Minimization of radioactive waste volume from nuclear power plants using precipitation-membrane technologies

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Abstract. The purpose of this study is the development and experimental testing on simulation solutions of a precipitation-membrane method for fractionation of liquid radioactive waste and sorption post-treatment of the filtrate. The choice of processing method is based on the analysis of factors affecting the efficiency of ion-exchange purification of solutions; properties of complex compounds of polyvalent metals; characteristics of commercially available membrane elements and economic aspects of the preparation and disposal of radioactive waste. The basic idea is to use the internal properties of solutions to isolate polyvalent cations and acidoligands in the form of poorly soluble compounds in the volume of an inert polypropylene element, which will increase the efficiency of ion-exchange post-treatment and reduce the amount of waste. The architecture and operating parameters of the experimental setup are designed to provide favorable conditions for the formation in solution of complexes (ion pairs) of polycharged cations with acid ligands of various nature.

1 Introduction

The chemical and radionuclide composition of a specific batch of liquid radioactive medium is determined by the conditions of its formation and is not the same even for the same-type NPPs after their mixing. However, it can be argued that the content of radionuclides in radwaste is six or more orders of magnitude less than that of ballast (non-radioactive) components [1-3]. Therefore, a reduction in the cost of radioactive waste processing can be achieved by excluding ballast components from the radwaste composition. Ballast components are not required for the formation of secondary radwaste, primarily biologically inactive compounds.

Homophase concentration can treat most types of radwaste. Due to this flexibility, homophase concentration is often used to maintain the volume in temporary radioactive concentrate storage tanks in Russian nuclear power plants. When using sorption technologies for decontamination of solutions, as a rule, the content of stable components determines the duration of the protective action of ion-exchange elements, including the “cesium-selective” sorbents widely used in nuclear power plants’ operation [4–6].

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predetermined instability of the composition makes it impossible to predict the volume of secondary radwaste. Knowing the chemical composition of the radwaste makes it possible to predict its volume after processing.

In our opinion, the development of modern liquid radioactive medium processing systems should take the following into account:

1. The minimum volume of radwaste that meets any acceptance criteria is achieved only when they are formed by low-soluble salts that include radionuclides as a natural component;
2. In the general case, liquid radioactive medium contains all chemical analogues of the main radionuclides;
3. The inclusion of radionuclides in the solid phase occurs together with their chemical counterparts, and the interfacial distribution of components obeys the general laws of the process.

Complex formation processes should be taken into account when developing systems to remove corrosion products from liquid radioactive medium [7]. Note that the formation of a complex form always precedes the formation of a precipitate. In this regard, a complex form is always present in solution along with the cationic form of the metal. This results in an excess of the analytical/total concentration over the equilibrium concentration.

The purification coefficient $K_{\text{pur}}$ of the solution will be determined by the ratio of the initial concentration of the carrier ion $\text{Me}_c$ and the solubility of the resulting precipitate. The carrier metal concentration in an equilibrium salt solution consists of two components: the cation concentration, which is determined by the solubility product, and the concentration of its complex form, which is also determined by the concentration of the free ligands. Therefore, an increase in the concentration of the precipitating anion in excess of the stoichiometrically required amount will result in a decrease in the equilibrium concentration of the metal. This will simultaneously increase the percentage of the coordination complex which will retain cations in solution. So, the precipitation methods can achieve the limited purification coefficients.

Non-selective concentration leads to an increase in the concentration of all salts, for example, by evaporation or reverse osmosis. Consequently, it increases the amount of coordination complexes which can contain all types of ligands. Note that at high concentrations, even nitrate ions are able to form with metals significant amounts of coordination complexes [8]. In turn, nuclear power plants bottoms are characterized by high concentrations of nitrate ions. Complexation leads to a decrease in the effective concentrations of removed cations even with weak ligands. This limits the efficiency of precipitation and sorption methods both thermodynamically and kinetically by minimizing the process time due to the productivity requirements and mass-size characteristics of the equipment.

We examined the microfiltration elements made of fibrous polypropylene and thin-film polyamide membranes. The aim of the work is to test their effectiveness in preparing nuclear power plants radwaste for final isolation.

2 Materials and methods

Schematic diagrams of experimental units for treatment from dispersed impurities, ensuring the quality of discharged water and the release of technogenic impurities are shown in Figures 1, 2 and 3, respectively.
Fig. 1. Schematic diagram of the system for purification from dispersed impurities. 1 – thin-layer sump; 2, 4 – water meter; 3 – double-flow filter with pre-washed membrane; 5 – intermediate tank of the second stage of purification.

The control over the establishment of a stationary regime was carried out by the values of the electrical conductivity of the flows with a two-point flow-through conductometer TDS-meter HM Digital, Inc TDS Monitor DM-1 (South Korea).

Fig. 2. Water quality assurance unit: schematic diagram (a) and photo (b). 1 – ion-exchange filter 2, 3 – reverse osmosis apparatus.

Reverse osmosis membranes of Vontron series ultra-low pressure 1812-50 (Vontron Technology Co., Ltd.) were used in the work. The ratio of permeate and concentrate flows and the operating pressure in the purge chamber were provided by the drainage controllers with the required flow rate. At the second stage of cleaning, a bypass valve with a response pressure of 0.6 MPa is additionally installed, which protects the feed pump from overload.

The study used commercially available cartridge filters based on fibrous polypropylene of the SL-10” standard with a declared pore size of 1-5 µm. The prepared filter element was placed in the housing of the Typhoon series, the standard connections of which provide the ability to work in the radial filtration mode. The working pressure allowed by the developer is 0.6 MPa.
Industrially produced macroporous acrylate cation exchanger H⁺-form Purolite C104 was used to purify technogenic waters from biologically hazardous components. Total capacity 4.7 eq/dm³. The volume of the filter load is 0.4 dm³.

![Diagram](image)

**Fig. 3.** Unit for separation of technogenic impurities: schematic diagram (a) and photo (b). 1 – nutrient tank, 2, 4, 7 – water flow meter, 3 – ion-exchange filter storage, 5, 6 – reverse osmosis apparatus, 8 – concentrate storage tank.

Ion concentrations were controlled using the methods according to the Russian State Standard GOST. Hardness salts and Ca²⁺ was determined trilonometrically with eriochrome black T and murexide, respectively. The concentration of iron compounds was determined photocolorimetrically with o-phenanthroline. Chloride ions were determined mercurimetrically using the diphenylcarbazone indicator; nitrate ions were determined photocolorimetrically with Griess reactive. Sulfate ions were determined turbidimetrically, bicarbonate ions were determined acidometrically with methyl orange indicator.
3 Results and discussion

3.1 Process solution preparation unit

Technogenic waters, which include liquid radioactive medium, are generally colloidal solutions, the dispersed phase of which are various suspensions and oil products, often artificially stabilized by various surfactants. These substances are deposited on the working surfaces of filtering equipment and lead to premature failure of equipment compared with the theoretically possible service life due to:

1. The formation of dynamic membranes, which lead to a decrease in equipment performance;
2. Blocking the active centers of ion exchangers. This leads to an increase in the height of the protective layer and, accordingly, to the deterioration of the filtrate quality.

In this regard, the main task of creating technologies for the processing of liquid radioactive medium, organized according to the principle of minimizing the volume of secondary radwaste, is the deep clarification of technological media transferred to final stages.

Traditional methods of liquid radioactive medium clarification, using forced coagulation of suspension and emulsion components and sorption of dissolved organic impurities by carbon materials, are generators of "excessive" secondary radioactive waste. This is due to the fact that the solid phase in contact with the treated solution will inevitably be contaminated with radionuclides [9, 10]. The minimum volume of secondary waste generated at this stage can be achieved only due to coagulation/coalescence of dispersed substances in the secondary energy minimum. For coagulation/coalescence, it is necessary to provide conditions for concentrating the suspension to a critical concentration of micellization.

To solve this problem, the most promising is the use of alluvial dynamic membranes, which, in principle, can provide the ultra-, micro-, and nanofiltration. In the considered case, such membranes can spontaneously form on various filter surfaces from the dispersed component of solutions [11].

For liquid radioactive medium processing, it is advisable to use industrially produced and, accordingly, commercially available components. This will reduce the capital and operating costs of the plants. In our opinion, commercially available polypropylene filter cartridges are the most promising carriers for sedimentary membranes [12, 13]. The main advantage of these elements is the inertness of the material and the possibility of a sharp decrease in the volume of waste elements by pressing.

Since the constant increase in the hydraulic resistance of the filter during operation is due to a continuous increase in the thickness of the washed microporous layer of the membrane, an increase in the duration of the element can be achieved by creating conditions that limit the rate of its growth. Theoretically, such conditions can be created in double-flow filters of radial filtration, in which the output of a clarified solution leads to an increase in the concentration of dispersed components in the purge solution. For cartridge elements, the occurrence of coagulation/coalescence in the supra-membrane space is a favorable factor that reduces the rate of membrane growth, since large particles that are weakly adhered to the substrate are easily washed off the surface during fluctuations in the longitudinal flow rate that are inevitable for such a regime. As follows from the data obtained on the experimental setup shown in Figure 1, after reaching the critical concentration of dispersed products, the processes of coagulation/coalescence of dispersed phases lead to the separation and accumulation of solid particles in a thin-layer sump.
Figure 4 shows data on changes in the main controlled parameters during operation. The experiments were carried out on model solutions similar in composition to the artesian district water of St. Petersburg.

The presented data shows that the initial period of operation, in which there is practically no pressure drop across the filter cartridge identified by control devices, is characterized by an increase in the concentration of iron compounds and organic substances, characterized by oxidizability, in the feed solution and filtrate. With an increase in the pressure drop, a sharp increase in the concentration of iron compounds in the feed water is observed with a simultaneous decrease in this indicator in the filtrate. This indicates the formation of an alluvial membrane. The process of formation of the primary layer, leading to a decrease in the free porosity of the substrate, ends after passing 20-25 m³/m² of the cartridge, which corresponds to the surface density of iron (III) oxyhydrate of about 5-7 g/m². At the same time, a noticeable increase in the pressure drop begins, accompanied by periodic jumps. By the time this paper was written, the average value of the differential had stabilized.

A sharp decrease in the concentration of iron compounds in the feed water may be associated with the achievement of a critical concentration. This starts the coagulation of iron(III) oxyhydrates. Note that at the same moment, a sharp decrease in the oxidizability of feed water is observed, which can only be explained by the adsorption of organic components by the developed surface of coagulating compounds.

The permeability of the filter cartridge with an increase in pressure drop during the formation of a dynamic membrane gradually decreases in accordance with the characteristic of the pump "flow-pressure" and decreases sharply at the moment of maximum opening of the bypass valve, which corresponds to the transition of the filter to the operating dual-flow mode. A further increase in the pressure drop is due to a smoothly increasing flow rate along the device purge line, which can be associated with an increase in the concentration of osmotically active particles in the concentrate. This leads to a decrease in the permeability of the filter cartridge precisely as an ultra- or nanofiltration element.
Further, the process solution clarification system acquires all the properties of a self-organizing one, which is able to maintain an average productivity and provides a high quality filtrate in terms of cations prone to the formation of polynuclear metal particles and organic components without dosing any reagents.

This fact is confirmed by the absence of an increase in the pressure drop across the cation exchange filters, which are installed on the concentration line. The pressure drop across these filters was due only to their own hydraulic resistance.

Thus, deposits of the solid phase did not appear on the frontal layer of the carboxylic cation exchanger after the process solution preparation block.

3.2 Unit for ensuring the quality of water removed from the technological cycle

The control tank ensures the quality of wastewater at all operating units of the liquid radioactive medium processing systems. The control tank is designed for short-term storage of deactivated solutions before receiving permits for the drain. Even an episodic stay of water of improper quality (further sent to re-treatment) in it, can lead to contamination of the next sewage portions.

![Graphs showing changes in concentration of iron compounds, permanganate oxidizability, pressure drop across the filter element, and flow rate during the operation of the unit.](image-url)
During the operation of the deactivation unit, deviations from the project regime may be observed due to many reasons. These are the instability of the composition of the clarified solution, the operation of pumping and dosing equipment and adjustment systems, the average daily temperature fluctuations. As a result, a dynamic settlement occurs due to the kinetic features of the processes or the creation of forms that are not active in the processes used.

Electrical conductivity and pH are the only two controlled indicators of the solution, whose changes characterize the stability of the system and can be tracked in real time.

Since the electrical conductivity of solutions most adequately allows one to evaluate the performance of demineralization systems, it is preferable to use reverse osmosis as a guarantee. Without questioning the existing filtration-capillary model, we note that the selectivity of modern polyamides-based membranes can also be determined by Donnan exclusion. The number of charge carriers in such membranes is determined by the degree of protonation of amino groups, which, in the general case, reaches the maximum value in weak acid media (pH <5.5). Based on this hypothesis, at the feeding lines, it is advisable to install filters loaded by weak acid carboxyl cations. The advantages of these materials are:

- High concentration of ionic groups, providing "internal" neutralization of almost any probable peak alkalinity values of solutions;
- "Hungry" regeneration mode;
- Reliable "instantaneous" fixation of the end of the working period when pH exceeds the specified value.

The concept of water quality assurance block is presented in Figure 2. To organize the system, a two-stage feed solution process was selected. Purified solution is the permeate of the apparatus operating in the most favorable conditions (the first in the course of the flow).

The feed solution for the second stage apparatus is a concentrate from the first stage of desalting. The permeate of this apparatus operating in more severe conditions is considered conditionally "dirty" and returns to the beginning of this block. This permeate is mixed with solution that comes from the cleaning unit and forms the feed solution of this system. This combined stream enters the cation exchange filter-corrector input.

The approach to the formation of the block was determined by the following considerations:

1. The most likely reason for the deterioration of the quality of purified water is that part of the extracted components is in a molecular form, so they are not trapped by filtration elements.

2. The Otswald’s dilution law states that the dilution is a fairly effective means of increasing the degree of dissociation of molecular forms. And the resulting ionic forms are more efficiently trapped by filtration equipment.

3. The cation-exchange filter, by sorbing some of the cations, reduces the salt load on the reverse osmosis units.

Unfortunately, we are not able to quantify the effectiveness of the work of this block, since the concentrations of the cations of the metals of interest and chloride ions are below the determination limit used in our laboratory methods. So, wastewater obtained during the experiment can be used for laboratory purposes.

It should be noted that the two discussed blocks are of general-purpose [14]. Adapting blocks to specific technological processes occurs only at the stage of hardware selection in accordance with the performance requirements and its manufacturer. This choice is also based on the convenience of mounting and subsequent maintenance.
3.3 Unit for separation of man-made products from liquid radwaste

The obvious requirements for storage filters are to achieve the maximum possible (including those defined by radiation safety standards) sorption capacity for target components, which is implemented for a specific brand of sorbent: (a) when aligning the concentrations of recoverable ions at the input and output of the filter; (b) while maintaining the maximum possible concentration of extractable components in the feed solution under given conditions.

The first condition is determined by the prevalence of the limiting dynamic capacity, achieved in the mode “up to a complete breakthrough of the target components”, over the working dynamic capacity, implemented in the purification mode “up to a given value of the concentration of the component in the filtrate”.

The second condition is a consequence of the exchange isotherm, which, as a rule, is linear in the region of ultralow concentrations.

In contrast to the systems discussed above, the organization of this block must be strictly related to the radiochemical composition of the processed solution. The radiochemical composition should be understood not only as the volume specific activity of the solution for individual radionuclides, but primarily as the specific activity of an isotope per mass of all its chemical analogues.

During the development of the block, it was assumed that:

1. Crossing the border between medium-level and high-level waste at any stage of the process is unacceptable.

2. Selective separation of liquid radioactive medium components with the formation of secondary radwaste that meets all the criteria for acceptability for "eternal" isolation or long-term uncontrolled storage can only be provided by methods that lead to the formation of poorly soluble inorganic substances.

3. All other methods, the use of which is dictated by the logistics of the process, should be considered as auxiliary, with the sole purpose of providing optimal conditions for the incorporation of radionuclides into the phase of poorly soluble compounds of their chemical analogues.

The first provision is determined by the only possible technical means for conditioning and transporting radioactive waste – a container of the NPC-1500 type (non-returnable protective container) and its analogues. It should be noted that the same containers are suitable as biological protection when individual elements of the complex are placed in them and the spent components are buried without their decontamination.

The second position follows from the very fact that the leaching of components is difficult, which is limited not only by the diffusion coefficient of the component in the matrix, but also by the limitation of its concentration, as well as the compatibility of such mineral-like structures with any binders, primarily cements [15, 16].

The last requirement means the need to use commercially available components and focus on the processes, the preference for the use of which is determined by the availability of an energy source.

In this regard, we note that reverse osmosis concentration systems show good results in the processing of liquid radioactive medium with low (<5 g/dm³) salt content [17]. However, if there is a sufficient amount of thermal energy (for example, exhaust gases from diesel generator sets or pyrolysis plants [18, 19]), it is preferable to use evaporation, which is less sensitive to this indicator, to concentrate solutions.

The widely advertised ion-selective sorption of radionuclides [20], even if it really exists, is based on materials produced in extremely limited quantities. This circumstance makes them unsuitable materials for organizing replicated technologies, especially those designed for rapid deployment. Precipitation technologies are focused on products of heavy inorganic synthesis, the chemical properties of which do not depend on the manufacturer.
The theoretical coefficient of purification \( (K_{\text{pur}}) \) of a solution from radionuclides using precipitation methods of this type can be estimated from the following relationship:

\[
K_{\text{pur}} = \frac{A_{\text{initial}}}{A_{\text{final}}} = \frac{[\text{Me}_c]}{S_c} = \frac{[\text{Me}_c]}{M + A \sqrt{MSP_c}}
\]

where \( A_{\text{initial}} \), \( A_{\text{final}} \) is volumetric specific activity of the solution for radionuclides of a given grade; \([\text{Me}_c]\) is radionuclide carrier metal concentration; \( S_c \), \( SP_c \) are the solubility of a salt in its saturated solution and the product of the solubility of the precipitated metal salt; \( M \), \( A \) are stoichiometric coefficients.

The most probable carriers for activated corrosion products are the corrosion products of structural materials – iron (II) and nickel (II), and the natural carrier for \(^{90}\)Sr are calcium ions. The table shows the properties of low-solubility compounds that are most preferred because (a) they most closely meet the acceptance criteria for "eternal" isolation, (b) they correspond to the possibilities of technological support of the processes, and (c) they provide a sufficient value of the decontamination factor \( \sim 1000 \).

**Table 1.** Properties of poorly soluble compounds of doubly charged metals capable of acting as carriers of radionuclides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility product</th>
<th>Salt solubility, M</th>
<th>Metal solubility, mg/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCO₃</td>
<td>1.05⋅10⁻¹⁰</td>
<td>1.0⋅10⁻⁵</td>
<td>0.58</td>
</tr>
<tr>
<td>NiCO₃</td>
<td>1.3⋅10⁻⁷</td>
<td>3.6⋅10⁻³</td>
<td>201</td>
</tr>
<tr>
<td>FeCO₃</td>
<td>3.5⋅10⁻¹¹</td>
<td>5.9⋅10⁻⁶</td>
<td>0.303</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>1.1⋅10⁻¹⁰</td>
<td>1.1⋅10⁻⁵</td>
<td>0.99</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>3.8⋅10⁻¹⁰</td>
<td>1.9⋅10⁻⁵</td>
<td>0.78</td>
</tr>
<tr>
<td>CoC₂O₄</td>
<td>6.3⋅10⁻⁸</td>
<td>2.5⋅10⁻⁴</td>
<td>14.8</td>
</tr>
<tr>
<td>NiC₂O₄</td>
<td>4⋅10⁻¹⁰</td>
<td>2⋅10⁻³</td>
<td>1.14</td>
</tr>
<tr>
<td>FeC₂O₄</td>
<td>2⋅10⁻⁷</td>
<td>4.5⋅10⁻³</td>
<td>252</td>
</tr>
<tr>
<td>CoS</td>
<td>4⋅10⁻¹¹</td>
<td>6.3⋅10⁻¹¹</td>
<td></td>
</tr>
<tr>
<td>NiS</td>
<td>3.2⋅10⁻¹⁹</td>
<td>5.6⋅10⁻¹⁰</td>
<td>3.13⋅10⁻⁵</td>
</tr>
<tr>
<td>FeS</td>
<td>5⋅10⁻¹⁸</td>
<td>2.2⋅10⁻⁹</td>
<td>1.23⋅10⁻³</td>
</tr>
<tr>
<td>SrSO₄</td>
<td>3.2⋅10⁻⁷</td>
<td>5.6⋅10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>CaSO₄</td>
<td>2.5⋅10⁻⁵</td>
<td>5⋅10⁻²</td>
<td>2000</td>
</tr>
<tr>
<td>SrHPO₄</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaHPO₄</td>
<td>2.5⋅10⁻⁷</td>
<td>5⋅10⁻³</td>
<td>200</td>
</tr>
</tbody>
</table>

The concentration of carriers in the solution should exceed the values given in the table by several times. Therefore, the main task should be considered the joint accumulation of radionuclides and ionic forms of carriers that are capable of forming a matrix material. The concentration of carriers can be in the range of 0.1-5 mg/dm³.

To implement this direction, the system shown in Figure 3 seems to be the most acceptable. Reverse osmosis devices 5, 6 ensure trapping of at least 99.5% of all cationic impurities, providing the possibility of almost complete retention of non-ferrous metal ions by the sorption filter 3. The \( \text{H}^+ \)-form of the complexing cation exchanger 3 ensures the accumulation of cationic forms of corrosion products. The resulting weak acid medium enhances the salt-retaining properties of the membrane, prevents deposits on the mass-transferring surfaces, and provides stabilization of the cationic forms of metals. Salts of
alkali and alkaline earth metals, freed from non-ferrous metal ions and, accordingly, activated corrosion products, accumulate in the storage tank.

Experimental dependences of the concentration of doubly charged metal ions and membrane permeability at an operating pressure of 0.6 MPa on the concentration of alkaline earth metal salts in the storage tank were obtained. It was shown that significant changes in the membrane permeability begin only after the total concentration of hardness cations exceeds 40-50 meq/dm$^3$, with the proportion of calcium of 60% or 450-600 mg/dm$^3$. At these carrier concentrations, the use of precipitation in the form of carbonate seems to be the most acceptable. As an alternative, ammonium phosphate precipitation is considered, in which ammonium magnesium phosphate and calcium (strontium) monohydrogen phosphate are formed. Subsequent alkalization of the solution converts monohydrophosphates into orthophosphates, the solubility of which is much lower.

4 Conclusions

It is shown that a correct combination of sedimentation-membrane methods makes it possible to guarantee fulfillment of all existing environmental quality standards for wastewater obtained during the decontamination of radioactively contaminated medium.

The set of methods we used guarantee that the required quality of aqueous solutions will be reached. It minimizes the amount of secondary radwaste compared to other methods, therefore reducing the cost of processing liquid radioactive medium.

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