thermostat. The experiment control and data recording were computerized.

Based on the temperature vs. time plots for the samples studied, reference sample (air-dry quartz sand), or the reaction vessel wall, we elucidated the conditions at which the sample temperature abruptly changes.

We tested samples of VP-1AP anion exchanger in the nitrate form, both moist and air-dry, in particular, that dried from HNO_3 solutions to the air-dry state, and the sorbent- HNO_3 mixture.

RESULTS AND DISCUSSION

VP-1AP anion exchanger, air-dry or moist.

Moist VP-1AP anion exchanger does not degrade up to 100°C . After moisture removal and further heating of VP-1AP at $200\text{--}210$ ($20\text{--}50 \text{ cm}^3$ samples) and $220\text{--}260^\circ\text{C}$ ($4\text{--}6 \text{ cm}^3$ samples), the temperature in the sorbent phase changed jumpwise by $50\text{--}70^\circ\text{C}$ in parallel with ejection of charred anion exchanger granules from the open vessel. At the moment of the temperature jump, the flame appeared, as recorded with a photodiode.

Figure 2 shows a typical plot of the temperature variation with time in the anion exchanger bulk. Immediately before the temperature jump, the temperature in the anion exchanger ceases to grow for a relatively brief period and may even decrease. It can be assumed that, immediately before the jump in the warming-up rate for the anion exchanger samples, the temperature curve responds to the endothermic decomposition of HNO_3 . On attaining the thermal explosion onset temperature, the acid decomposition tends to accelerate, and the amount of NO_2 becomes sufficient for rapid exothermic oxidation of the anion exchanger.

It should be noted that there was no evidence of the sorbent degradation at heating of the anion exchanger before the onset of the exothermic process. This finding was also supported by our thermogravimetric studies [3].

Our measurements showed that, at the time of the temperature jump, the bulk anion exchanger exhibits a significant temperature gradient, as seen from the temperature curves shown in Fig. 3. Exothermic process is initiated in the local zone(s) of the ion exchanger characterized by the worst heat removal con-

ditions (in deep-lying layers). As the heat conductivity of the dry ion exchanger is low, the temperature gradients are significant even for small volumes of the ion exchanger.

Condensed reaction products are charred anion exchanger granules sintered into black caked fragments, plus a minor amount of a black tarry liquid.

The appearance of a flame, as well as the character of the exothermic processes initiated by heating the NO_3 form of VP-1AP anion exchanger, suggest that these processes can be regarded as thermal explosions. The primary prerequisites to their initiation are the drying and heating of the anion exchanger to the appropriate onset temperatures.

Thermal explosion of the NO_3 form of VP-1AP anion exchanger occurs at very high rates; at the thermal explosion moment, the anion exchanger temperature increases at a rate of $7\text{--}10 \text{ deg s}^{-1}$. The fact that the thermal explosion products contain nonoxidized and partly oxidized anion exchanger granules even with 4 cm^3 samples suggests that, because of a high degradation rate, the reaction vessel content is blown out at a time when the bulk of the anion-exchanger has not yet fully reacted.

Mixtures of the NO_3 form of VP-1AP anion exchanger with HNO_3 solutions. Heat treatment of VP-1AP anion exchanger samples in 4 and 7 M HNO_3 solutions at 40 and 60°C is not accompanied by gas evolution. Noticeable amounts of gaseous products appear only at heating temperatures as high as $95\text{--}100^\circ\text{C}$. Studies of gas evolution upon heating the VP-1AP anion exchanger samples (Fig. 4) show that the gas evolution rates are significant [on the $0.2\text{--}0.6 \text{ l min}^{-1} (I_{\text{sorb}})^{-1}$ level] in the initial heat-treatment period (first $\sim 20\text{--}30$ min). Further heating decelerates evolution of gaseous products to $0.01\text{--}0.02 \text{ l min}^{-1} (I_{\text{sorb}})^{-1}$, and within 3–4 h gas evolution virtually ceases. At the HNO_3 concentrations within 4–12 M, the maximum gas evolution rates linearly increase with increasing HNO_3 concentration in the aqueous phase. "Active" gas evolution can be due either to oxidation of the products of the anion exchanger synthesis or impurities contained in the sorbent that are more reactive than the sorbent matrix, or to air release from the resin pores. The sorbent itself is very stable under these conditions.

The anion exchanger samples pretreated with 4–12 M HNO_3 solutions for 100 h at 100°C and washed to remove water-soluble degradation products exhibit the same gas evolution trends as the mixtures with the initial sorbent. However, the volumes of the gaseous

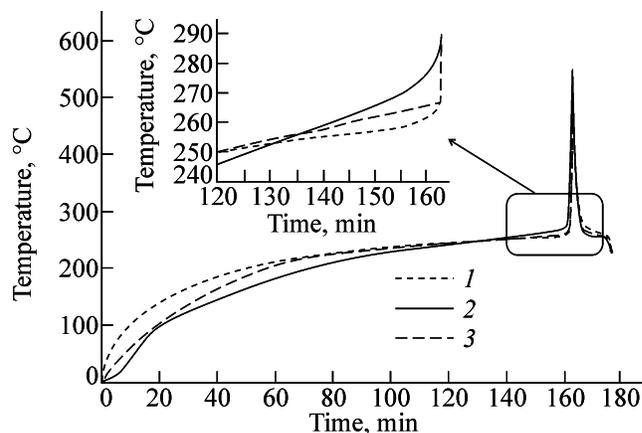


Fig. 3. Temperature gradient in the bulk of the VP-1AP sorbent in the NO_3 form upon heating in an open vessel: (1) cell wall temperature, (2) VP-1AP sample temperature measured at the cell center (separated from the bottom by 7 mm), and (3) VP-1AP sample temperature measured at a distance of 3–4 mm from the cell wall (separated from the bottom by 7 mm).

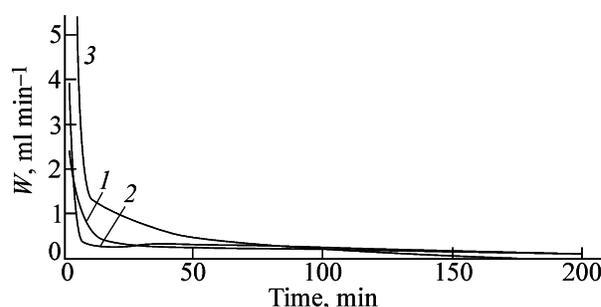


Fig. 4. Variation of the gas evolution rate in heat treatment of VP-1AP anion exchanger in HNO_3 solution of the concentration (1) 4, (2) 7, and (3) 12 M. Volume of the swollen anion exchanger 10 ml.

products and the gas evolution rates are significantly lower in this case [under $0.01 \text{ l min}^{-1} (I_{\text{sorb}})^{-1}$]. Thus, the heat resistance of the anion exchanger increases after washing off its degradation products.

At temperatures above 100°C , the exothermic processes initiated by heating the anion exchanger– HNO_3 mixtures proceed similarly to air-dry and moist samples.

Figure 5 presents typical plots of the temperature variation on heating the anion exchanger mixtures with 3–12 M HNO_3 .

Upon drying, a portion of HNO_3 and NO_2 remains in the micropores of the anion exchanger, and the latter gets "enriched" in the oxidant. This is responsible for certain distinctions in the initiation of the exothermic processes in mixtures compared to the air-dry anion exchanger in the NO_3 form.

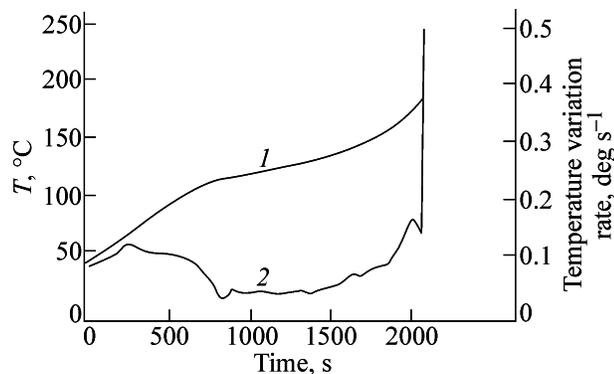


Fig. 5. Temperature variation with time upon heating the VP-1AP anion exchanger–HNO₃ mixtures in open vessels: (1) temperature of the anion exchanger–HNO₃ mixture and (2) temperature variation rate (for curve 1).

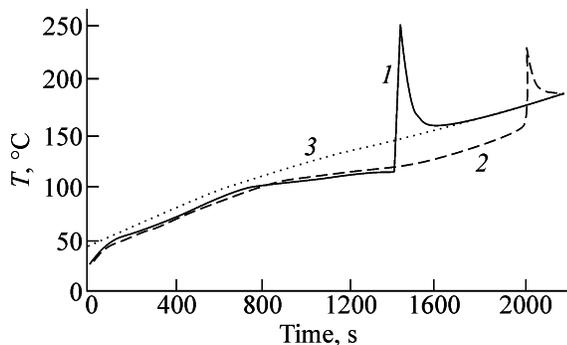


Fig. 6. Temperature variation with time in the irradiated (5 MGy) and reference samples of VP-1AP anion exchanger when heated in open vessels: (1) temperature of the irradiated sample, (2) temperature of the reference sample, and (3) temperature of the cell wall.

Above 100°C, the endothermic vaporization of the aqueous phase in mixtures occurs in parallel with oxidation of the anion exchanger with HNO₃ and NO₂, which is accompanied by evolution of gaseous products. Evidently, oxidation is accompanied by heat release, but the endothermic process prevails as long as the sorbent granules are separated by the aqueous phase. At a certain moment at 130–150°C, the amount of the heat released begins to exceed that of the heat lost by the aqueous phase vaporization. The temperature of the mixture tends to rise to the “onset” temperature of the thermal explosion, which by 20–50°C exceeds that of the exothermic processes. The exothermic process initially proceeds in a local volume of the mixture, at a considerable distance from the external heating source, whereupon it spreads throughout the mixture bulk.

Thermal explosion was recorded upon heating the mixtures of the NO₃ form of the anion exchanger with

3–12 M HNO₃. It should be noted that increase of the HNO₃ concentration in the mixture tends to reduce the onset temperature of exothermic processes. The minimal “onset” temperature of thermal explosion recorded for a mixture with 12 M HNO₃ was 127°C. It should be noted that keeping this mixture at 120 ± 5°C for 25 h was not accompanied by self-heating.

The influence exerted by the HNO₃ concentration can be explained by increase in the amount of the oxidant occurring in the sorbent phase, which results in a more profound oxidation of the sorbent matrix and formation of a larger amount of degradation products and active centers in the sorbent matrix; this is responsible for the reduced onset temperature of exothermic reactions (130–150°C).

The condensed reaction products are both variously colored (from the initial color to black) granules and caked charred lumps.

Preheating the anion exchanger in HNO₃ solutions tends to reduce the onset temperature of exothermic processes in mixtures, which initiates thermal explosions. In particular, for mixtures with 7 M HNO₃ preheated for 100 h at 40, 60, and 100°C the onset temperatures of exothermic processes are estimated at 185, 180, and 130°C, respectively. In mixtures with 12 M HNO₃ preheated for 100 h at 100°C, thermal explosion occurs at 120°C.

Figure 6 illustrates how irradiation affects the thermochemical degradation dynamics, with VP-1AP–7 M HNO₃ mixture irradiated at a 5 MGy dose as an example. It is seen that, in the irradiated mixture, thermal explosion occurs at a lower temperature compared to nonirradiated mixture. It was found that, after irradiation with an external γ -source at a dose of up to 5 MGy, thermal explosion in mixtures occurs at temperatures as low as 114–116°C. This is preceded by exothermic processes initiated in the irradiated mixture at 80–90°C, which are accompanied by gas evolution. The condensed products of degradation of irradiated and nonirradiated mixtures differ in the external appearance as well. In the former case, the products are, essentially, black powders with different particle size (in particular, finely divided powder, dust), and the anion-exchanger granules degrade virtually completely. In the case of nonirradiated mixture, these are black, charred granules which preserved their form plus partially caked lumps.

The fact that the heat resistance of the irradiated mixtures decreased to such a significant extent can be attributed to the radiolysis-induced formation of easily oxidizable degradation products. Also, additional

“enrichment” of the mixture with NO_2 yielded by HNO_3 radiolysis cannot be ruled out.

However, after washing the irradiated sorbent with water, its mixtures with HNO_3 ignite at the same temperatures as the nonirradiated sorbent. Hence, the heat resistance of the ion exchanger is strongly affected by the radiolysis products.

Thus, studies on thermal degradation dynamics of the NO_3 form of the VP-1AP anion exchanger and its mixtures with HNO_3 suggest that heating them to temperatures close to 100°C in open vessels in the presence of the aqueous phase presents no hazard, provided that the forming gases are removed.

The NO_3 form of the VP-1AP anion exchanger can ignite if two conditions are met simultaneously: the anion exchanger granules are not separated by the aqueous phase (drying) and the ignition temperature is attained. In the anion exchanger– HNO_3 mixtures, oxidative processes occur even without drying, as suggested by evolution of gaseous products, but these processes acquire the character of a thermal explosion only when the two above-mentioned conditions are met.

It is highly probable that these conditions will be met when the sorbent phase contains radionuclides characterized by significant heat evolution capacity. In this case, even without external heating, the anion exchanger– HNO_3 mixtures within a certain period could get dried and heated to thermal explosion “onset” temperatures, which are not so high. This does not require drying and warming-up of the entire sorbent bulk; for ignition and development of exothermic oxidation processes, it is sufficient that a fairly small layer (or zone) of the sorption mixture get dried.

This is exactly the situation dealt with at the Mayak Production Association, where the plutonium column was damaged. We suggested in [2] that drying of the upper layer of the column, containing about 100 g of ^{238}Pu , was responsible for the warming-up

of the sorbent to 109°C and its conversion from the moist to air-dry state within 1.5–2 h and further warming-up to 160 – 200°C (within 30–40 min, as suggested by thermophysical calculations) and thermal explosion.

Our previous studies [2–4] showed that exothermic oxidative processes can start below 160°C , and in the case of sorbents irradiated to 5 MGy, even below 100°C . The sorbent temperature sensor can give no response because of a large distance separating it from the warming-up site and low heat conductivity of the dry anion exchanger. To ensure fire and explosion safety of the processes utilizing VP-1AP anion exchanger, the highest priority in preventive measures should be assigned to monitoring of the aqueous phase level above the sorbent.

In the presence of sorbed plutonium hexanitrate complexes, the anion exchanger should get “enriched” with the oxidant, thus substantially complicating the situation. The influence of the sorbed hexanitrate complexes on the safety of the anion-exchange processes is beyond the scope of this study, though, in our opinion, this is a very urgent problem.

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