



# Article Removal of Cs-137 from Liquid Alkaline High-Level Radwaste Simulated Solution by Sorbents of Various Classes

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Abstract: The present work describes the results of the removal of cesium by sorbents of various classes from highly mineralized alkaline solutions simulating the clarified phase of storage tanks with high-level radioactive waste (HLW) of the Mayak Production Association. Within the scope of the performed works, inorganic sorbents of the Clevasol<sup>®</sup> and Fersal brands, as well as resorcinol-formaldehyde ion-exchange resins (RFRs: RFR-i, RFR-Ca, and Axionit RCs), were used. The sorbents' characteristics under both static and dynamic conditions are presented. The Fersal sorbent has demonstrated the best sorption characteristics in the series of sorbents under study. The disadvantage of inorganic sorbents is the loss of mechanical strength upon cesium desorption, which complicates their repeated use. It has been demonstrated that RFRs, despite their lower selectivity towards cesium and adsorption capacity, can be used many times in repeated sorption-desorption cycles. The latter makes RFRs more technologically attractive in terms of the total volume of decontaminated HLW. However, RFRs tend to be oxidized during storage, which results in the formation of carboxyl groups and a decrease in sorption characteristics—this must be further taken into account in the real processes of liquid radioactive waste (LRW) management.

**Keywords:** selective sorbents; resorcinol–formaldehyde resin; adsorption; cesium; liquid radioactive waste

# 1. Introduction

The necessity to process liquid alkaline high-level wastes (HLW) from storage tanks of the Mayak Production Association and, subsequently, transfer them to a stable matrix form is an important and urgent task. To process HLW, schemes were suggested involving the sorption removal of Cs-137 as the main dose-forming radionuclide of the waste from the supernatant. After removal of Cs-137, the decontaminated waste can be solidified by cementation, resulting in solid waste in the intermediate-level category (ILW). The ferrocyanide sorbent FS-10 was chosen for the selective removal of Cs-137 from HLW [1]. However, the disadvantage of using the FS-10 sorbent consists in the need for preliminary neutralization of HLW to pH 6–8 due to the fact that sorbents based on poorly soluble transition metal ferrocyanides undergo destruction in alkaline media [2]. For this reason, the search continues for sorption materials capable of selectively removing Cs-137 from alkaline HLW without prior neutralization.

As the above-mentioned sorption materials, one can consider resorcinol-formaldehyde resins (RFR), which at present are actively used to remove cesium from alkaline radioactive waste streams [3]. The selectivity of RFR towards some single-charge cations changes as follows:  $Na^+ < K^+ < Rb^+ < Cs^+ < H^+$  [4]. This property makes it possible to reversibly remove cesium from alkaline LRW with subsequent desorption with suitable acid solutions [5–7].



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The mechanism of cesium adsorption is related to the occurrence of ion exchange on deprotonated functional groups [8]. The selectivity of ion-exchange resins towards cesium can be explained by the predominance of the stage of transfer of alkaline metal cations from the liquid phase of the polymer to its solid phase over the stage of electrostatic binding with ion-exchange groups [9,10]. Another model explaining the nature of selectivity suggests that swelling in alkaline media results in an increase in the osmotic pressure in the resin and, consequently, a tension in the polymer network. Sorption of low-hydration cesium and rubidium is preferential in comparison with that of sodium and potassium, as it allows reducing the polymer network tension [11].

Sphere-granulated RFRs (sRFR) became widely used [12–14] due to their advantage of reducing hydrodynamic resistance as well as greater mechanical strength as compared to granular ion-exchangers [14–16]. To solve the problem of RFR oxidation in alkaline media, samples with improved chemical resistance and selectivity to cesium were prepared [7].

Inorganic sorbents can serve as a cheaper and more effective alternative for selective ion-exchange resins to solve the problem of treating LRW with complex chemical composition. The Clevasol<sup>®</sup> sorbent, commercially manufactured by the French company LEMER PAX Innovative, can be considered as such an alternative. The sorbent is marketed as an effective material for the removal of radionuclides from solutions in a broad pH range [17].

The Clevasol<sup>®</sup> sorbent comprises a polymer structure with high selectivity to a number of cations, especially cesium, silver, and thallium [18]. Due to its mechanical strength and large particle size, the sorbent can be used under dynamic conditions as a load for adsorption columns. It was shown that the Clevasol<sup>®</sup> sorbent effectively removed Cs<sup>+</sup> from nitric acid solutions at concentrations of 1–8 mol/dm<sup>3</sup> ( $K_d$  for Cs<sup>+</sup> greater than 10<sup>4</sup> cm<sup>3</sup>/g) [19]. Composite sorbents were prepared by embedding the Clevasol<sup>®</sup> sorbent particles into the polyvinyl alcohol (PVA) cryogel [20]. According to the authors, this material can be used as part of anti-migration barriers due to its high distribution coefficients for Cs<sup>+</sup> and Sr<sup>2+</sup>. The information on the sorbent composition and a detailed mechanism of the adsorption process is a commercial secret of the LEMER PAX Innovative company.

The Institute of Physical Chemistry and Electrochemistry RAS, in collaboration with Komfinservis LLC, has developed a novel inorganic sorbent of the Fersal brand based on modified nickel ferrocyanide selective to cesium ions. Insoluble ferrocyanides of transition metals and sorbents on their basis demonstrated good results in the processes of cesium ion removal. The mechanism of cesium adsorption on ferrocyanides of transition metals is known in detail and is related to the exchange of potassium and, partially, transition metals by cesium [21–23]. Despite the fact that the sorption-active phase of a sorbent is represented by nickel ferrocyanide, earlier performed tests demonstrated the possibility of cesium removal from alkaline solutions [24].

The above-mentioned materials can be used in the processes of decontamination of highly mineralized alkaline LRW from cesium. However, to choose the most effective sorbent in order to optimize the LRW treatment process, it is necessary to compare their sorption characteristics towards cesium under identical experimental conditions simulating the real ones to a maximal degree. The earlier published results on cesium removal from liquid media do not enable one to conduct this comparison since they were obtained under different experimental conditions using different criteria of efficiency assessment. At the same time, despite the encouraging prospects of the available sorption materials for HLW treatment, there is a necessity for a preliminary assessment of the sorption characteristics and features of the cesium extraction process on the mentioned sorption materials under practically real-life conditions. The present work was devoted to the study of the physical-chemical and sorption characteristics of RFRs: RFR-i, RFR-Ca, and Axionit RCs, as well as inorganic sorbents Clevasol<sup>®</sup> and Fersal, in order to determine the most promising of them in terms of the decontamination of alkaline HLW from cesium radionuclides.

### 2. Materials and Methods

## 2.1. Sorbents

The following resorcinol-formaldehyde ion exchange resins were used in the present work:

- Axionit RCs, the sample was synthesized and provided for experiments by JSC "Axion—Rare and Noble metals". Two batches of RFR, synthesized in 2017 (Axionit RCs 2017) and 2022 (Axionit RCs 2022), respectively, were used in the study.
- RFR-i is an experimental laboratory sample, synthesized and provided for testing by the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences (Vladivostok, Russia).
- RFR-Ca is an experimental laboratory sample with a porous surface morphology, synthesized and provided for testing by the Institute of Chemistry of the Far Eastern branch of the Russian Academy of Sciences (Vladivostok, Russia).

The following inorganic sorbents were used in the present work:

- Sorbent of the Fersal brand, an inorganic composite sorbent based on modified nickel ferrocyanide. According to the X-ray fluorescence analysis data, the sorbent contains %: N—24.38; O—56.83; Si—9.46; K—0.20; Fe—1.87; Ni—2.86; Cs—3.65. It is supplied in the K<sup>+</sup>—form. The cesium sorption proceeds through the exchange of K<sup>+</sup> ions in the sorbent phase with the Cs<sup>+</sup> ions in the solution. The sorbent is manufactured by the LEMER PAX Innovative company, France. A sample for tests was provided by the official distributor of this sorbent in Russia—Komfinservis LLC (Russia).
- Sorbent of the Clevasol<sup>®</sup> brand, a macroporous inorganic polymer. According to the X-ray fluorescence analysis data, the sorbent contains %: B—83.0; O—6.27; Na—0.46; S—6.86; Cl—3.44. It is supplied in the H<sup>+</sup>—form. The cesium sorption proceeds through the exchange of H<sup>+</sup> ions in the sorbent phase by the Cs<sup>+</sup> ions in the solution. The sorbent is manufactured by the LEMER PAX Innovative company, France. A sample for testing was provided by the official distributor of this sorbent in Russia—Komfinservis LLC (Russia).

Figure 1 shows SEM images of the sorbents under study. Resorcinol-formaldehyde resins comprise monolithic, glasslike structures. The sorbent Axionit RCs 2022 comprises regular spherical granules with smooth surfaces. The sorbents RFR-i and RFR-Ca are represented by granules of an irregular shape with surface chips formed during grinding. A specific feature of the sorbent RFR-Ca is the presence of micropores formed as a result of the dissolution of a part of CaCO<sub>3</sub> preliminarily introduced into the oligomeric phase at the initial synthesis stage.

The sorbent of the Clevasol<sup>®</sup> brand is represented by granules of an irregular shape, containing large fissures and cracks. Granules of the Clevasol<sup>®</sup> sorbent are formed through the agglomeration of smaller particles of irregular and spherical shapes. Granules of the Fersal sorbent are monolithic and do not contain fissures and cracks. As can be seen on the insert with large magnification, the surface of the Fersal sorbent granules includes pores with an average diameter of 5–6.5  $\mu$ m, which probably ensures high accessibility of adsorption sites.

The resorcinol-formaldehyde resins Axionit RCs, RFR-i, and RFR-Ca were converted to a working sodium form prior to the experiments and sequentially treated with the following under static conditions:  $HNO_3$  solution with a concentration of 1 mol/dm<sup>3</sup>, distilled water, and NaOH solution with a concentration of 1.0 mol/dm<sup>3</sup>. Then the sorbents were washed with distilled water and dried in the air at a temperature of 60 °C to a constant weight. The Clevasol<sup>®</sup> and Fersal sorbents were preliminary sieved to obtain a fraction of 0.25–0.50 mm and then dried in air at a temperature of 60 °C to a constant weight.



**Figure 1.** SEM images of sorbents, (**a**) Clevsol, (**b**) Fersal, (**c**) RFR-i, (**d**) RFR-Ca, (**e**) Axionit RCs 2022. The bulk weight ( $d_{bw}$ , g/cm<sup>3</sup>) of the sorption materials was calculated by Formula (1):

$$d_{\rm bw} = \frac{m_s}{V_{\rm (dry)}},\tag{1}$$

where  $m_s$  is the mass of the sorbent (g) and  $V_{(dry)}$  is the volume of dry sorption material (cm<sup>3</sup>). The arithmetic mean of the three parallel definitions was taken as the test result, and the relative discrepancy should not exceed 5%.

The specific volume value ( $V_{\text{specvol}}$ , cm<sup>3</sup>/g) was calculated by Formula (2):

$$V_{\rm (specvol)} = \frac{V_{\rm (svel)}}{m_s},\tag{2}$$

where  $V_{(svel)}$  is the volume of the swollen sorption material (cm<sup>3</sup>).

The arithmetic mean of three parallel definitions was taken as the test result, and the relative discrepancy must not exceed 5%

Table 1 shows the physical-chemical characteristics of the sorption materials; errors do not exceed 5%. A characteristic difference between ion-exchange resins and inorganic sorbents is their significant swelling, which increases during the transition from distilled water to an alkaline model solution and must be taken into account when using this class of sorption materials. Strong swelling may be accompanied by an increase in the hydrodynamic resistance of the stationary sorbent layer, as well as the rupture of the column; therefore, ion-exchange resins were soaked under a layer of distilled water before the experiment.

Indicator	The Value of the Indicator for the Sorbent							
Indicator	RFR-Ca	RFR-i	Axionit RCs	Fersal	Clevasol			
Granule size (mm)	0.25-1.0	0.25-1.0	0.25-0.80	0.25-3.0	0.25-1.0			
Bulk weight (g/cm <sup>3</sup> )	0.61	0.68	0.82	0.53	0.52			
$d_{\rm bw}$ (cm <sup>3</sup> /g)	1.63	1.47	1.22	1.87	1.92			
$V_{(\text{specvol})}$ (cm <sup>3</sup> /g)	2.73	2.08	3.29	1.87	1.92			
$V_{(\text{specvol})}$ in model solution * (cm <sup>3</sup> /g)	2.87	2.16	3.40	1.87	1.92			

Table 1. Physical and chemical characteristics of the studied sorption material.

\* HLW simulated solution.

## 2.2. Compositions of Model Solutions

The sorption characteristics of Cs-137 were evaluated using model solutions of the following composition:

- NaNO<sub>3</sub> solutions of concentrations at 0.5, 1.0, 2.0, and 3.0 mol/dm<sup>3</sup>, pH = 13. pH adjustment was carried out with NaOH solution;
- KNO<sub>3</sub> solutions of concentrations at 0.1, 0.25, 0.5, and 1.0 mol/dm<sup>3</sup>, pH = 13. pH adjustment was carried out with NaOH solution;
- NaOH + NaNO<sub>3</sub> solutions with constant sums of concentrations of NaOH + NaNO<sub>3</sub> = 3.5 mol/dm<sup>3</sup>, containing 0.1, 0.25, 0.50, 1.0, 1.5, and 2.0 mol/dm<sup>3</sup> of NaOH and 3.4, 3.25, 3.0, 2.5, 2.0, and 1.5 mol/dm<sup>3</sup> of NaNO<sub>3</sub>;
- Model solution simulating the clarified phase of HLW storage tanks of the Mayak Production Association with the following composition, g/dm<sup>3</sup>: NaOH—100, NaNO<sub>3</sub>—128, Al(NO<sub>3</sub>)<sub>3</sub> × 9H<sub>2</sub>O—82.5 (6.0 by Al), K<sub>2</sub>CrO<sub>4</sub>—7.72, CsNO<sub>3</sub>—0.0733 (0.050 by Cs), density—1.190 g/cm<sup>3</sup> [1].

Model solutions were prepared by dissolving the corresponding salts in distilled water. Sodium hydroxide was introduced as a concentrated solution.

Prior to the sorption experiments, the model solutions were labeled with Cs radionuclide in an amount of about  $10^5$  Bq/dm<sup>3</sup> and then held for more than 3 days to achieve equilibrium between the active and inactive components of the solution. The specific activity of Cs-137 was determined by a direct radiometric method on the 661 keV gamma line using the SCS-50M spectrometric complex (Green Star Technologies, Russia). The geometry of the measuring sample was a Petri dish, the sample volume was  $20 \pm 2$  cm<sup>3</sup>, the measurement time was 300 s, and the relative error of measuring activity was no more than 15%.

The C-13 NMR spectra of the polymers in the solid phase were recorded using a Bruker Avance AV-300 spectrometer (Rheinstetten, Germany) with a proton resonance frequency of 300 MHz. To record the spectra, the method of rotating samples at a magic angle (MAS) was used. Tetramethylsilane was used as a standard for carbon nuclei. The chemical shift reference (CS) was set in a separate experiment. The determination error for chemical shift (CS) was 0.3 ppm, while for the intensity of the spectral line it was 5% of its area. The spectra were recorded at 300 K.

## 2.3. Evaluation of Sorption Characteristics under Static Conditions

Sorption characteristics under static conditions were evaluated as follows: A sample weight of air-dry sorption material of  $0.10 \pm 0.01$  g was placed in a polyethylene container, into which 20 cm<sup>3</sup> of the model solution was poured (W/T ratio = 200 cm<sup>3</sup>/mg), after which it was stirred for 24 h. After that, the solid phase was separated from the solution by filtering through a white ribbon paper filter, and the specific activity of Cs-137 was determined in the filtrate.

Based on the results of the analyses, the values of the distribution coefficient ( $K_d$ ) Cs-137 were calculated; see Equation (3).

$$K_d = \frac{A_0 - A_{\text{(resact)}}}{A_{\text{(resact)}}} \times \frac{V_{\text{(solut)}}}{m_s},\tag{3}$$

where  $A_0$  and  $A_{\text{(resact)}}$  are the initial specific activity of Cs-137 in the solution and the residual activity of Cs-137 in the solution after sorption, respectively (Bq/cm<sup>3</sup>), and  $V_{\text{(solut)}}$  is the volume of the liquid phase (cm<sup>3</sup>).

The value of static exchange capacity (SEC, mg/cm<sup>3</sup>) in solutions with a macro concentration of stable cesium was calculated using Equation (4):

$$SEC = \frac{C_0 - C_{(resid)} \times V_{(solut)}}{m_s \times V_{(specvol)}},$$
(4)

where  $C_0$  and  $C_{\text{(resid)}}$  are the initial and residual concentrations of cesium in solution, respectively (mg/cm<sup>3</sup>).

The measurement error for the confidence probability 0.95 (p < 0.05) was estimated on the basis of three parallel measurements of the solution gamma-activity using the one-sample t-criterion.

#### 2.4. Evaluation of Sorption Characteristics under Dynamic Conditions

Sorption characteristics under dynamic conditions were evaluated as follows: First,  $3.0 \text{ cm}^3$  of the sorption material held under a layer of water for more than 12 h was transferred to a polypropylene sorption column with an inner diameter of 8.5 mm. Percolation of the HLW model solution was carried out by a peristaltic pump from Longerpump (China), model BQ-50J at a speed of  $10.0 \pm 0.5 \text{ cm}^3$ /h. The rate of solution percolation was selected based on the fact that to establish equilibrium under dynamic conditions, the contact time must be at least  $10t_{0,5}$ , where  $t_{0,5}$  is the time of half-exchange. Based on the data of [25], the time of half-exchange of cesium ions on selective absorbents is about 1–2 min, so the contact time must be at least 20 min, which corresponds to the specific filtration rate of 3 BV/h.

Filtrates after the column were collected by fractions, and the residual specific activity of Cs-137 was determined. Based on the results of the filtrate analysis, the output adsorption curves were constructed in coordinates f(DF) = BV, where BV is the bed volume calculated as the ratio of the sorbent volume in the column (cm<sup>3</sup>) to the volume of the solution being passed (cm<sup>3</sup>), and DF is the decontamination factor for dynamic conditions, which was calculated by the Formula (5):

$$DF = \frac{A_0}{A_{\text{(filtrate)}}},\tag{5}$$

where  $A_{\text{(filtrate)}}$  is the specific residual activity of Cs-137 in the filtrate (Bq/cm<sup>3</sup>).

When using an HLW simulated solution containing stable cesium, the dynamic exchange capacity up to reaching a given slip (DEC,  $mg/cm^3$ ) was calculated as an integral of the dependence of the amount of adsorbed cesium on the amount of the fed solution (6).

$$DEC = \int_0^n f\left(\frac{\left(C_0 - C_{(\text{filtrate})}\right)V_{(i)}}{V_{(\text{svel})}}\right) dV_{(t)},\tag{6}$$

where  $C_{\text{(filtrate)}}$  is the residual concentration of cesium in the *i*-th fraction of the eluate (mg/cm<sup>3</sup>),  $V_{(i)}$  is the volume in the *i*-th fraction of the eluate (cm<sup>3</sup>), *m* is the mass of the sorbent (g), an dV (*i*) is the volume of the fed solution (cm<sup>3</sup>).

To determine the total dynamic exchange capacity (TDEC, mg/cm<sup>3</sup>) for the output curves of cesium adsorption in coordinates  $f(C_{\text{(filtrate)}}/C_0) = t$ , the Thomas model (7)–(9) was used as follows:

$$\frac{C_{\text{(filtrate)}}}{C_0} = \frac{1}{1 + e^{(a-b\times t)}},\tag{7}$$

$$a = \frac{K_{\rm Th} \times {\rm TDEC} \ \times m}{Q},\tag{8}$$

$$\mathbf{b} = \mathbf{K}_{\mathrm{Th}} \times C_0,\tag{9}$$

where  $K_{\text{Th}}$  is the adsorption rate constant (cm<sup>3</sup>/mg × h), m is the mass of the sorbent (g), Q is the volume rate of the solution (cm<sup>3</sup>/h), and t is the duration of the experiment (h). The experimental data were processed using Veusz software (ver. 3.4) [26].

#### 2.5. Desorption of Cs-137 and Regeneration of Sorbents

After the sorption of Cs-137 from the HLW simulated solution was completed, the sorbent in the column was washed with distilled water with a volume of 30 cm<sup>3</sup> at a rate of 6–9 cm<sup>3</sup>/h to remove the residues of the solution. Then a desorbing solution was fed through the column with the washed sorbent using a peristaltic pump at a rate of 2.5–3.0 cm<sup>3</sup>/h (0.8–1.0 BV/h). The eluates after the column were collected by fractions, and the residual specific activity of Cs-137 in them was determined. Based on the results of the filtrate analysis, the output desorption curve was constructed with the coordinates Des% = f(BV). The degree of desorption of cesium (Des, %) under dynamic conditions was calculated by the Equation (10):

$$Des\% = \left(\frac{\sum_{1}^{i} V_{(el)} \times C_{(eluate)}}{C_{DEC}}\right) \times 100,$$
(10)

where  $C_{\text{(eluate)}}$  is the concentration of the cesium in the *i*-th fraction of the eluate (mg/cm<sup>3</sup>),  $V_{\text{(el)}}$  is the volume of the eluate (cm<sup>3</sup>),  $C_{\text{DEC}}$  is the amount of the adsorbed cesium (mg), and *i* is the ordinal number of the eluate fraction.

For the repeated sorption of cesium, the RFR-i and RFR-Ca ion exchange resins were washed with water to remove acid residues and treated with a 1.0 M NaOH solution to transform them into sodium form. The volume of a 1.0 M NaOH solution was 30 cm<sup>3</sup>, and the transmission rate of the solution was  $2.5 \text{ cm}^3/\text{h}$ .

Under dynamic conditions, the error with the confidence probability 0.95 (p < 0.05) for a single measurement of the solution gamma-activity was determined using the Equation (11).

$$SD = \frac{\sqrt{n}}{t} \times 1.96 \tag{11}$$

where *n* is the quantity of registered impulses and *t* is the measurement time (min).

#### 3. Results and Discussion

Figure 2 shows the results for the values of the Cs-137 distribution coefficients and the static cesium capacity for various sorbents during sorption from a model HLW solution containing a stable cesium isotope in macro concentrations. Based on the results obtained, the efficiency of the sorption materials in terms of cesium removal from the HLW simulated solution under static conditions can be put in the following order: Fersal > RFR-i > Axionit RCs 2022~RFR-Ca > Axionit RCs 2017 > Clevasol<sup>®</sup>. One should mention that the storage of Axionit RCs ion exchange resin for 5 years led to a decrease in SEC by 10% and  $K_d$  Cs-137 by 25% due to oxidation processes that negatively affected sorption characteristics [27]. In order to exclude the oxidation of RFR for a long time, the storage must be carried out in an inert nitrogen atmosphere at a pressure of 0.26 bar [28].



**Figure 2.** Sorption-selective characteristics of the sorption materials under study in the HLW simulated solution: (a) SEC, (b) value of  $K_d$  Cs-137.

The dependencies of the values of the Cs-137 distribution coefficients on the studied sorbents on the concentration of NaNO<sub>3</sub>, KNO<sub>3</sub>, and NaOH are shown in Figure 3. For the Axionit RCs 2022 ion exchange resin, curves are not presented since its sorption characteristics are similar to those of RFR-Ca. According to the presented results, when the concentration of NaNO<sub>3</sub> and KNO<sub>3</sub> increases, the values of  $K_d$  Cs-137 naturally decrease due to an increase in competitive adsorption. In NaNO<sub>3</sub> solutions, the highest values of  $K_d$ Cs-137 were obtained for the sorbents Fersal, RFR-i, and RFR-Ca. One can note that, in the presence of Na<sup>+</sup> ions, the values of  $K_d$  Cs-137 for different sorbents are similar except for Clevasol® and Axionit RCs 2017. K<sup>+</sup> ions manifest a greater competitive effect than Na<sup>+</sup>, thus reducing the  $K_d$  Cs-137 values by 0.5 orders of magnitude on average. The exception is the Fersal sorbent, whose efficiency is equally high in both NaNO<sub>3</sub> and KNO<sub>3</sub> solutions due to its extremely high selectivity towards Cs<sup>+</sup> ions. With an increase in the concentration of NaOH, the  $K_d$  Cs-137 value for the Fersal sorbent gradually decreases, while for the ion-exchange resins Axionit RCs, RFR-I, and RFR-Ca, on the contrary, the efficiency of Cs-137 extraction increases. This is related to an increase in the degree of deprotonation of functional hydroxyl groups as the concentration of hydroxide ions increases [11].

Figure 4 shows the output curves of the dependence of the decontamination factor on the volume of the fed solution (bed volumes). The sorption characteristics of RFR-I and RFR-Ca ion exchange resins were additionally tested in three consecutive sorption cycles (Figure 3b). The dependence curves f(DF) = BV were interpolated by the Akima spline, which was later used to determine the number of bed volumes fed before reaching a preset cesium breakthrough into the filtrate. For the sorbents Fersal, RFR-I, and RFR-Ca, 50% cesium breakthrough was calculated using the Thomas model (Equation (7)), since the obtained curves of the efficiency of Cs-137 extraction from the model HLW solution did not reach the set values.

To understand the processes of oxidation of RFRs during storage in air, NMR spectra of C-13 (Figure 5) were obtained, as well as those of RFR-I, which was stored in H-form in plastic containers for 6, 15, and 21 months.

Table 2 shows the values of chemical shifts and the corresponding peak areas. Relative integral intensities of the spectrum components were determined by fitting a calculated resonance line to the experimental one using the least squares method by means of independently developed software.



**Figure 3.** Dependence of the distribution coefficient of Cs-137 on the concentration of (**a**) NaNO<sub>3</sub>, (**b**) KNO<sub>3</sub>, (**c**) NaOH.



**Figure 4.** Curves of the dependence of the decontamination factor on the volume of the fed model solution: (**a**) sorbents Fersal, Clevasol<sup>®</sup>, Axionit RCs 2017, Axionit RCs 2022, (**b**) removal of Cs-137 in three repeated sorption cycles on RFR-I and RFR-Ca.



**Figure 5.** C-13 NMR spectra of RFRs; (a) RFR-i, (b) Axionit RCs, 1—RFR-i stored for 6 months, 2—RFR-i stored for 15 months, 3—RFR-i stored for 21 months, 4—Axionit RCs 2017, 5—Axionit RCs 2022. Asterisks mark the spinning sidebands.

Organic	RFR-i Stored for 21 Months		RFR-I Stored for 15 Months		RFR-I Stored for 6 Months		Axionit RCs 2018		Axionit RCs 2022	
Group	Area (%) *	CS, ppm *	Area (%)	CS, ppm	Area (%)	CS, ppm	Area (%)	CS, ppm	Area (%)	CS, ppm
-CH <sub>2</sub> -(4,6')	12.9	19.3	11.1	19.2	13.2	24.3	10.8	19.6	10.6	21
-CH <sub>2</sub> -(4,2')	10.4	29.1	13.6	28.3	8.2	32.7	7.5	29.1	9.5	30.2
-CH2-C6H6	-	-	-	-	-	-	6.7	40.2	7	42.1
-CH <sub>2</sub> OH	8	50.6	6.5	52.2	10	56.2	5.9	51.7	6.8	53.8
hemiformals	-	-	-	-	-	-	-	-	2.1	91
C <sub>2</sub> , C <sub>6</sub>	2.7	105	3.9	104.8	6.7	106.6	-	-	-	-
$C_4$	32.3	117.9	22.1	120.8	26.9	120.1	31	117.6	29	119.2
$C_5$	12.2	131.4	15.6	129.9	14.8	129.5	12.9	131.4	10.4	130.7
>C=C<	-	-	-	-	-	-	3.7	141	4.6	140.7
C <sub>1</sub> , C <sub>3</sub>	17.5	151.8	23.2	151.2	15.4	154.2	16.4	151.2	16.6	151.7
R-COO-, >C=O	4.1	160.1	4.1	159.1	4.7	160.9	5.1	160.2	3.3	158.2

Table 2. Values of chemical shifts and corresponding peak areas on the C-13 NMR spectra of the RFRs.

\* Errors for the area fractions and CS values are  $\pm 2\%$  and 0.3 ppm, respectively.

The C-13 NMR spectra of RFR-i and Axionit RCs revealed characteristic features indicating a change in the molecular structure of ion-exchangers during storage. Axionit RCs are characterized by the presence of an additional peak around 90.6 ppm related to hemiformals [29], which, however, disappears during storage, probably due to oxidation processes. In the spectrum of Axionit RCs, there are peaks around 42.1 and 140.9 ppm, which were not described in the works on RFRs and can be attributed to the benzylmethylene radical [30] and alkenes [31], respectively. The presence of these peaks can be explained by the impurities in the form of organic compounds used as an emulsifier to produce spherical resin granules.

RFR-i is characterized by the presence of a peak around 106 ppm, which can be related to the carbon of the aromatic ring of resorcinol both at the C2 position not associated with the methylene bridge and at the C6 position [32]. The area of this peak gradually decreases during the storage of ion-exchange resin, which can be explained by the formation of para-quinone during oxidation with oxygen in the air [33].

A common feature of both ion exchange resin samples is a peak around 160 ppm, which appears after 21 months of storage. This peak is presumably determined by the formation of quinone and carboxylate groups [33,34]. The formation of carboxylates and quinones during oxidation is probably one of the main reasons for the decrease in the efficiency of Cs-137 extraction by RFRs.

Therefore, the negative effects of the RFR oxidation process are more pronounced under dynamic conditions, making it impossible to use resin as a sorption load in columns. Thus, during the decontamination of alkaline LRW, it is necessary to use fresh batches of RFR, and the long-term storage must be carried out in an inert atmosphere.

According to the volume of the fed model solution before attaining the 50% cesium breakthrough into the filtrate (DF 2, Table 3), the order of sorbents changes and looks as follows: Fersal > RFR-i > RFR-Ca~Axionit RCs 2022 > Clevasol<sup>®</sup>. This can be explained by the fact that, at high SEC values (Figure 2a), the efficiency of cesium removal by RFR-i resin at the initial stage is presumably limited by mass transfer in the grain volume.

**Table 3.** The number of bed volumes of the solution passed before reaching the preset cesium breakthrough into the filtrate.

Removal Efficiency		Axionit	nit Axionit				RFR-i		RFR-Ca			
		RCs	RCs	Clevasol®	Fersal	A	dsorption C	Cycle	Adsorption Cycle			
%	DF	2022	2017			1	2	3	1	2	3	
99	100	$41\pm 2$	0	$22\pm1$	$127\pm 6$	$30 \pm 1$	$45\pm2$	$89\pm4$	$44\pm 2$	$31\pm2$	$29\pm1$	
95	20	$56\pm3$	$9\pm0.5$	$27\pm1$	$160\pm 8$	$50\pm3$	$65\pm3$	$157\pm8$	$53\pm3$	$40\pm2$	$37\pm2$	
90	10	$63\pm3$	$10\pm0.5$	$32\pm2$	$177\pm9$	$63 \pm 3$	$78\pm4$	$195\pm9$	$57\pm3$	$45\pm2$	$42\pm2$	
50	2	$83\pm4$	$13\pm0.5$	$45\pm2$	$237\pm12~{}^{*}$	$117\pm6$ *	$153\pm8$	$298\pm15~{*}$	$77\pm4$	$73\pm4$	$59\pm3$	

\* Values calculated using the Thomas model.

The disadvantage of the Fersal and Clevasol<sup>®</sup> sorbents is the loss of mechanical strength during the desorption of cesium, which makes it impossible to reuse them. Granules of the ion-exchange resins RFR-i and RFR-Ca after desorption remained in their original form and were used for the resorption of cesium.

Figure 6b shows the output sorption curves of Cs-137 on the ion exchange resins RFR-I and RFR-Ca during the first, second, and third sorption cycles. During three repeated sorption-desorption cycles using RFRs, changes in sorption characteristics are observed (Table 3). For RFR-Ca, there is a decrease in the volume of the solution fed before reaching a preset cesium breakthrough into the filtrate due to oxidation at low percolation rates of the model HLW solution. On the contrary, for RFR-I, an increase in the sorption resource was observed, which was associated with the gradual transition of the ion-exchange resin to the operating mode. This transition can be associated with a number of reasons, such as the gradual removal of potassium ions [35], non-reacted reaction products from the polymer matrix, and an increase in the mass transfer rate in the bulk of the resin grain.

To calculate the theoretical value of TDEC, we used the output curves of the dependence  $f(C/C_0) = t$  (Figure 6), which were approximated by nonlinear regression using the Thomas equation (Equation (7)). Table 4 shows the calculated parameters of the Thomas model equation for the sorbents Fersal, RFR-I, and RFR-Ca. The coefficient of determination exceeds 0.95, which indicates a good agreement of the experimental values with the Thomas model.



**Figure 6.** Dependence curves of  $C/C_0$  on time: (a) sorbents Fersal, Clevasol<sup>®</sup>, Axionit RS 2017, Axionit RS 2022, (b) extraction of Cs-137 in three repeated sorption cycles on RFR-I and RFR-Ca; the dotted lines are curves obtained by the nonlinear regression equation of the Thomas model.

Parameters of the Thomas Equation		RFR-Ca					
	Α	dsorption Cycl	e	A	Fersal		
	1	2	3	1	2	3	
а	$7.7\pm0.5$	$5.3\pm0.3$	$7.8\pm0.3$	$5.4\pm0.2$	$4.3\pm0.2$	$6.3\pm0.4$	$9.1\pm0.3$
b	$0.43\pm0.03$	$0.24\pm0.01$	$0.33\pm0.01$	$0.15\pm0.01$	$0.09\pm0.01$	$0.7\pm0.1$	$0.13\pm0.01$
R <sup>2</sup>	0.9961	0.9909	0.9972	0.9891	0.9886	0.9125	0.9943
$K_{\rm Th}  ({\rm cm}^3/{\rm mg} \times {\rm g})$	8.69	4.79	6.55	3.03	1.84	1.42	2.54

Table 4. Calculated parameters of the Thomas model equation.

For the Clevasol<sup>®</sup> and Axionit RCs sorbents, as the volume of the fed solution increases, the value of the ratio  $C_0/C$  begins to exceed one (Figure 6a), which indicates the desorption process, presumably associated with the chemical destruction of the sorbents. For this reason, the Thomas model was not used for cesium output curves obtained with Clevasol<sup>®</sup> and Axionit RCs sorbents.

The presence of a macro concentration of a stable isotope of cesium in the LRW imposes high requirements for the sorption materials in regard to the value of the dynamic exchange capacity. The latter is caused by the fact that, despite the high selectivity of the sorption materials for cesium, along with a decrease in the value of the dynamic exchange capacity, the volume of liquid waste decontaminated from cesium will also decrease.

To calculate the total dynamic exchange capacity, the experimental values were extrapolated to the values of total cesium saturation using the Thomas equation with the parameters given in Table 3. Figure 7 shows the theoretical integral curves obtained for the saturation of sorbents with cesium under dynamic conditions.



Figure 7. Integral curves of the adsorption of cesium from the HLW simulated solution.

Table 5 shows the calculated values of the dynamic exchange capacity before attaining a preset cesium breakthrough into the filtrate, as well as the theoretical values of the total dynamic capacity. According to the results obtained during the first cycle, the Fersal sorbent has the largest capacity for cesium among the other investigated sorption materials.

**Table 5.** Values of the dynamic exchange capacity (mg/cm<sup>3</sup>) before reaching a preset cesium break-through into the filtrate, and values of the total dynamic exchange capacity calculated using the Thomas model.

Removal Efficiency		RFR-Ca				RFR-i				
0/	Adsorption Cycle Adsorption Cycle				vcle	RCs 2022	Clevasol	Fersal		
%	DF	1	2	3	1	2	3	-		
99	100	$2.1\pm0.1$	$1.5\pm0.1$	$1.4\pm0.1$	$1.5\pm0.1$	$2.2\pm0.1$	$2.2\pm0.1$	$2.5\pm0.1$	$1.0\pm0.1$	$6.2\pm0.3$
95	20	$2.6\pm0.1$	$1.9\pm0.1$	$1.8\pm0.1$	$2.4\pm0.1$	$3.1\pm0.2$	$7.6\pm0.4$ $^1$	$2.9\pm0.1$	$1.2\pm0.1$	$7.8\pm0.4$
90	10	$2.8\pm0.1$	$2.2\pm0.1$	$2.0\pm0.1$	$3.0\pm0.1$	$3.8\pm0.2$	$9.3\pm0.4$ $^1$	$3.2\pm0.2$	$1.5\pm0.1$	$8.6\pm0.5$
50	2	$3.4\pm0.2$	$3.0\pm0.2$	$2.5\pm0.1$	$5.0\pm0.3$ $^1$	$6.31\pm0.3$	$13.1 \pm 0.8$ $^{1}$	$3.8\pm0.2$	$1.9\pm0.1$	$10.8\pm0.5$ $^1$
TE	DEC	$3.8\pm0.2^{\ 1}$	$3.5\pm0.2^{\ 1}$	$2.8\pm0.1~^1$	$5.8\pm0.3$ $^1$	$7.61\pm0.4$	$14.7\pm0.8$ $^1$	$4\pm0.2$ $^1$	$2\pm0.1$ $^2$	$11.7\pm0.4~^1$

<sup>1</sup> The value calculated using the Thomas model. <sup>2</sup> Maximum value before desorption.

The RFR-Ca resin is characterized by a decrease in the theoretical value of TDEC, which is associated with chemical and physical degradation, whereas the accumulation of ionizing radiation dose can also intensify this process [36]. RFR-I, with the number of adsorption cycles increasing, is characterized by an increase in the theoretical value of TDEC, which, at the third adsorption cycle, is comparable to the value obtained for the Fersal sorbent. This indicates the high chemical stability of the RFR-I ion exchange resin and its gradual transition to operating mode. The increase in the total dynamic exchange capacity can also be explained by an increase in the number of exchange groups due to the oxidation of methyl groups to carboxyl groups [37].

Solutions of HNO<sub>3</sub> were used for the desorption of Cs-137. One should mention that, at room temperature, 2.0–3.0 M solutions of HNO<sub>3</sub> lead to changes in RFR after 24 h due to its nitration [38]. Nitration of RFRs with 0.5–1.0 M HNO<sub>3</sub> solutions occurs when heated to 55 °C or after prolonged exposure for 70 days [38,39]. Nitration of RFRs is accompanied by the destruction of the polymer matrix as well as a decrease in the sorption capacity [40]. Therefore, in terms of the volume of the desorbing solution consumed, the time of desorption, and the destruction of the polymer matrix, the optimal concentration of the HNO<sub>3</sub> solution is 1.0 mol/dm<sup>3</sup> [6]. The solution of HNO<sub>3</sub> at a concentration of 7.5 mol/dm<sup>3</sup> was used as a desorbing solution for the sorbents Fersal and Clevasol<sup>®</sup>. The rate of feeding of the desorbing solution was 2.3 cm<sup>3</sup>/h (0.77 BV/h). The curves of desorption of Cs-137 from various sorbents are shown in Figure 8.



**Figure 8.** Cs-137 desorption: (**a**) integral desorption curves, (**b**) output desorption curves. Desorbing solutions: 7.5 mol/dm<sup>3</sup> HNO<sub>3</sub> used for Fersal and Clevasol<sup>®</sup> sorbents, 1.0 mol/dm<sup>3</sup> HNO<sub>3</sub> used for RFRs sorbents.

Ion-exchange resins have an advantage over inorganic sorbents in requiring solutions with lower concentrations of HNO<sub>3</sub>, which is important for reducing the corrosion of equipment. The curves obtained for ion-exchange resins RFR-I and RFR-Ca indicate a wide desorption front. This feature could be associated with a low mass transfer rate inside the resin grain or a significant decrease of the resin volume due to a large difference between bulk weight and specific volume value, which leads to sorbent compaction in the column, thus preventing the normal flow of the desorbing solution. Despite some differences, the results presented in Figure 8 show that, with the exception of the Fersal sorbent, when 10 bed volumes of the HNO<sub>3</sub> solution are fed, the desorption efficiency exceeds 99%, which is consistent with the known published data [3].

## 4. Conclusions

The sorption characteristics of resorcinol-formaldehyde resins Axionit Cs, RFR-i, and RFR-Ca as well as inorganic sorbents of Clevasol<sup>®</sup> and Fersal brands towards cesium ions in model-simulated solutions of high-level alkaline waste streams from the Mayak Production Association have been evaluated. The studied sorbents can be arranged in the following order in terms of their sorption characteristics in the HLW simulated solution under static conditions: Fersal > RFR-i > Axionit RCs 2022~RFR-Ca Axionit RCs 2017 Clevasol. The Fersal sorbent is characterized by the highest selectivity towards cesium ions. Along with the increase in NaOH concentration in solution, the efficiency of the Fersal sorbent decreases, whereas that of resorcinol-formaldehyde resins increases. It has been demonstrated that, under dynamic conditions, the resource of the Fersal sorbent until the 1% cesium breakthrough is a minimum 2.5-fold larger in comparison with other sorption materials. The disadvantage of inorganic sorbents consists of a loss of mechanical strength upon cesium desorption by a 7.5 M solution of HNO<sub>3</sub>. Using RFRs, cesium can be desorbed by a 1 V solution of HNO<sub>3</sub> without a loss of the granule's mechanical strength. Within three

repeated sorption-desorption cycles, RFR-i has the best values of resource and full dynamic exchange capacity, as compared with the porous RFR-Ca. A common disadvantage of RFRs is worsening of sorption characteristics as a result of oxidation accompanied by the formation of quinone and carboxylate groups. Based on the obtained results, one can conclude that in the decontamination of high-level wastes in the storage tanks of the Mayak Production Association, the sorbent of the Fersal brand and the resorcinol-formaldehyde resin RFR-I can be used. However, taking into account repeated use in sorption-desorption cycles and the total amount of the decontaminated HLW, resorcinol-formaldehyde resins can turn out to be more preferential.

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## References

- Kozlov, P.V.; Kazadaev, A.A.; Makarovskii, R.A.; Remizov, M.B.; Verbitskii, K.V.; Logunov, M.V. Development of a Process for Cesium Recovery from the Clarified Phase of High-Level Waste Storage Tanks of the Mayak Production Association with a Ferrocyanide Sorbent. *Radiochemistry* 2016, *58*, 295–301. [CrossRef]
- Milyutin, V.V.; Mikheev, S.V.; Gelis, V.M.; Kozlitin, E.A. Sorption of Cesium on Ferrocyanide Sorbents from Highly Saline Solutions. *Radiochemistry* 2009, 51, 298–300. [CrossRef]
- 3. Fiskum, S.K.; Pease, L.F.; Peterson, R.A. Review of Ion Exchange Technologies for Cesium Removal from Caustic Tank Waste. Solvent Extr. Ion Exch. 2020, 38, 573–611. [CrossRef]
- 4. Aleman, S.; Hamm, L.; Smith, F. Ion Exchange Modeling Of Cesium Removal From Hanford Waste Using Spherical Resorcinol-Formaldehyde Resin; Technical Report WSRC-STI-2007-00030; Washington Savannah River Site (SRS): Aiken, SC, USA, 2007.
- Fiskum, S.K.; Blanchard, D.L.; Arm, S.T.; Peterson, R.A. Cesium Removal from Simulated and Actual Hanford Tank Waste Using Ion Exchange. Sep. Sci. Technol. 2005, 40, 51–67. [CrossRef]
- Milyutin, V.V.; Zelenin, P.G.; Kozlov, P.V.; Remizov, M.B.; Kondrutskii, D.A. Sorption of Cesium from Alkaline Solutions onto Resorcinol-Formaldehyde Sorbents. *Radiochemistry* 2019, *61*, 714–718. [CrossRef]
- Tokar, E.; Tutov, M.; Kozlov, P.; Slobodyuk, A.; Egorin, A. Effect of the Resorcinol/Formaldehyde Ratio and the Temperature of the Resorcinol–Formaldehyde Gel Solidification on the Chemical Stability and Sorption Characteristics of Ion-Exchange Resins. *Gels* 2021, 7, 239. [CrossRef]
- Miller, H.S.; Kline, G.E. Reactions of Cesium in Trace Amounts with Ion-Exchange Resins. J. Am. Chem. Soc. 1951, 73, 2741–2743. [CrossRef]
- 9. Kargov, S.I.; Shelkovnikova, L.A.; Ivanov, V.A. The Nature of Ion Exchange Selectivity of Phenol-Formaldehyde Sorbents with Respect to Cesium and Rubidium Ions. *Russ. J. Phys. Chem. A* 2012, *86*, 860–866. [CrossRef]
- Samanta, S.K.; Misra, B.M. Ion Exchange Selectivity of a Resorcinol-Fqrmaldehyde Polycondensate Resin for Cesium in Relation to Other Alkali Metal Ions. *Solvent Extr. Ion Exch.* 1995, 13, 575–589. [CrossRef]

- Hubler, T.L.; Franz, J.A.; Shaw, W.J.; Bryan, S.A.; Hallen, R.T.; Brown, G.N.; Bray, L.A.; Linehan, J.C. Synthesis, Structural Characterization, and Performance Evaluation of Resorcinol-Formaldehyde (R-F) Ion-Exchange Resin; Technical Report PNL-10744; Pacific Northwest Laboratory: Richland, WA, USA, 1995.
- 12. Duignan, M.R.; Nash, C.A. Removal of Cesium from Savannah River Site Waste with Spherical Resorcinol Formaldehyde Ion Exchange Resin: Experimental Tests. *Sep. Sci. Technol.* **2010**, *45*, 1828–1840. [CrossRef]
- Adamson, D.J. Pilot-Scale Hydraulic Testing of Resorcinol Formaldehyde Ion Exchange Resin. In Proceedings of the Fluids Engineering Division Summer Meeting, Vail, CO, USA, 2–6 August 2009; Volume 43727, pp. 545–553. [CrossRef]
- Duignan, M.R.; Nash, C.A.; Punch, T.M. High Aspect Ratio Ion Exchange Resin Bed—Hydraulic Results for Spherical Resin Beads. Sep. Sci. Technol. 2008, 43, 2943–2979. [CrossRef]
- 15. Brooks, K.P.; Augspurger, B.S.; Blanchard, D.L.; Cuta, J.M.; Fiskum, S.K.; Thorson, M.R. Hydraulic Testing of Ion Exchange Resins for Cesium Removal from Hanford Tank Waste. *Sep. Sci. Technol.* **2006**, *41*, 2391–2408. [CrossRef]
- Fiskum, S.K.; Augspurger, B.S.; Brooks, K.P.; Buchmiller, W.C.; Russell, R.L.; Schweiger, M.J.; Snow, L.A.; Steele, M.J.; Thomas, K.K.; Wallace, D.E.; et al. *Comparison Testing of Multiple Resorcinol-Formaldehyde Resins for the River Protection Project—Waste Treatment Plant*; Technical Report PNWD-3387 WTP-RPT-103, Rev 0; Savannah River Technology Center, Department of Energy 1000 Independence Ave.: Washington, DC, USA, 2004; p. 2978.
- Clevasol<sup>®</sup>—A Novel Cation Exchange Resin for Isotope Capture. Available online: https://www.lemerpax.com/en/products/ clevasol-en/ (accessed on 25 April 2023).
- Yakushev, A.; Turler, A.; Dvorakova, Z.; Bremen, K. CLEVASOL, a Novel Radiation Hard Cation Exchanger Suitable for Treatment of Liquid Radioactive Waste with High Salinity. In Proceedings of the APSORC'13—5th Asia-Pacific Symposium on Radiochemistry Kanazawa, Kanazawa, Japan, 22–27 September 2013; p. 133.
- 19. Lin, M.; Kajan, I.; Schumann, D.; Türler, A.; Fankhauser, A. Selective Cs-Removal from Highly Acidic Spent Nuclear Fuel Solutions. *Radiochim. Acta* 2020, 108, 615–626. [CrossRef]
- Chaplin, J.D.; Berillo, D.; Purkis, J.M.; Byrne, M.L.; Tribolet, A.D.C.C.M.; Warwick, P.E.; Cundy, A.B. Effective <sup>137</sup>Cs<sup>+</sup> and <sup>90</sup>Sr<sup>2+</sup> Immobilisation from Groundwater by Inorganic Polymer Resin Clevasol<sup>®</sup> Embedded within a Macroporous Cryogel Host Matrix. *Mater. Today Sustain.* 2022, 19, 100190. [CrossRef]
- Haas, P.A. A Review of Information on Ferrocyanide Solids for Removal of Cesium from Solutions. Sep. Sci. Technol. 1993, 28, 2479–2506. [CrossRef]
- 22. Loos-Neskovic, C.; Fedoroff, M. Fixation Mechanisms of Cesium on Nickel and Zinc Ferrocyanides. *Solvent Extr. Ion Exch.* **1989**, 7, 131–158. [CrossRef]
- 23. Lee, E.F.T.; Streat, M. Sorption of Caesium by Complex Hexacyanoferrates. v. a Comparison of Some Cyanoferrates. J. Chem. Tech. Biotechnol. 1983, 33, 333–338. [CrossRef]
- Milyutin, V.V.; Nekrasova, N.A.; Kozlov, P.V.; Markova, D.V.; Feoktistov, K.A. Extraction of cesium from model solutions of highly active alkaline wastes on an inorganic ferrocyanide sorbent of the brand Fersal. *Vopr. Radiatsionnoy Bezop.* 2022, 3, 22–27. (In Russian)
- Milyutin, V.V.; Gelis, V.M.; Leonov, N.B. Study of the Sorption Kinetics of Cesium and Strontium Radionuclides by Sorbents of Different Classes. *Radiochemistry* 1998, 40, 418–420. (In Russian)
- 26. Sanders, J. Veusz—A Scientific Plotting Package. Available online: https://veusz.github.io/ (accessed on 25 April 2023).
- Hubler, T.L.; Shaw, W.J.; Brown, G.N.; Linehan, J.C.; Franz, J.A.; Hart, T.R.; Hogan, M.O. Chemical Derivation to Enhance the Chemical/Oxidative Stability of Resorcinol-Formaldehyde (R-F); Resin Technical Report No. PNNL–11327; Pacific Northwest National Laboratory: Richland, WA, USA, 1996.
- Russell, R.L.; Fiskum, S.K.; Smoot, M.R.; Rinehart, D.E. Cesium Isotherm Testing with Spherical Resorcinol-Formaldehyde Resin at High Sodium Concentrations; Technical Report PNNL-25277; Pacific Northwest National Laboratory (PNNL): Richland, WA, USA, 2016.
- Kim, M.G.; Wu, Y.; Amos, L.W. Polymer Structure of Cured Alkaline Phenol–Formaldehyde Resol Resins with Respect to Resin Synthesis Mole Ratio and Oxidative Side Reactions. *J. Polym. Sci. Part A Polym. Chem.* 1997, 35, 3275–3285. [CrossRef]
- Christiansen, A.W. Resorcinol-Formaldehyde Reactions in Dilute Solution Observed by Carbon-13 NMR Spectroscopy. J. Appl. Polym. Sci. 2000, 75, 1760–1768. [CrossRef]
- Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. Tables of Spectral Data for Structure Determination of Organic Compounds; Springer Science & Business Media: Berlin/Heidelberg, Germany, 2013; ISBN 978-3-662-10207-7.
- Werstler, D.D. Quantitative <sup>13</sup>C n.m.r, Characterization of Aqueous Formaldehyde Resins: 2. Resorcinol- Formaldehyde Resins. Polymer 1986, 27, 757–764. [CrossRef]
- Hubler, T.L.; Franz, J.A.; Shaw, W.J.; Hogan, M.O.; Hallen, R.T.; Brown, G.N.; Linehan, J.C. Structure/Function Studies of Resorcinol-Formaldehyde (R-F) and Phenol-Formaldehyde (P-F) Copolymer Ion-Exchange Resins; Technical Report PNNL-11347 Richland; Pacific Northwest National Laboratory: Washington, WA, USA, 1996.
- 34. Pratt, L.M.; Szostak, R.; Khan, I.M. Alkaline degradation of resorcinol- formaldehyde resins: Solid-State nmr, thermal adsorption and desorption analysis, and molecular modeling. *J. Macromol. Sci. Part A Pure Appl. Chem.* **1997**, *34*, 281–289. [CrossRef]
- 35. Arm, S.T.; Blanchard, D.L. *Pre-Conditioning and Regeneration Requirements of Ground Gel Resorcinol Formaldehyde Ion Exchange Resin;* Technical Report WTP-RPT-104, PNWD-3390; Battelle–Pacific Northwest Division, Richland: Washington, DC, USA, 2004.

- Fiskum, S.K.; Colburn, H.A.; Rovira, A.M.; Allred, J.R.; Smoot, M.R.; Peterson, R.A.; Landon, M.R.; Colosi, K.A. Cesium Removal from AP-105 Hanford Tank Waste Using Spherical Resorcinol Formaldehyde Resin. *Sep. Sci. Technol.* 2019, 54, 1932–1941. [CrossRef]
- 37. Shelkovnikova, L.A.; Gavlina, O.T.; Ivanov, V.A. Stability of Phenol-Formaldehyde Ion-Exchange Sorbents in Aqueous Solutions. *Russ. J. Phys. Chem. A* 2011, *85*, 1652–1659. [CrossRef]
- King, W.D.; Fondeur, F.F.; Wilmarth, W.R.; Pettis, M.E.; McCollum, S.W. Reactivity of Resorcinol Formaldehyde Resin with Nitric Acid. Sep. Sci. Technol. 2006, 41, 2475–2486. [CrossRef]
- 39. Russell, R.L.; Rinehart, D.E.; Brown, G.N.; Schonewill, P.P.; Peterson, R.A. *Ion Exchange Kinetics Testing with SRF Resin*; Technical Report PNNL-21109; Pacific Northwest National Laboratory: Richland, WA, USA, 2012.
- 40. Arm, S.T.; Blanchard, D.L.; Fiskum, S.K.; Weier, D.R. *Chemical Degradation of SuperLig*<sup>®</sup> 644 Ion Exchange Resin; Technical Report PNWD-3315; Battelle-Pacific Northwest Division: Richland, WA, USA, 2003.

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