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Porous Resorcinol-Formaldehyde Resins (RFR) as Sorbents for Radiocesium Removal

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Abstract. Porous resorcinol-formaldehyde resins were fabricated by leaching an inorganic filler introduced earlier into the polymer and by polymerization of the emulsion dispersed medium. The sorption properties of the fabricated materials with respect to the micro-quantities of ^{137}Cs were investigated under dynamic conditions at high feeding rates of a model highly mineralized alkaline solution. It has been shown that the fabricated ion exchangers are characterized with high decontamination factors in comparison with the initial nonporous resin.

1. Introduction

Accumulation and subsequent evaporation of liquid radioactive wastes (LRW) in order to reduce their volume results in formation of evaporator concentrates produced by respective devices at nuclear power plants (NPP). Evaporator concentrates comprise highly mineralized alkaline solutions (high pH), whose activity is mainly caused by the presence of ^{137}Cs radionuclide [1]. The generally accepted methods of processing and conditioning of evaporator concentrates include immobilization into solid matrices, mainly cement ones, which results in the increase of the volume of wastes to be sent to final disposal. To reduce the quantity of the conditioned wastes, ^{137}Cs radionuclides can be preliminarily removed from evaporator concentrates using the selective sorption and producing small volumes of the radionuclide concentrate [2]. Granulated and composite sorbents based on ferrocyanides of transition metals (Ni, Co, and Cu) [3–5] and low-acidity phenol-aldehyde cation exchangers [6, 7] have found an extensive application in selective removal of ^{137}Cs from liquid media. General disadvantages of ferrocyanide sorbents include their peptization and fast dissolution in alkaline media [8, 9], which serves as a reason of the reduction of their operation resource and/or even complete material destruction.

The above disadvantages are not associated with resorcinol-formaldehyde resins (RF-resins) belonging to the group of phenol-aldehyde thermoreactive polymers of the resol type and comprising low-acidity cation exchangers. Such ion exchangers are capable to remove selectively Rb and Cs from alkaline media with high Na$^+$ ions content [10]. As compared to phenol-formaldehyde resins belonging to the same group of ion exchangers, RF-resins are characterized with the best sorption characteristics, which is the result of the presence of a large number of functional –OH groups in the polymer structure [11, 12]. Because of their unique sorption properties, RF-resins are applied for removal and concentration of ^{137}Cs radionuclides from alkaline liquid radioactive wastes, including evaporator concentrates. For example, there exists the experience of using RF-resins in treatment of

highly mineralized LRW [13, 14]. Besides, an efficient method for decontamination of radioactively-contaminated spent ion-exchange resins from ^{137}Cs by RFR was suggested [15].

However, phenol- and, especially, RF-resins are known to be chemically unstable and undergo gradual oxidation at a prolonged exposure in alkaline media, which results in the decrease of selectivity with respect to Cs$^+$ ions [11]. Oxidation mainly affects methylene bridges and aromatic resorcinol rings, which results in the decrease of total number of functional groups [16]. The authors of [17] assumed that oxymethylene bridges ($-CH_2-O-CH_2-$) and methylol groups ($-CH_2-OH$) are oxidized until carboxyl groups, which are not specific with respect to Cs, but increase the ion exchanger capacity.

RF-resins are mainly applied under dynamic conditions, when ion exchanger is used as a bed of the sorption column with subsequent of liquid radioactive wastes through a stationary layer of the material [18]. Under dynamic conditions, the kinetic characteristics of the ^{137}Cs sorption process are mainly limited by mass transfer inside the ion exchanger grain – gel diffusion. In this case, the improvement of kinetic characteristics of ion exchange would enable one to increase the linear rate of feeding the solution to be decontaminated through a stationary layer of the RF-resin with preservation of high decontamination factors (DF) for ^{137}Cs and, thus, to decrease the treatment time and ion exchanger destruction.

The decrease of the RFR crosslinking degree for the above purposes is not reasonable due to possible decrease of the resin chemical stability [19]. One of the ways of improving the kinetic characteristics of the ion exchange process consists in formation of a polymer porous structure, for example, through introduction of an inorganic filler with its subsequent leaching or polymerization of the dispersed medium of highly concentrated emulsion [20].

2. Experimental

Resorcinol ($C_6H_6O_2$), sodium hydroxide (NaOH), nitric acid (HNO_3), formalin, and sodium nitrate ($NaNO_3$) were purchased from Nevareaktiv, Russia. All chemicals were of the analytical grade and used as received without further purification. Carrier free radiocesium (^{137}Cs) was obtained from A.I. Leypunsky Institute of Physics and Power Engineering in the chloride form in 1 M hydrochloric acid solution and diluted prior to use.

The initial RF-resin (RFR-i) was obtained according to the technique described in [19]. Solidification was carried out at 200–210 °C for 6 h in air, after which it was ground and washed with 1 M solution of HNO_3.
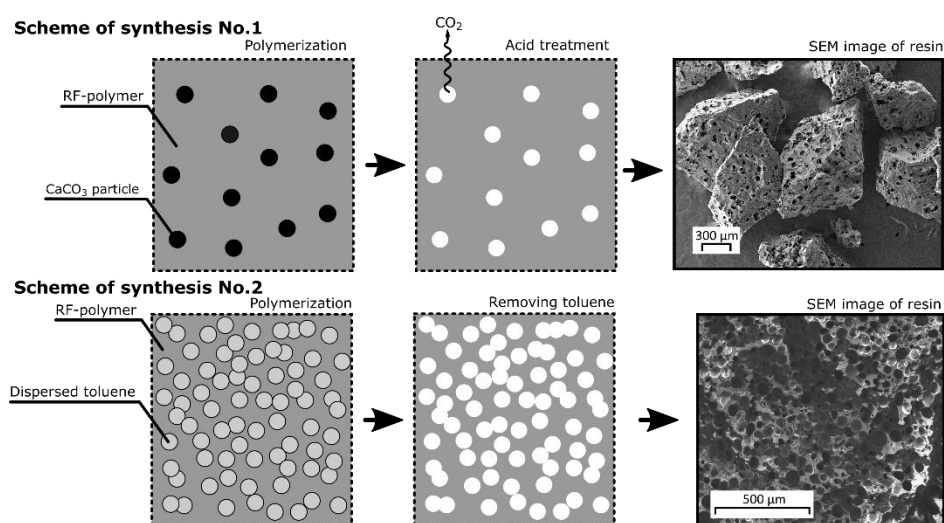

Figure 1. Schemes of synthesis of SEM-images of ion exchange resins.

Samples marked as "porous" were obtained in accordance with two different schemes. Figure 1 shows the methods of synthesis and SEM-images of the fabricated ion exchangers. According to the first scheme, ion exchangers were fabricated through introduction of a thin powder of $CaCO_3$ into the reaction mixture with subsequent solidification of the resorcinol-formaldehyde polymer and treatment by 1 M solution of HNO_3. A sample of the RFR-10 resin was obtained through introduction of $CaCO_3$ in the quantity of 10 % of the mass of initial components used at synthesis, whereas the RFR-25 ion exchanger was fabricated though addition of 25 % $CaCO_3$.

According to the second synthesis scheme, resin samples were obtained through addition of toluene into the liquid reaction mixture. The obtained polymer was solidified and sequentially washed by 1 M solution of HNO_3 and 1 M solution of NaOH. The following samples were obtained: RFR-25t, RFR-35t, and RFR-65t differing in the quantities of 25, 35, and 65 % of toluene from total mass of initial components used in synthesis.

To estimate the efficiency of absorption of ^{137}Cs radionuclide by ion exchange resins under dynamic conditions, 1 ml of a sample of a grain size of 0.5–1.0 mm was placed into a column of an internal diameter of 1 cm. A model solution containing 1.25 mol/l of $NaNO_3$ and 0.75 mol/l of NaOH and labeled with ^{137}Cs radionuclide ^{137}Cs (500-1000 Bq ml^{-1}) fed through a column at a rate of 50 ml h^{-1}. After feeding 200–300 ml of the solution, the experiment was stopped, and resins were washed by 1 M solution of HNO_3 in order to desorb ^{137}Cs – the process completeness was estimated on the eluate specific activity. Thereafter, resins were washed by distilled water, and the sorption cycle was repeated. The results of ^{137}Cs removal as a function of $\log(C/C_0)$ on bed volumes of the fed model solution are shown in Figure 3 and 4, where C – the initial solution activity (Bq cm^{-3}), C_1 – the residual solution activity (Bq cm^{-3}).

Kinetic characteristics of the ion exchange process were determined under static conditions using a model solution labeled with ^{137}Cs radionuclide at a rate m/V = 0.001 g ml^{-1}. In the process of stirring, solution samples were taken within certain time periods and analyzed for the residual activity. The degree of equilibrium attainment (F) in the moment τ was calculated from the analysis results according to the formula: (1)
where $A(\tau)$, $A(max)$ – the initial sorbent activities on the radionuclide in the moment τ and at maximal sorption, respectively (Bq ml^{-1}).

The half-exchange time ($t_{0.5}$) was determined graphically using the f(F)=τ dependence (Figure 2). The gel diffusion coefficients were determined using the formula (2): (2)
Where r – the average radius of the resin particle (cm); $t_{0.5}$ – the half-exchange time (min).

3. Results and Discussion

The results of studies of the ^{137}Cs sorption under static conditions demonstrated that porous resins were characterized with the desorption process, whose start time depends on synthesis and varies from 2 to 6 days. The desorption process is the result of resin destruction with simultaneous yellow or dark-orange coloring of the model solution, so that the point of attainment of the maximal ^{137}Cs sorption, after which the ion exchanger starts to destruct, was taken as A(max) in each individual case. For RFR-i, no ^{137}Cs desorption was observed even upon 13-day contact with the model solution.

It is worth mentioning that in f(F)=τ coordinates the experimentally obtained values are satisfactorily approximated by a linear function ($r^2 > 0.95$), which indicates to limitations of the ion exchange process, first of all, by mass transfer inside the ion exchanger grain. In spite of chemical destruction of porous samples in alkaline solutions, they are characterized with larger D values and smaller $t_{0.5}$ ones (Table 1).

Figure 2 shows kinetic curves of ^{137}Cs sorption from the model solution. It was revealed that resins obtained through $CaCO_3$ leaching were characterized with better kinetic parameters than the samples fabricated in accordance with the second scheme that, probably, contains a system of closed macropores. In case of introduction of an inorganic filler, more clearly expressed increase of kinetic parameters of the ion exchange process is observed at the synthesis stage (Table 1). Destruction of $CaCO_3$ in the process of acidic treatment results in CO_2 formation and active release from the polymer

matrix through cleavages and fractures, which excludes the formation of isolated cavities in the resin grain bulk.
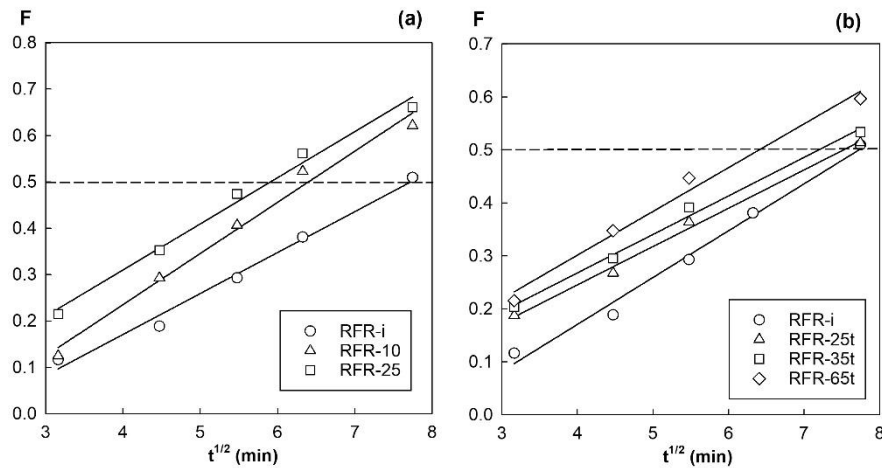

Figure 2. Kinetic curves of ^{137}Cs sorption.

Table 1. Internal diffusion coefficients (D) and half-exchange times ($\tau_{0,5}$) at sorption of ^{137}Cs micro-quantities.

	$D \times 10^7$ (cm^2 min^{-1})	$t_{0.5}$ (min)
RFR-i	7±1.0	60±10
RFR-10	10±0.5	45±10
RFR-25	12±0.5	28±10
RFR-25t	7.4±0.2	57±10
RFR-35t	8±0.7	52±10
RFR-65t	10±0.5	41±10

The results of ^{137}Cs removal from the model solution under dynamic conditions demonstrate that the sorption properties of the initial RF-resin and porous samples differ significantly (Figure 3). Within three sequential sorption cycles, the efficiency of ^{137}Cs removal increases, which is related to the achievement of proper working conditions of ion exchange resins. The best parameters characterize the RFR-10 resin sample, which removes ^{137}Cs twofold more efficiently in comparison with the initial RFR-i sample. However, the sorption properties of RFR-25 and RFR-i samples in the second and third cycles are compatible. The latter is related to the fact that the RFR-25 sample, having the largest surface area, dissolves at a markedly more intensive rate under effect of the model alkaline solution.

Figure 4 shows the results of ^{137}Cs removal under dynamic conditions by ion exchange resin samples obtained through polymerization of the emulsion dispersed medium. As in the previous case, the samples properties are different, which results from synthesis peculiarities. The RFR-25t resin has the bets sorption characteristics, and one can conclude that an optimal quantity of the added toluene must not exceed 25 % of the initial reagent mass. The increase of the specific surface area due to addition of larger toluene quantities (35 and 65 %) increases the rate of ion exchangers dissolution in an alkaline solution, thus decreasing the efficiency of ^{137}Cs absorption. For example, the RFR-i and RFR-35t resins are characterized with compatible sorption parameters, whereas the RFR-65t resin manifested the lowest degrees of radionuclide removal in three sorption cycles.
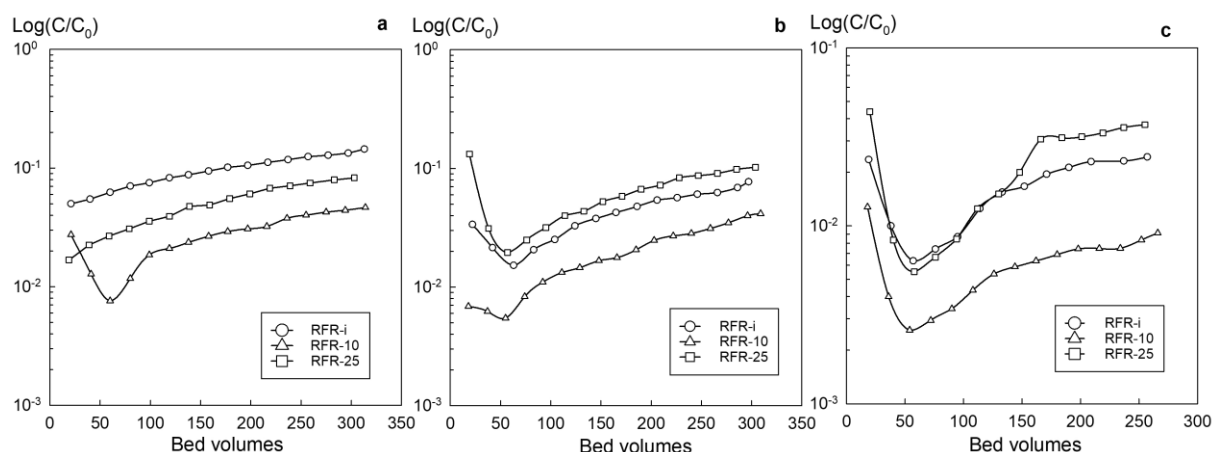
Figure 3. Sorption of ^{137}Cs from model solutions under dynamic conditions, a – 1st sorption cycle, b – 2nd – sorption cycle, c – 3rd sorption cycle.
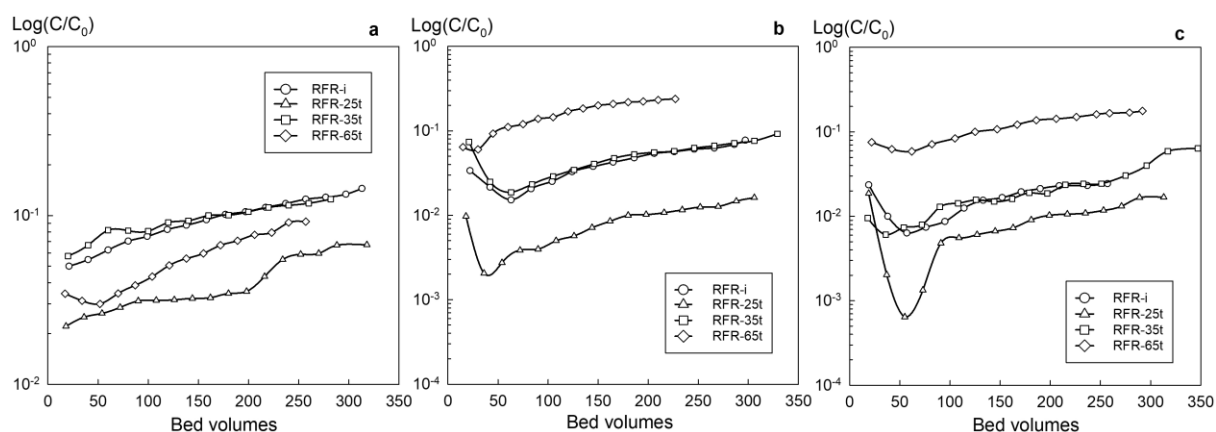

Figure 4. Sorption of ^{137}Cs from model solution under dynamic conditions, a – 1st sorption cycle, b – 2nd sorption cycle, c – 3rd sorption cycle.

4. Conclusions

RF-resins have been fabricated through introduction of an inorganic filler (CaCO$_3$) into the reaction mixture or polymerization of the dispersed medium of highly concentrated emulsion (in toluene) and their sorption characteristics have been studied. The fabricated resins can be applied in situations, when high efficiency of ^{137}Cs removal from liquid media at high linear rates of the solution feed is required.

5. References

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