

# Prospects for Using Weakly Dissociated Ion Exchange Resins in Special Water Treatment Systems at VVER-Based Nuclear Power Plants for Reducing the Volume of Radioactive Waste Generated

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**Abstract**—Minimizing the amount of liquid radioactive waste generated during operation of nuclear power plants is among the important problems that have to be solved to enhance the nuclear power industry safety and economic indicators. For this purpose, it is proposed that the ion-exchange materials applied in the active water treatment systems of new power units equipped with VVER-type reactors be used only once (without regenerating them). In so doing, measures should be taken to dramatically reduce the consumption of ion-exchange resins by using materials having a higher ion-exchange capacity than the currently used universal ion-exchange resins. In addition, it is necessary to improve the ion-exchange treatment technology to achieve a higher extent of filling sorbents with the target components, primarily, with radionuclides to be buried. In this context, the properties of weakly dissociated ion-exchange resins made on the basis of acrylic acid and divinylbenzene copolymers are considered. The selected line of research is theoretically substantiated, and the results from laboratory investigations on treating model flows are presented, including those for elaborating the regeneration modes of weakly dissociated ion-exchange resins, the use of which makes it possible to fix biologically dangerous components in mineral-like structures with the minimal amount of compounds to be buried. It is shown that sequential subjecting of alkali flows contaminated with radionuclides to ion-exchange treatment in the carbonaceous resin–sulfonic cation resin system results in that the solution becomes dealkalized under the effect of carbonaceous resin, after which cesium radionuclides are removed by means of sulfonic cation resin. Such redistribution of functions helps to decrease the concentration of alkali-metal and ammonium ions that compete with  $^{134}$ ,  $^{137}$ Cs radionuclides for sorption vacancies, due to which the sorbent to be buried is filled with radioactive substances to the maximal extent, thus resulting in a smaller amount of generated radioactive waste.

**Keywords:** liquid radioactive wastes, active water treatment, carbonaceous resin, weak-base anion resin, deamination, boron-containing water

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Application of the technology for boiling down mixed salt flows (spent decontaminating compositions, regenerating solutions from active water treatment systems, steam generator flushing water, etc.) that was adopted in the early 1960s made it possible to set up conditions for safe and compact storage of wastes at the sites of nuclear power plants (NPPs) for their design service life. However, the situation has been changed after law [1] and legislatively supported directives on the radioactive waste lifecycle final stage were adopted [2–6]. According to law [1], limits have been imposed on the waste storage time at NPPs. Moreover, boiled down radioactive media in which the content of so-called ballast salts poorly compatible with the cement matrix is several orders of magnitude higher than the concentration of radionuclides are a source of additional radiation risks and unreasonably high costs [7] both in preparing and burying these wastes.

At present, application of nonreusable ion-exchange filter charges is proposed in new NPP designs for improving the liquid radioactive waste (LRW) treatment technology [8]. In the opinion of the developers, this measure will make it possible to radically decrease the amount of radioactive substances to be buried. According to the results of our investigations, the amount of ion-exchange materials that would be consumed in the adopted modes of operation in case of using them only once (without regeneration) is a factor of 5–7 more than the amount of radioactive salts that can be separated from spent regenerating solutions by evaporation or crystallization.

Below, we present data on decreasing the amount of radioactive waste and optimizing its content from NPPs through the use of commercially available weakly dissociated ion-exchange resins in special water treatment (SWT) systems.

**Deamination of water flows.** Almost all flows arriving to SWT plants contain ammonia, and it is particularly its concentration that determines the service life of cation resins. At present, ammonia–morpholine or ammonia–ethanolamine water chemistry has been adopted in all NPP power units equipped with new-generation VVER reactors in accordance with the valid regulatory documents for the secondary coolant circuit [9–12]. In view of this, the media arriving to the condensate polishing plant (CPP) and to the steam generator (SG) blowdown water purification system contain ammonia and monoethanolamine.

Radioactivity accumulates in the CPP filters at existing NPPs due to the following two factors:

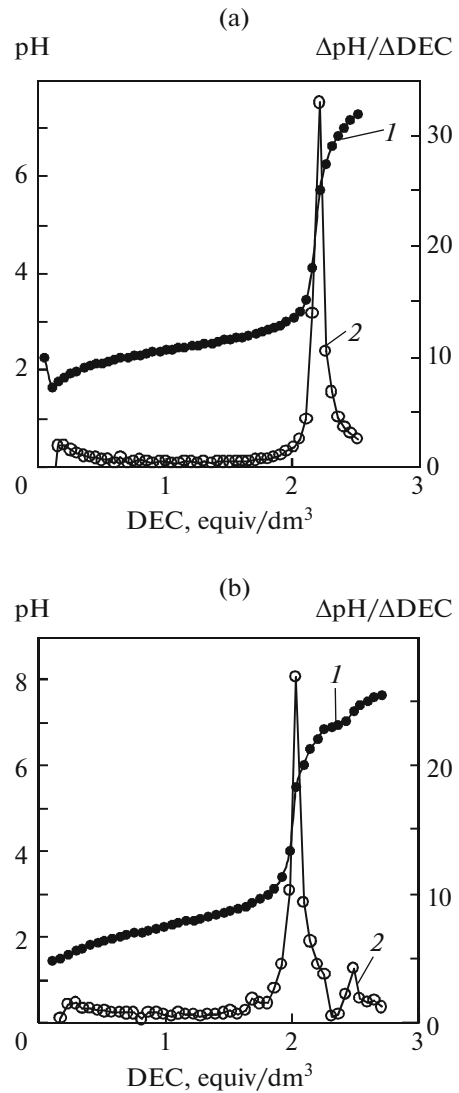
(1) Eddy-current-based systems for examining the state of SG heat-transfer tubes have been put in use at Russian NPPs. If the examination results indicate that the permissible discontinuity criterion is exceeded, a decision to blank off the faulty tube is taken. The blank-off criterion is defined according to [13], and its value corresponds to 70% of the tube wall thickness for the commissioned power units. Owing to this measure, a significantly smaller amount of primary-to-secondary leaks in SGs has been achieved at the operating NPPs.

(2) Owing to replacement of the turbine condenser tube systems' material by stainless steel or titanium, a lower amount of cooling water inleakages in the condensers has been secured. It should also be noted that the available field experience points to the possibility of power unit operation with the SG feed water H-cationated sample conductivity ( $\chi_H$ ) below its standardized value when the CPP is either disconnected or operates with degraded throughput capacity.

Selective separation of ammonia and monoethanolamine, due to which a much longer service life of regular sulfonic cation resins can be obtained and the amount of spent regenerating solutions can be kept to a minimum, can be implemented by subjecting the flows to prefiltering by means of passing them through carbonaceous resins whose affinities are inverted with respect to the affinities of sulfonic cation resins that are regularly used at NPPs [14–16].

To verify this working hypothesis, we carried out investigations on subjecting chloride solutions of salts to deamination by means of Tokem-200 carbonaceous resin.

Figure 1 shows a typical pattern of the filtrate pH value as a function of the resin dynamic exchange capacity (DEC). The integral dependence is essentially the classic titration potentiogram. Therefore, the position of the peak on the differential dependence corresponds to the point at which the weak acid (the cation resin ionogenic groups) and base (amine compound) mutually neutralize each other. The fundamentals and specific features of the potentiometric resin testing method are described in [17, 18].



**Fig. 1.** (1) Integral and (2) differential dependences of the filtrate pH value on the Tokem-200 cation resin dynamic exchange capacity in absorbing (a) ammonia and (b) monoethanolamine at a filtration rate of 25 m/h.

It follows from the obtained data (see Fig. 1) that the Tokem-200 resin exchange capacity is approximately 3.0 equiv/dm<sup>3</sup> for ammonia and 2.6 equiv/dm<sup>3</sup> for monoethanolamine, which is almost a factor of two higher than the total dynamic exchange capacity of sulfonic cation resins.

The amount of acid required to fully recover the Tokem-200 carbonaceous resin properties during its regeneration is several times smaller than that for the regularly used sulfonic cation resin (Fig. 2), and, accordingly, a smaller amount of secondary waste will be generated.

Thus, in our opinion, the use of weak-acid cation resins as a charge for the prefilter in the regular active water treatment system allows a longer service life of

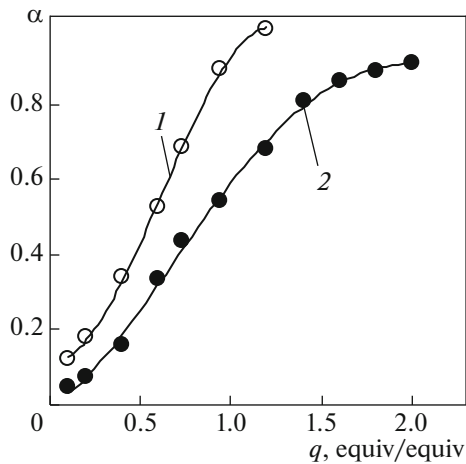


Fig. 2. Effect of nitric acid specific consumption  $q$  on the dynamic exchange capacity recovery ratio  $\alpha$  of (1) acrylate (Tokem-200) and (2) sulfonic (KU-2-8) cation resins.

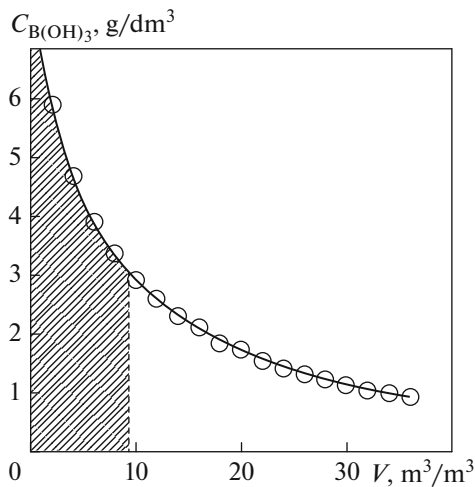


Fig. 3. Variation of boric acid concentration  $C_{B(OH)_3}$  in the filtrate of spent AV-17-8 anion resin during its hydrolysis versus the flushing water specific volume  $V$ .

sulfonic cation resins to be achieved along with obtaining higher concentration (specific activity) of fission products and activated corrosion products contained in them. In this case, the approach according to which the ion-exchange materials are used only once (without regenerating them) can be regarded as a really economically efficient technique for optimizing the LRW processing cycle at NPPs [8].

In addition, good prospects seen in the use of this method stem from the following factors. Since the macrochemical composition of water flows existing at VVER-based NPPs is predominantly represented by potassium, lithium, and ammonia ions and by monoethanolamine and morpholine, it is unlikely that any significant amounts of radioactive cesium can accu-

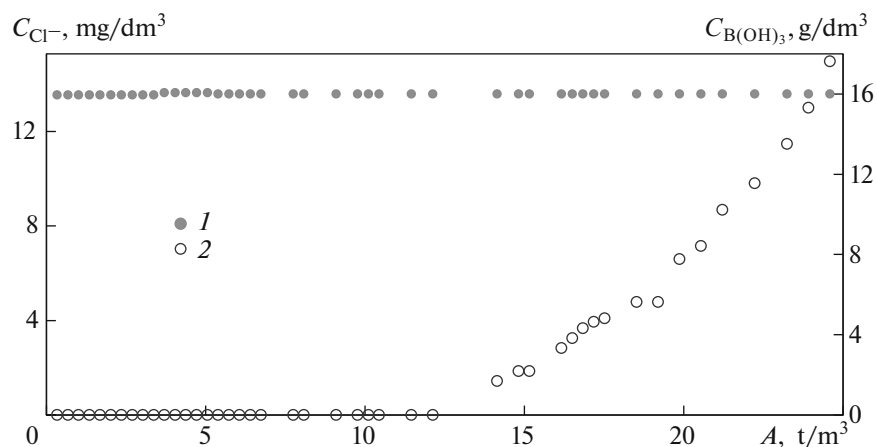
mulate in the weak-acid cation resin. The radionuclides of alkali-earth and nonferrous metals can be absorbed, even though with moderate efficiency, by carbonaceous resin and form strong complex compounds with ionogenic groups. However, if some arrangements are even taken for removing them from the cation resin in the lean regeneration mode at  $q = 1.0$  equiv/equiv (see Fig. 2), this will be performed with extremely poor efficiency.

Although the outspoken hypothesis needs confirmation by carrying out special investigations, there are grounds to believe that regeneration solutions of weak-acid cation resins will fall under the category of nonradioactive chemical waste, which can be reprocessed separately from LRWs by using less expensive methods, e.g., by oxidizing amine compounds with hypochlorites. In principle, such an approach is in good consistency with the Rosenergoatom Concern's concept that stipulates separation of flows.

During its long-term operation, H-form weak-acid cation resin accumulates quite significant quantities of activated corrosion products. The question of whether or not it is advisable to bury these expensive cation resins still remains to be answered, the more so that relatively weak acids as sulfanic and oxyethylidenediphosphonic (OEDP) acids are suitable for regenerating them, the use of which opens the possibility in principle to fix desorbed radionuclides in the form of mineral-like structures. Thus, in the case of using sulfanic acid, oxidation of amine groups with chlorinated lime yields gypsum and chalk, which behave as matrix materials for activated corrosion products. OEDP-based regenerating solution can be neutralized with lime milk with subsequently subsection of the phosphate groups to thermal hydrolysis in alkali medium, which will facilitate generation of water-resistant apatite-like structures.

Apparently, application of these technologies can be regarded as a promising alternative to the regenerationless method of treating weak-acid cation resins [19].

**Purification of boron-containing flows.** In accordance with [8], the approach according to which strong-base anion resins are used only once in the boric acid purification systems makes it possible to completely exclude ingress of boron-oxygen compounds into the reservoirs for temporarily storing radioactive concentrates. However, the authors of [8] do not take into account that the boric acid salts absorbed by anion resin are subjected to hydrolysis, due to which they will inevitably transfer into a soluble form when the spent anion resin undergoes backwashing and hydraulic reloading. It follows from the data shown in Fig. 3 that up to 35 kg  $H_3BO_3$  per cubic meter of ion-exchange resin may enter into transport water at the design flowrate of water for hydraulic reloading (the hatched area), and these borates will be forwarded to the LRW storage reservoirs.



**Fig. 4.** Concentrations of (1)  $C_{B(OH)_3}$  and (2)  $C_{Cl^-}$  in the filtrate versus the specific amount of boric acid  $A$  in purifying technical boric acid solution and at a specific ion-exchange resin load of  $20 \text{ m}^3/(\text{m}^2 \text{ h})$ .

The only way in which the ingress of oxygen boron compounds into NPP radioactive wastes can be prevented or radically decreased is to use low-base anion resins that do not contain hydroxyl groups, which cannot in principle absorb boric acid from process solutions. This latter circumstance is of fundamental importance because it has been proven that anion resins in hydroxyl form are able to absorb undissociated boric acid according to the chemisorption mechanism [20, 21].

In neutral solutions, the sorption of anions by weak basic ion exchangers is provided by the deprotonated of water. In acidic solutions, the protonation of group is carried out by protons of the solution with compensation of the group charge by anions. At the same time weak boric acid at  $\text{pH} < 5$  is in molecular form and it is not involved in the processes of ion exchange.

The process boric acid solutions removed from the reactor plant are predominantly neutral or alkaline in nature, which is governed by the availability of alkali metal ions (primarily  $\text{Li}^+$  and  $\text{K}^+$ ) and ammonia ions in them, the charges of which can be partially compensated by anion forms of oxygen boron compounds. The buffer properties of the solutions arriving for purification facilitate the use of weak-acid cation resin.

Figure 4 shows data on the variation of filtrate concentration when technical boric acid solution is purified by treating it with a combination of S-104 H-form carbonaceous resin, KU-2-8 H-form sulfonic cation resin, and Purolite A-100 weak-base anion resin with methylene dimethyl amine groups in the form of free base with the equal volumes of filtering beds.

It can be seen that the proposed ion-exchange system is almost inert with respect to boric acid while ensuring a high separation ratio of strong acid anions  $\text{Cl}^-$ . Breakthrough of  $\text{Cl}^-$  anions was recorded even before cations began to break through. This may only

take place if ionogenic groups of weak-acid cation resin (the exchange capacity of which under the considered conditions is, as a minimum, commensurable with that of sulfonic cation resin) are involved in the process of removing cations from the buffer solution that are contained in it. Thus, the strong-acid cation resin plays the role of a fine purification filter in this pair by predominantly absorbing microamounts of cations (including, primarily, cesium radionuclides), the breakthrough of which through weak-acid cation resin is unavoidable, a feature due to which the obtained boric acid concentrate quality complying with the standard requirements is ensured.

Thus, the following conclusion can be drawn: application of weakly dissociated ion-exchange resins in active water treatment systems of NPPs in a goal-seeking manner makes it possible to achieve a significantly smaller amount of radioactive concentrates and to optimize their composition without the need of making radical changes in the currently used process circuit arrangements.

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