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Analysis of Cation Resins for WWER-1000 Reactor Coolant Purification Filters

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Abstract

The paper considers filtration equipment used for coolant purification in WWER-1000 reactors, which plays an important role in providing an optimal water-chemical regime, reducing radioactive contamination of equipment and extending the service life of reactor components. The operating features of ion-exchange filters are investigated and directions for their modernization are determined. The design and characteristics of cation exchange filters are analyzed and key factors affecting their efficiency are highlighted, including the replacement of ion-exchange resins and optimization of the regeneration process. A comparative analysis of nuclear-grade ion-exchange resins, such as Lewatit MonoPlus S 108 H, Purolite® NRW100 and DIAION™ SKN1, is carried out, and their suitability for cation exchange filters modernization is evaluated. Cation exchange filter parameters are calculated for different ion-exchange resins, such as operational exchange capacity, intervals between regenerations and acid amount for filter regeneration. It was determined that Lewatit MonoPlus is the optimal resin for cation exchange filters due to its higher exchange capacity (2 g-eq/L), longer intervals between regenerations (22 regenerations per year) and lower cost.

Keywords: WWER-1000 reactor; coolant; purification system; cation exchange filter; regeneration; ion exchange resin.

1. Definition of the problem to be solved

Nowadays, nuclear power units with WWER-1000 reactors play an important role in electricity production in Ukraine. The efficiency and safety of their operation largely depend on providing an optimal water-chemical regime. The primary circuit of the power unit, where the coolant circulates, operates under conditions of high temperature and pressure, as well as ionizing radiation, which creates significant technical challenges, including corrosion of structural materials, wear of mechanical equipment, formation of deposits in the core, damage to fuel rod cladding, and contamination of reactor systems [1], [2]. Consequently, the urgent tasks are preventing corrosion, minimizing the radioactive deposits, and ensuring the stable reactor performance. The water-chemical regime solves these challenges while reducing radiation exposure to personnel by limiting the formation of radioactive aerosols and deposits. This simplifies equipment maintenance, lowers radiation doses, minimizes radioactive emissions, and supports environmental protection [3], [4].

At Ukrainian nuclear power plants with WWER-1000 reactors, a mildly alkaline, reducing, ammonia-potassium water-chemical regime with boric acid regulation is used. The water in WWER reactors serves a dual purpose: it acts as a coolant, transferring heat from the reactor core, and as a neutron moderator for nuclear fission reactions. Boric acid (H_3BO_3) is used to ensure reactor controllability. The acid content in the coolant depends on the core neutron physical characteristics. The primary reagent for maintaining the required pH level in the primary circuit is potassium hydroxide

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(KOH), which creates a mildly alkaline medium to minimize corrosion of the primary circuit metal. To establish a reducing medium, ammonia (NH_3) is added to the coolant to provide an optimal content of dissolved hydrogen, which appears as a result of its radiolytic decomposition. This helps suppress the formation of radiolytic oxygen and prevents corrosion of stainless steel [3]–[6]. Consequently, the feedwater for the primary circuit is prepared by deionization, degassing and removing residual oxygen by dosing hydrazine hydrate ($N_2H_4 \cdot H_2O$).

Special attention is given to providing the concentration of corrosive impurities (oxygen, chloride, fluoride, and sulfate ions) below permissible levels. Reactor water treatment systems SVO-1 and SVO-2 are used to purify the coolant from dispersed corrosion products and radionuclides, and to promptly adjust the water-chemical regime parameters in case of deviations from specified values [3]. These systems must be appropriately designed and operated to ensure effective coolant purification.

2. Analysis of recent publications and research works on the problem

Issues related to preventing corrosion in primary circuit equipment and coolant treatment are the subject of numerous studies [5]–[12]. Significant attention is given to the system for purifying the organized leakages and blowdown water from the primary circuit of WWER-1000 reactors, as well as improving the performance of its main components – ion-exchange filters, which are responsible for deep removal of dissolved ionic impurities, elimination of excess alkalinity, and some colloidal and finely dispersed suspended solids [6]–[8].

The productivity of the coolant purification system, i.e., the volume of coolant flowing through the filters per time unit, typically amounts to only a few percent of the total coolant flow through the reactor core. A portion of the coolant flow, known as blowdown, is continuously or periodically removed from the primary circuit, passes through cooling and filtration systems, and then the purified coolant is returned to the circuit. According to [6], [13], the nominal productivity of the purification system can vary in the range from 10 to 30 m^3/h, allowing a flexible response to changes in coolant quality and purification needs [6], [13].

The efficiency of the purification process is evaluated by purification coefficients, which indicate how many times the content of a specific impurity decreases after passing through the filtering element. For modern ion-exchange filters, these coefficients can reach 90–99% or higher for most dissolved ionic impurities. The efficiency of mechanical filters depends on their design and is characterized by the minimum particle size they can retain with high effectiveness [13].

Ion-exchange resins and other filtering materials sorb and accumulate significant amounts of radionuclides during operation. These are primarily corrosion activation products from structural materials (Co-58, Co-60, Mn-54, Fe-59) and fission products from nuclear fuel that may enter the coolant (Cs-137, I-131) [9], [12]. High levels of accumulated activity require the implementation and strict adherence to special radiation safety measures during all stages of system operation, maintenance, and especially during the replacement of spent filtering materials [1].

Radioactive substances accumulated on the filters generate heat due to radioactive decay. This residual heat release can significantly heat ion-exchange resins and other filtering materials, particularly when coolant flow stops through the filter or during their unloading. Therefore, resins must be heat-resistant, or systems and procedures must be provided to ensure their cooling [9].

Spent ion-exchange resins and mechanical filter elements are classified as radioactive waste. Their collection, transportation, processing, conditioning, and long-term storage or disposal must be carried out according to the special procedures and regulatory requirements to minimize impacts on personnel and the environment [1], [11].

Over time, as power units are operated and because of the increased requirements and safety standards for coolant purification efficiency, the reactor purification systems need modernization. Equipment is physically aging, while water treatment and purification technologies continue to develop [8], [9]. Therefore, this article is devoted to analyzing the current state of ion-exchange materials and justifying directions for ion-exchange filter modernization, which are the key elements of purification systems.

3. Formulation of the goal of the paper

The aim of this study is to determine the directions for modernizing ion-exchange filters of the coolant purification system of the WWER-1000 reactor, conduct a comparative analysis of known nuclear-grade cation resins, and calculate the parameters of cation exchange filters when using different types of resins.

4. Presentation and discussion of research results

4.1. Directions for ion-exchange filters modernization

An ion-exchange filter is a vertical cylindrical apparatus made from corrosion-resistant materials, designed for purifying the coolant from impurities (Fig. 1). The main components of the filter are the housing, upper and lower drainage-distribution devices (typically made as perforated plates or slotted caps), a layer of ion-exchange resin, loading and unloading hatches for fresh and spent resin, nozzles for inlet and outlet water, regeneration reagents, and air release, as well as devices for monitoring the quality of purified water and the resin characteristics. The drainage-distribution devices ensure uniform water flow distribution through the resin layer and prevent the loss of resin particles from the filter [13].

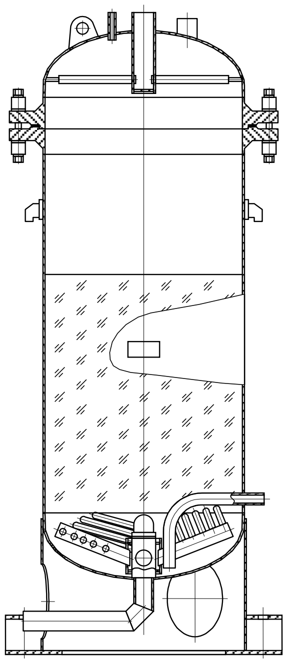

Fig. 1. Longitudinal cross-section of a cation exchange filter.

Contaminated water is fed into the filter's upper part, flows downward through the layer of ion-exchange resin where the ion-exchange process occurs, and purified water is removed from the filter's lower part. The type and properties of the ion-exchange resin and the filtration rate are the key factors influencing purification efficiency and filter cycle duration. The purification system at Ukrainian NPP uses nuclear-grade cation exchange resin AMBERLITE™ IRN77 H, which looks like translucent amber-colored spherical granules, and the strongly basic polystyrene gel anion exchange resin AMBERLITE™ IRN78 in hydroxyl form, which looks like gray spherical granules [14].

When the exchange capacity of the resin is exhausted, i.e., it becomes saturated with absorbed ions and can no longer effectively purify water, it should be regenerated or replaced. Regeneration is the restoration of the resin's exchange capacity by treating it with solutions of appropriate reagents. For example, cation resins in H^+ form are regenerated using hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) solutions [9]. For ion-exchange filters in the primary circuit of WWER-1000 nuclear power plants, when the reagent is already exhausted and no longer suitable for regeneration, the spent resin is entirely replaced with fresh resin. The spent resin is solid radioactive waste that must be sent for specialized processing and disposal.

The efficiency of ion-exchange filters, particularly the duration of the filter cycle (the period of filter operation between regenerations or resin replacements), depends on several factors. The most significant factors are the properties of the ion-exchange resin, such as its type, exchange capacity, wear degree, and presence of contaminants; the content of impurities in the inlet water (higher impurity concentrations lead to faster resin exhaustion); coolant temperature (high temperatures can cause resin thermal degradation and reduce its exchange capacity); water flow rate (high flow rates may result in incomplete ion exchange due to insufficient contact time, while low flow rates may lead to inefficient use of the filter volume); coolant pH (affects the dissociation degree of the resin's ionogenic groups and the form of certain impurities in the solution); the presence of suspended solids and organic compounds (these can mechanically contaminate the resin layer, coat granules and block access to ionogenic groups, which reduces efficiency and increases hydraulic resistance); radiation impact (can cause resin degradation, structural changes and decrease in the exchange capacity and mechanical strength) [13], [15].

The authors analyzed known examples of ion-exchange filter modernization and innovations in water treatment, identifying the following key proposals.

• *Introduction of new ion-exchange materials and multilayer loading*: development, testing, and implementation of modern ion-exchange resins with improved characteristics, such as higher exchange capacity, enhanced selectivity for specific ions (e.g., cobalt or cesium ions), better mechanical strength, and greater thermal and radiation resistance [16]–[19]. This would extend the filter life and reduce the volume of liquid radioactive waste.

• *Improvement of filter design*: extending filter life by using more durable materials for the housing and its components; optimizing the internal filter structure to improve coolant flow hydrodynamics. This includes developing and applying more efficient drainage-distribution systems that ensure uniform flow distribution across the filter's cross-section and prevent the formation of stagnant zones or channels that reduce the efficiency of the resin layer [8], [9].

• *Improvement of control, management, and diagnostic systems*: implementing modern measuring technologies and automated control systems, including filters with integrated sensors that enable real-time monitoring of their operation and prediction of resource exhaustion. This allows for more precise and timely control of water-chemical regime parameters, the condition of filtering materials (e.g., exhaustion degree), and more effective control of the purification system [5], [9].

• *Optimization of blowdown-feedwater system for the primary circuit*: research for determining the optimal operating modes for the blowdown-feedwater system, which provides the required coolant quality while reducing the volume of blowdown water. This helps reduce the amount of liquid radioactive waste [9], [13].

4.2. Calculation of cation filter parameters using different ion-exchange resins

The authors have analyzed modern nuclear-grade ion-exchange resins, such as Lewatit® MonoPlus S 108 H, Purolite® NRW100, and DIAION™ SKN1, including their physicochemical properties and potential application in cation filters [17]–[19]. A comparative analysis of the physicochemical properties of nuclear-grade ion-exchange resins is presented in Table 1.

Table 1. Characteristics of ion-exchange resins.

Parameter	Unit	AMBERLITE™ IRN77 H	Lewatit MonoPlus S 108 H	Purolite® NRW100	DIAION™ SKN1
Uniformity coefficient	-	<1.2	1.05(+/- 0.05)	1.1(+/- 0.05)	1.2(+/- 0.05)
Average granule diameter	mm	< 0.3 (0.2 %) > 1.180 (3%)	0.65(+/- 0.05)	0.8(+/- 0.05)	0.7(+/- 0.05)
Total exchange capacity	g-eq/L	> 1.9	2.0	1.8	1.7
Maximum water content	%	49-55	47-53	45-50	54
Maximum operating temperature	°C	120	120	120	120
Specific acid amount for regeneration	g-eq/L	6.21	2	6	4
Operating flow rate	m^3/hour	< 60	< 60	< 40	< 40

Lewatit MonoPlus S 108 H is a strong-acid cation exchange resin that is universal for water demineralization at industrial steam generators and purification systems, and for mixed filters combined with anionites. It provides low organic carbon content and resistance to oxidation, which is especially important for the nuclear industry. Thanks to its specialized manufacturing process, the resin exhibits exceptional chemical, osmotic, and mechanical stability, ensuring low leaching even at high temperatures, in the presence of oxidants, or during external regeneration [17].

Purolite® NRW100 is a strong-acid cation exchange resin with exceptional chemical and mechanical stability, which ensures its durability under challenging conditions, such as high temperatures or oxidant impact. Its monodisperse structure with minimal content of fine particles reduces hydraulic resistance and promotes uniform regenerant flow, thereby improving the efficiency of hydrochloric acid during regeneration. Its resistance to oxidation and low leaching level make it suitable for nuclear industry applications [18].

DIAION™ SKN1 is a strong-acid cation exchange resin specifically developed for the nuclear industry, particularly for coolant purification, radioactive waste processing, and purification of spent fuel storage pool systems, where high purity and low organic carbon content are necessary. The resin is chemically and mechanically stable at high temperatures and radiation. The resin's exchange capacity loss is only 2–5% per year with proper operation, making it cost-effective for long-term use [19].

The authors calculated the cation exchange filter parameters for different resins, including operational exchange capacity, duration between regenerations and acid amount for regeneration. The results of the filter parameter calculations using AMBERLITE™ IRN77 H, Lewatit MonoPlus S 108 H, Purolite® NRW100, and DIAION™ SKN1 resins are presented in Table 2. The formulas in Table 2 use the following labeling: D is the filter diameter; h is the height of the filtration zone; k_f is the coefficient of ionite filling with H^+ ions; E_t is the total exchange capacity; W is the coefficient of ion filling; d_{ion} is the resin grain diameter; C_{cat} is the average total cation concentration in the resin; k_{ef} is the regeneration efficiency coefficient; k_{pr} is the coefficient of incomplete utilization of the protective layer; H_{bf} is the water hardness before the filter; H_{af} is the water hardness after the filter; n_{if} is the number of ion-exchange filters; W_a is the specific acid amount.

Table 2. Parameters of cation exchange filters for different ion-exchange resins.

Parameter	Formula	AMBERLITE™ IRN77 H	Lewatit Mono Plus S 108 H	Purolite® NRW100	DIAION™ SKN1
Filter surface area, m^2	$f = \frac{\pi \cdot D^2}{4}$	0.785	0.785	0.785	0.785
Total volume of cation exchanger in the filter, m^3	$V_{cat} = f \cdot h$	0.942	0.942	0.942	0.942
Height of the protective filtration layer, m	$h_{pr} = 0.11 \cdot W^{0.5} \cdot d_{ion}^2 \cdot \log(C_{cat})$	0.0754	0.088	0.134	0.103
Equilibrium exchange capacity, $\frac{\text{g-eq}}{\text{m}^3}$	$E_e = (1 - k_f) \cdot E_t$	1881	1900	1782	1649
Working exchange capacity, $\frac{\text{g-eq}}{\text{m}^3}$	$E_w = k_{ef} \cdot E_e \cdot \left(1 - (1 - k_{pr}) \cdot \frac{h_{pr}}{h}\right)$	1647.18	1652.5	1512.95	1423.6
Number of regenerations per year	$n = \frac{Q \cdot (H_{bf} - H_{af}) \cdot 10^3 \cdot 24}{V_{cat} \cdot n_{if} \cdot E_w}$	22.572	22.5	24.57	26.12
Duration between regenerations, days	$T = \frac{1}{n}$	16.17	16.22	14.859	13.98
Acid amount for regeneration, kg	$Q_a = \frac{E_w \cdot W_a \cdot V_{cat}}{1000}$	6.21	6.23	8.555	5.367

Comparative analysis of the operational exchange capacity (Fig. 2), the duration between regenerations (Fig. 3), and the acid amount for regeneration for different cation exchange resins (Fig. 4) is presented below.

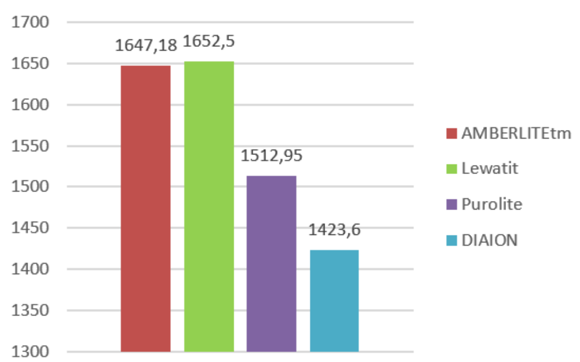

Fig. 2. Operational exchange capacity of cation resins.

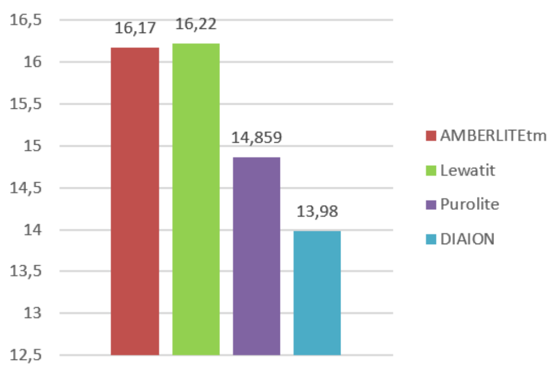

Fig. 3. Duration between regenerations for cation resins in days.

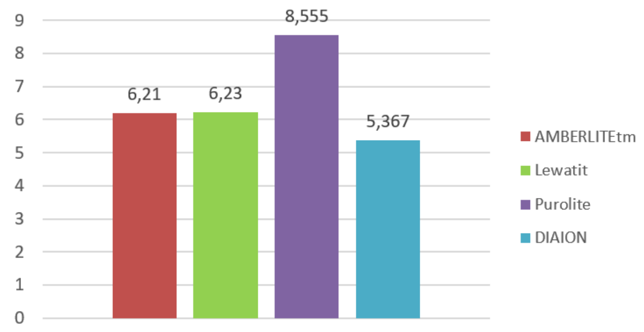

Fig. 4. Acid amount for regeneration of cation resins.

Analyzing the calculation results, the authors have concluded that the Lewatit® MonoPlus S 108 H resin offers advantages over the AMBERLITE™ IRN77 H resin, as it has a higher operational exchange capacity and a longer duration between regenerations.

Therefore, additional studies were conducted for the cation resin Lewatit® MonoPlus S 108 H. For this resin, the authors have analyzed the impact of the filter diameter within the range of 0.7 to 1.2 m on the filter's operational parameters. The calculation results are presented in Figures 5 and 6.

Based on the calculation results, the following conclusions were made:

- Increasing the filter diameter reduces the time between regenerations, increases acid consumption per regeneration, and requires modifications to the existing filter design, which is economically unfeasible.
- Increasing the height of the ion-exchange layer in the filter increases the resin's operational exchange capacity, positively affecting its productivity and efficiency; however, the costs for regenerating such a filter increase slightly. Therefore, for decisions regarding filter modernization, an additional economic analysis is necessary, considering the cost of acid amount for regeneration and the total expenses associated with modifying the filter design.

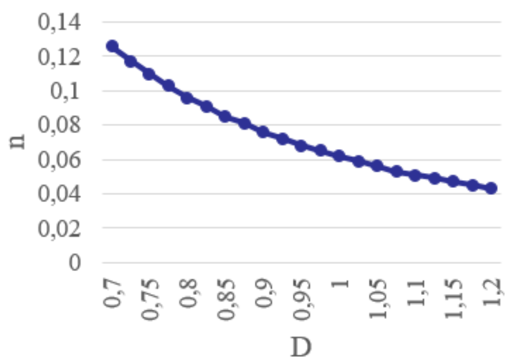

Fig. 5. Dependence of the number of regenerations on filter diameter.

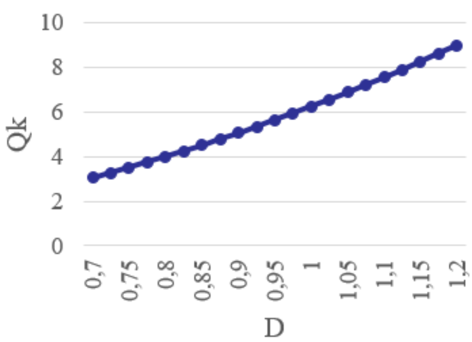

Fig. 6. Dependence of acid amount for regeneration on filter diameter.

The authors also analyzed the impact of the operational filtration height within the range of 0.8 to 1.5 m on the filter's characteristics. The calculation results are presented in Figures 7 – 9.

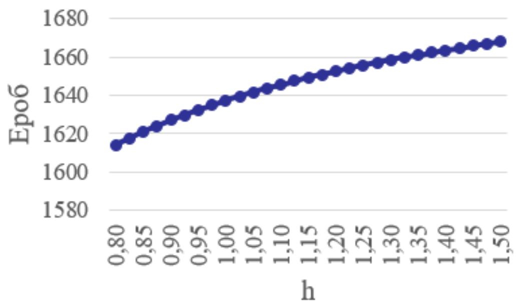

Fig. 7. Dependence of operational exchange capacity on the height of the working filter zone.

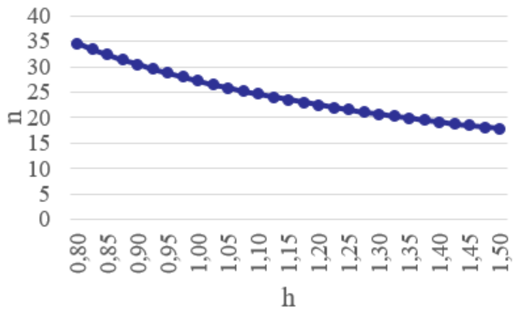

Fig. 8. Dependence of the number of regenerations per day on the height of the working filter zone.

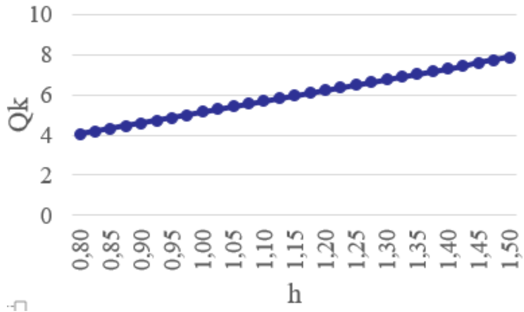

Fig. 9. Dependence of acid amount for regeneration on the height of the working filter zone.

5. Conclusion

The paper presents the operational features of ion-exchange filters used for purifying the coolant of the primary circuit of the WWER-1000 reactor, which play an essential role in enhancing the efficiency, safety, and cost-effectiveness of nuclear power plant operation. The directions for cation exchange filters modernization have been determined: using new ion-exchange resins; multilayer loading; reducing the volume of radioactive waste through optimized regeneration; using filters that do not require regeneration; extending the filters' service life by using more durable materials for housings and components; optimizing hydrodynamic regimes; implementing automated control and remote management systems, etc.

The nuclear-grade ion-exchange resins, such as Lewatit® MonoPlus S 108 H, Purolite® NRW100, and DIAION™ SKN1, were analyzed, including their physicochemical properties and potential for filter modernization. Cation exchange filter parameters, including operational exchange capacity, duration between regenerations, and acid amount for regeneration, were calculated. It was determined that the Lewatit® MonoPlus S 108 H resin provides a higher exchange capacity (2 g-eq/L), a longer duration between regenerations (22 regenerations per year), and a lower cost, making it suitable for replacing the existing AMBERLITE™ IRN77 H resin as part of filter modernization. The impact of the filter diameter within the range of 0.7–1.2 m and the height of the working filter zone within the range of 0.8–1.5 m on its performance was also analyzed, highlighting the need to balance increased productivity with regeneration costs.

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Аналіз катіонітових смол для очищення теплоносія реактора ВВЕР-1000

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Анотація

У статті розглянуто фільтрувальне обладнання для очищення теплоносія реактора ВВЕР-1000, яке відіграє важливу роль у підтримці оптимального водно-хімічного режиму, зниженні радіоактивного забруднення обладнання та продовженні терміну служби компонентів реакторної установки. Досліджено особливості експлуатації іонообмінних фільтрів та визначено напрямки їх модернізації. Проаналізовано конструкцію та характеристики катіонітового фільтра, визначено фактори, які впливають на ефективність роботи фільтрів, зокрема заміна іонообмінних смол та оптимізація процесу регенерації. Виконано порівняльний аналіз іонообмінних смол ядерного класу, таких як Lewatit MonoPlus S 108 H, Purolite® NRW100 та DIAION™ SKN1. Обґрунтовано можливості їх застосування для модернізації катіонітових фільтрів. Проведено розрахунки параметрів катіонітового фільтра при застосуванні різних іонообмінних смол, зокрема робочої обмінної ємності, тривалості між регенераціями та витрати кислоти на регенерацію фільтра. Встановлено, що оптимальним варіантом для застосування у катіоніовому фільтрі є смола Lewatit MonoPlus завдяки вищій обмінній ємності (2 г-екв/л), довшій тривалості між регенераціями (22 регенерації на рік) та низькій ціні.

Ключові слова: реактор ВВЕР-1000; теплоносій; система очищення; катіонітовий фільтр; регенерація; іонообмінна смола.