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Review

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## Selective ion-exchange sorbents for caesium extraction from alkaline radioactive solutions. Review

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### Abstract

This review covers studies dedicated to the search for and development of sorbents for the extraction of the caesium-137 radioactive isotope from highly mineralised, highly alkaline solutions that are waste products of nuclear plants. This isotope with a half-life of 30.2 years is one of the most significant contributors to the radioactivity of the waste. It was shown that phenolic sorbents play the key role in caesium extraction from such solutions, they are able to exchange ions on phenolic groups in alkaline solutions, exhibiting high selectivity to caesium against large amounts of sodium and potassium ions. The sorbents make it possible to filter large solution flows, as well as to elute concentrated caesium quantitatively and rapidly with a small volume of acid. We compared the selectivity of sorbents obtained by the condensation of phenol and diatomic phenols with formaldehyde as well as modern materials obtained by the condensation of calixarenes and resorcinarenes with aldehyde. It was shown that the latter do not have any advantage in selectivity and are of lower chemical stability. Therefore, resorcinol-based materials are considered the key element in solving the problem of extracting the caesium-137 isotope from alkaline solutions. We analysed the current state of the problem. This article explains the nature of the high selectivity of phenolic sorbents for caesium ions and why the special arrangement of functional groups of calixarene and resorcinarene resins does not result in increased selectivity as compared with conventional phenol- and resorcinol-based materials.

**Keywords:** Caesium-137 isotope, Highly mineralised alkaline solutions, Ion exchange, Sorbtion, Selectivity, Resorcinol-formaldehyde resin, Calixarene, Resorcinarene

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### 1. Introduction

The reviewed authors have a number of publications concerning the properties and applications of sorbents and ion exchangers based on phenol-formaldehyde resins (PFRs). When one of these studies [1] underwent the review phase in an international journal, one of the reviews clearly questioned the relevance and practical value of the study of ion exchange on phenolic groups. The reviewer added that such materials were considered long outdated in the field of ion exchange.

The reviewer's doubt and bemusement are understandable. After all, the whole era of research, production, and widespread use of synthetic organic ion exchange resins began as early as 1935 with the condensation products of phenols with formaldehyde [2]. The PFR was a polymeric matrix onto which ion-exchange groups such as sulphonic acid, carboxylic acid, phosphorus, and amine groups were grafted [3–8]. Sulphonic acid cation exchangers were the most common as they were widely used in the softening and demineralisation of natural water and other solutions. By the mid-50s, such ion-exchange resins were produced in at least 15 countries (including the USSR [3, p. 204]). However, starting with the mid-1940s, they were promptly superseded by more chemically and mechanically stable resins based on styrenedivinylbenzene copolymer.

Nevertheless, the reviewer of [1], following our response to the comment, was surprised to admit that phenol-formaldehyde sorbents were still relevant even in the late 1990s, as they were produced, researched, and used. Since then, another two decades have passed. But even now, studies in this field still attract attention regularly, they are often cited. Therefore, it seems that the long established data on the properties of phenolic sorbents is still relevant for some areas of research, which have become a priority only in recent years.

In this review, the authors pointed out the most significant properties of phenolic sorbents, the issues they helped to solve, and the origin of their most important property, selectivity for caesium ions.

### 2. Some information on the properties of phenol-formaldehyde adsorbents and ion exchangers, and the problems they solve

In our review we did not cover the abovementioned group of ion-exchange resins based on the PFRs with grafted acid or base groups, as they were described in a large number of monographs. We focused on the sorbents where the properties of the phenol-formaldehyde matrix and its ionexchange properties play the key role.

In the 1970s, Diamond Shamrock Chemical Co. [9], a US company, produced the Duolite S-761 sorbent with irregularly shaped grains in the form of splinters resulting from the crushing of PFRs. The sorbent was proposed for the removal of colouring and other organic substances from food processing solutions. Rohm&Haas offered a similar product called Amberlite XAD 761 (previously known as Duolite XAD 761) [10]. These sorbents were synthesised by the condensation of phenol and formaldehyde, they did not have any other ionexchange groups grafted into their structure other than phenolic groups. However, as the analysis in [11] showed, in addition to phenolic groups, they contained a rather large amount of methylol groups.

In addition, similar PFRs with grafted secondary and tertiary amino groups were produced under Duolite A-568, A-561, and A-7 brands as adsorbents of organic substances from liquid media. There are examples of their use in decolourisation of solutions of glucose and sodium glutamate and purification of citric acid during its extraction from products of enzymatic sugar processing.

PFR-based sorbents were used for these purposes due to a number of their specific properties [10]:

• Better adsorption properties towards substances with large molecules, which is attributed to the fact that their matrix is more hydrophilic compared to the polystyrene matrix and has a porous structure.

• Higher density (1.11 g/cm<sup>3</sup>) compared to the polystyrene matrix (1.04 g/cm<sup>3</sup>), which makes the adsorption layer more stable, and also gives other advantages for their practical use.

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• Better fluid permeability through the layer of adsorbents and ion exchangers based on the phenol-formaldehyde matrix with irregularly shaped grains (obtained by crushing a polycondensation resin) compared to the layer of the spherical grains of polystyrene ion exchangers.

In the USSR, in the mid-1980s, the technology for the synthesis of macroporous PFRs with spherical granules was developed at the Nizhny Tagil branch of NPO *Plastmasy* [12], and the first batches were produced. In addition to being used as molecular sorbents for organic substances, they were also intended to be used as intermediates for further transformation into activated macroporous carbon with spherical granules. However, the current list of products by the manufacturing plant, which is now called Uralchimplast, does not include such products.

The main feature of the PFR-based sorbents is their high ion-exchange selectivity for caesium and rubidium ions. This property was long ago revealed and studied in sulphonic acid cationexchangers based on PFRs in neutral and alkaline solutions [13–16]. In the USSR in the 1960s, processes for separating high purity caesium and rubidium compounds from alkali metal mixtures on sulphophenolic cationite [17–20] were developed as part of a state programme.

The PFRs without other types of ionogenic groups besides phenolic ones also exhibit high ion-exchange selectivity for caesium and rubidium ions in alkaline solutions [2-23]. When interacting with an alkaline solution, hydrogen from phenolic groups is substituted by alkali metal cations, and the interchange of metal cations may occur. It is possible to extract Cs<sup>+</sup> and Rb<sup>+</sup> ions from alkali metal mixtures using macroporous PFRs with spherical granules produced by the Nizhny Tagil branch of NPO *Plastmasy* [1, 24]. In the 1980s, as part of the state programme aimed at creating a technology for complex seawater processing with the recovery of valuable minerals, a method for rubidium extraction from seawater concentrates containing a large excess of potassium ions was developed. It was based on using macroporous PFRs [1, 24–26]. Due to the major changes in the former Soviet Union at the turn of the 1980s and 1990s, the programme was discontinued. However,

the technologies developed at that time will undoubtedly be in demand in the future, when the use of the ocean's mineral resources will inevitably become a pressing issue.

### 3. Selective extraction of <sup>137</sup>Cs from alkaline waste from nuclear plants

The most significant issue that explains the ongoing attention to phenolic sorbents is the extraction of radioactive caesium during the processing of nuclear waste in many countries. The key challenge is to extract caesium from solutions that are characterised by high salt content (up to 300-350 g/l) and are highly alkaline. For example, there are five large radioactive waste sites in the USA [27], particularly in South Carolina (Savannah River Site) and Washington (Hanford Site), where weapons-grade plutonium was produced. The scale of this issue was outlined in [28]: "In the previous decade, the government spent about \$60 billion on abatement measures, most of which, however, resulted only in isolation. At least another \$200 billion and 70 years are estimated to be required for remedial measures in more than 100 areas in the United States that have been involved in the national nuclear weapons programme". In 1982, the US Congress passed the Nuclear Waste Policy Act. It launched a major project to develop a technology for processing accumulated radioactive waste into forms safe for long-term storage. A schedule for the construction of an underground facility for permanent storage of high-level radioactive waste was set [29, p. 537]. Since the late 1980s, extensive work was carried out to develop the technology and construct a processing facility for waste stored in the state of Washington [30]. The ultimate goal of the entire process is to compact the radioactive elements in order to reduce their volume, then vitrify them with borosilicate glass, and place them in stainless steel containers, first at the temporary storage facility, and then in a permanent storage facility. Already by 2005, the main stages of the technology had been designed [30] and construction had started [31]. However, there were uncertainties and concerns about the concentration of <sup>137</sup>Cs, even after construction had started. Even in 2020, the construction of the processing facilities, including the caesium removal unit, was far from complete [32]. Notably,

the US Government Accountability Office noted a steady increase in the cost of the project.

The <sup>137</sup>Cs and <sup>90</sup>Sr isotopes, which are  $\beta$ -emitters with half-lives of 30.2 years and 28.8 years, are major contributors to the radioactivity of the waste, and they also account for 95% of the heat release during waste storage. When radioactive waste is processed in the form of liquid solutions, these isotopes must be removed at the very beginning of the process, which turns out to be the most difficult challenge. This is why the separation of <sup>137</sup>Cs is called the bottleneck of the whole process. First, there are huge volumes of solutions from which <sup>137</sup>Cs has to be concentrated. Furthermore, the solutions have very high concentrations of alkali and sodium, reaching respectively ~1.7 M and 5.0 M (Table 1). It has also been noted that the composition of the solutions in different storage tanks may vary.

**Table 1.** Main components of the solution kept atthe Hanford site in Washington before theextraction of radioactive caesium [33]

Ion	Concentration, mol/l	Ion	Concentration, mol/l
Na⁺	4.99	OH⁻	1.68
<b>K</b> <sup>+</sup>	0.12	$Al(OH)_4^-$	1.72
$Cs^+$	5.0·10 <sup>-4</sup>	NO <sub>3</sub>	1.67
Rb <sup>+</sup>	5.0·10 <sup>-5</sup>	$NO_2^-$	0.43
		CO <sub>3</sub> <sup>2–</sup>	0.23
		SO <sub>4</sub> <sup>2-</sup>	0.15
		F-	0.09

A large number of alternative materials for caesium extraction have been considered, including the most advanced ones (phenolbased extractants, crown ethers, calyxarenes, and inorganic sorbents and ion exchangers, etc.). Nevertheless, a key role in caesium extraction has been assigned to phenolic sorbents, which exhibit high ion-exchange selectivity for caesium against large excess of sodium and potassium ions. They also make it possible to filter large flow of solution and to elute concentrated caesium quantitatively and rapidly with a small volume of acid [34–36].

The use of the Duolite CS-100 ion exchanger was considered. It is a product of condensation of resorcylic acid with formaldehyde (besides two hydroxyl groups as substituents, the benzene ring also contains a carboxyl group). Its ability to sorb <sup>137</sup>Cs from low-activity solutions has been known since the 1960s. But the focus was on the resorcinol-formaldehyde sorbent (RFS), synthesised similarly to the PFRs, which turned out to be more selective and capacious. (It should be noted that obtaining of RFS was mentioned as early as in [2], 1935.) The technology for obtaining of sorbents with irregularly shaped grains was developed, it was implemented by Boulder Scientific Co, a US company [38–41].

Unfortunately, RFS, like all phenolic sorbents, has low chemical stability in alkaline media in the presence of oxygen dissolved in solutions and allows a relatively small number of sorptiondesorption cycles [40]. (Our publication [42] was devoted to the issue of chemical stability of phenolic sorbents. It was shown that methylol groups were oxidised in alkaline media with formation of carboxylic groups and gradual destruction of the grains). Therefore, the US project further attempted to overcome this disadvantage. Sinvent A/S, a company from Norway, developed a method for introducing RFS into polystyrene-type spherical granules [43]. This method is based on the technology for obtaining low cross-linked monodisperse spherical styrene-divinylbenzene copolymer granules (0.1 wt. %), developed earlier by one of the authors of the method. The granules are hydrophilised by the introduction of sulpho groups or quaternary ammonium bases. To obtain the sorbent, water and reagents for the synthesis of RFS are added to a certain amount of dried monodisperse polystyrene granules. Once the granules have swollen substantially and the reagents are introduced, a polycondensation reaction is carried out. However, no details were disclosed regarding the type of granules used in the production of the sorbent for further testing in the extraction of radioactive caesium.

The possibility of producing sorbents with phenolic groups by condensation of calixarenes and resorcinarenes with formaldehyde or other aldehyde was also considered as a possible solution to the issue. Calixarenes and resorcinarenes, known since the 1940s [44–46], are products of cyclic oligomerisation of phenols with formaldehyde. Their molecules can be formed by different numbers of phenolic or resorcinol nuclei, for example, as shown in Figure 1.

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Interest in compounds of this type increased dramatically in the 1970s and 1980s. This was caused by an overall burst of activity in the new field of supramolecular chemistry. It was expected that they, as well as other "highly organised" compounds (crown ethers, cavitands, and spherands) would provide significantly higher selectivity for complexation with metal ions and bring separation technologies to a much higher level. It was taken into account that calixarene adopts a specific conformation so that the aromatic rings and alkyl substituents such as tert-butyl, as shown in Figure 2, form the central ring rim and the upper rim, while the hydroxy substituents are located in the lower part of the macrocycle. Such a structure is sometimes called a "basketball hoop", its characteristic parameters are expected to ensure high ionic selectivity.

In the early 1980s, it was found in [47, 48] that during the diffusion transfer of alkali metal hydroxides through a liquid membrane containing various calixarenes, it shows high selectivity for Rb<sup>+</sup> and Cs<sup>+</sup> ions versus other alkali metal ions (the experiment is shown schematically in Fig. 3). In these experiments, a solution of calixarene in an organic solvent was placed between a solution of alkali metal hydroxides and pure water. The diffusion transfer of alkali metal hydroxides into water gradually occurred. The caesium hydroxide output was 20 times that of rubidium and 50 times that of sodium. The p-tert-butyl- and p-tert-pentylcalix[4]arenes were observed to have the highest selectivity.

However, the use of calixarenes directly in such experiments or in conventional extraction techniques is complicated by many drawbacks.

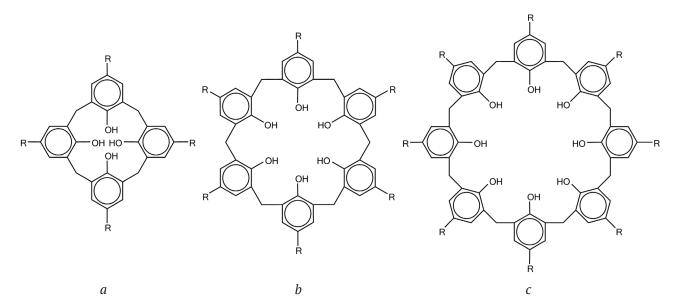
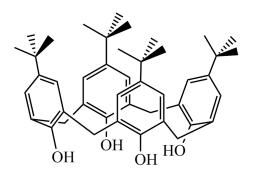
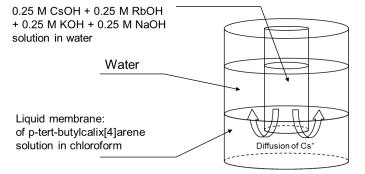


Fig. 1. Structure of calyx[4]arene (a), calyx[6]arene (b), and calyx[8]arene (c) (R – alkyl substituents)





**Fig. 2.** The "basketball hoop" conformation of tert-butylcalix[4]arene

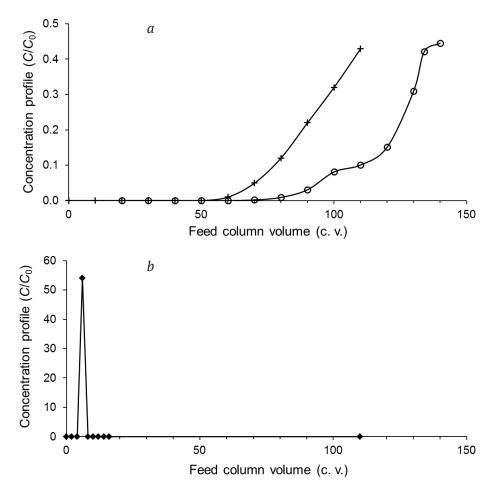
**Fig. 3.** Schematic of a diffusion transfer experiment in a liquid membrane cell

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Among them are the need to use hydrophobic solvents, the formation of emulsions, and solvent losses when using aqueous solutions. The most important disadvantage is a very low rate of diffusion of the extracted ions from one phase to another, etc. Subsequently, IBC Advanced Technologies, Inc. founded by the authors of works [47, 48] and specialising in obtaining and promoting macrocyclic reagents and technologies involving them, developed a method for obtaining sorbents with calixarene groups [49]. The patents describe the condensation of calyx[6]arene, calyx[8]arene, or propylresorcin[4]arene with phenol or resorcinol and formaldehyde in the presence of NaOH. The resulting resin is then crushed into fragments. From the information available in the open sources, it is not possible to say for sure, which of the materials under the trade mark SuperLig 644 obtained using this technology were chosen for further testing in order to develop the technology for <sup>137</sup>Cs extraction from radioactive waste in Hanford (Washington State, USA) [33, 50–54].

The scheme of the caesium extraction by sorption includes: 1) filtration of the treated alkaline solution through a column filled with one of the ion-exchange materials mentioned above until the breakthrough of caesium, and 2) subsequent elution of caesium from the ionexchanger with 0.5 M of nitric acid. Fig. 4 shows examples of the output curves of radioactive caesium sorption on the SuperLig 644 ion exchanger, and its elution with nitric acid from [27]. The two output curves in the upper figure represent two slightly different compositions of the initial solution, in particular, the sodium content was 5.0 M in one solution and 5.7 M in the other.

In experimental studies, SuperLig 644 showed no significant advantage in the volume of the



**Fig. 4.** Output curves of radioactive caesium sorption using the SuperLig 644 ion exchanger (a) and its elution with nitric acid (b) [27]

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treated solution (and hence selectivity) and in quality of acid elution (it was possible to achieve approximately 100-fold concentration of radioactive caesium) compared to the RFS. SuperLig 644 proved to be the least chemically stable sorbent, capable of withstanding only 5 or 6 sorption-desorption cycles. Upon reaching the limit, the used material has to be replaced and disposed of (it must be treated as a radioactive material). Moreover, SuperLig 644 turned out to be the most sensitive to temperature. At 45 °C, it almost lost its capacity for <sup>137</sup>Cs, while the conventional RFS retained its sorption capacity [51]. Another important consideration when selecting materials is that the SuperLig 644 ion exchanger is also the most expensive. Therefore, the RFS was considered a better option among these two materials, as it is more chemically stable.

In Russia, radioactive caesium in waste from nuclear facilities is mainly contained in nitric acid solutions. Highly selective ferrocyanide sorbents and corresponding technologies have been developed and successfully used for its extraction for a long time [55]. But there is a problem with caesium extraction from high salt alkaline boiler residues from evaporators at nuclear power plants, as their salt content reaches 300–350 g/l and their pH > 13 [56]. Ferrocyanide sorbents, like most inorganic sorbents, are unstable in such alkaline solutions. So, for the extraction of <sup>137</sup>Cs, Axion-RNM (from Perm) developed a technology and produced pilot batches of AXIONIT RCspk sorbents with granules obtained by crushing RFS and AXIONIT RCs-gran sorbents based on RFSs impregnated in spherical sulphonated polystyrene granules [56, 57]. During tests with solutions simulating high salt alkaline boiler residues from nuclear power plants evaporators, the sorbents showed high selectivity for caesium as well as good chemical and hydromechanical stability in alkaline media.

In Russia, the methods for the production of resorcinarene sorbents have also been developed. In particular, C-phenylcalix[4]resorcinarene (Fig. 5) is obtained by the condensation of resorcinol with benzaldehyde. It is used to produce a polymer in the form of spherical granules by catalytic resol polycondensation with formaldehyde, taken in the ratio of 1 : 3 [58].

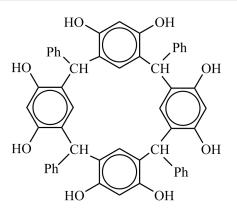


Fig. 5. Structure of C-phenylcalix[4]resorcinarene

In our article [59], we studied the selectivity of  $Cs^+-Rb^+$  ion exchange (1 : 1) from 0.1 M of alkaline solutions using the RFS and a sorbent based on C-phenylcalix[4]resorcinarene. The results were compared with the data for the PFR-based sorbent. It turned out that this sorbent showed no advantage over PFR and even exhibited a slightly lower selectivity.

Thus, sorbents based on phenol, resorcinol, calixarenes, and resorcinarenes show high selectivity to caesium ion (and also rubidium) compared with other alkali metal ions. Particularly remarkable is the fact that the sorbents based on calixarenes and resorcinarenes did not exhibit the advantage over other materials of the group. Although we expected them to perform better, given the expectations which are usually associated with the use of macrocyclic reagents in the field of separation of substances. Therefore, the issue of explaining of such results remains urgent.

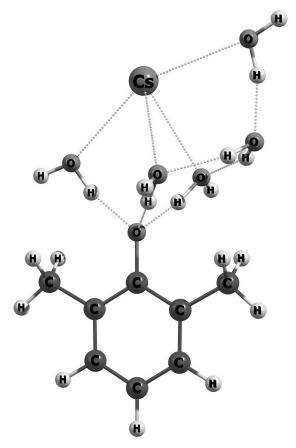
# 4. The origin of the ion-exchange selectivity of phenol-type sorbents for caesium ions

Previously [14, 60, pp. 65-88], the high selectivity for caesium and rubidium ions was explained by the fact that phenols or phenolic groups can form complexes with large caesium and rubidium ions. However, some researchers believe that this mechanism cannot explain the increased selectivity (61).

The features of the formation and structure of such complexes were studied using quantum chemistry methods. For instance, we used the density functional method in our study [62]. The calculations showed no particular binding

ability of caesium and rubidium ions to phenolate ions compared to other alkali metal ions. On the contrary, water molecules compete with the phenolate anion for binding to all alkali metal cations. Only three water molecules are enough to displace the phenolate anion into the second coordination sphere of any alkali metal ion. If more water molecules are added, the phenolate anion is always in the second coordination sphere (Fig. 6). The binding energy of  $(CH_3)_2PhO^-$  with the  $Me^+(H_2O)_n$  hydrated cation decreases irrespective of *n*, the number of water molecules in the aqua complex. It decreases in the same order as the hydration energy, i.e.,  $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ .

The calculations also showed that the calyx[4]arene anion, obtained by the removal of one hydrogen atom from one of the four OH-groups, also has no specific selectivity for caesium and rubidium ions in the absence of water molecules [59]. In this case, the energy of the cation binding to the calyx[4]arene anion also decreases under the sequence of  $Li^+ > Na^+ > K^+ >$ 



**Fig. 6.** Structure of the aqua complex of the  $Cs^{+}(H_2O)_5$  ion with the 2,6-dimethyl-phenolate anion

Rb<sup>+</sup> > Cs<sup>+</sup>. The numerical values of the energy of binding to the calix[4]arene anion are also close to the corresponding values for binding to the phenolate anion (even slightly lower than them). It should also be noted that the caesium ion in the optimised structure of the complex is positioned far away from the oxygen "crown", whereas the lithium ion is positioned almost in the plane of the crown. Thus, the modelling demonstrated that the special order of the functional groups of the calixarene and resorcinarene resins cannot cause an increase in selectivity for caesium ion compared to conventional PFRs and RFSs.

On our initiative, our colleagues in studies [63, 64] carried out molecular modelling of the interaction of alkali metal cations with the calyx[4]arene anion in the presence of 291 water molecules using the molecular dynamics method. The calculations showed that in the presence of water molecules the binding of Rb<sup>+</sup> and Cs<sup>+</sup> cations to the calyx[4]arene anion is much greater than that of Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> cations. The authors attributed this to the fact that smaller cations with a lower coordination number exhibit greater disruption of the hydrate shell when they bind to the calix[4]arene anion.

Thus, the selectivity for caesium and rubidium ions during ion exchange on all phenolic ion exchangers is due to other features.

Usually, during the ion-exchange process, the transfer of ions from an external solution into the ion-exchanger, which is a concentrated polyelectrolyte solution, is accompanied by their considerable dehydration. When an alkali metal ion is transferred from an external solution into the sorbent, its complex with the anion is broken. The ion undergoes partial dehydration with subsequent binding to phenolic groups:

$$Me_{2}^{+}(H_{2}O)_{n} \cdot Cl^{-} \xrightarrow{-mH_{2}O, -Cl^{-}}$$

$$\rightarrow Me_{2}^{+}(H_{2}O)_{n-m} \xrightarrow{+PhO^{-}} Me_{2}^{+}(H_{2}O)_{n-m} \cdot PhO^{-}.$$

$$(1)$$

At the same time, the smaller ion 1, which was originally in the ion exchanger, is transferred in the opposite direction:

$$Me_{1}^{+}(H_{2}O)_{n} \cdot Cl^{-} \xleftarrow{+mH_{2}O, +Cl^{-}} (2)$$

$$\leftarrow Me_{1}^{+}(H_{2}O)_{n-m} \xleftarrow{-PhO^{-}} Me_{1}^{+}(H_{2}O)_{n-m} \cdot PhO^{-}.$$

If we assume that the structures of similar complexes of the  $M_1^+$  and  $M_1^+$   $\mu$   $M_2^+$  alkali metal

ions are the same (although this is not necessarily true), then the entropic component of the ion exchange reaction can be neglected. Thus, the Gibbs energy of the ion exchange reaction is determined by the hydration energies of ions and the energies of their interaction with fixed groups in the PFRs and with anions in the solution:

$$\Delta G = (\overline{E}_{\text{binding},\text{Me}_2} - \overline{E}_{\text{binding},\text{Me}_1}) - (E_{\text{binding},\text{Me}_2} - E_{\text{binding},\text{Me}_1}).$$
(3)

The first difference reflects the difference in binding energies of the ions (dehydrated) exchanged with the phenolate ions in the ion exchanger. The second reflects the difference in binding energies of the ions exchanged with water and the anion in the external solution. As shown by the calculations from [62], these two differences are positive and quite close. The selectivity in the ion-exchange system is determined by the delicate balance between them. Since the value of  $\Delta G$  is determined simultaneously by four large values of the formation energies of the different complexes, it cannot be expected that quantum chemistry calculations can quantitatively predict selectivity in an ion-exchange system. However, expression (3) evidently shows that formation of aqua complexes of alkali metal ions in a solution contributes to a decrease in selectivity of smaller ions in comparison with larger ions in terms of binding to phenolic groups.

Thus, the only explanation for the selectivity of PFRs and other phenolic compounds for caesium and rubidium ions is the dominance of the ion dehydration stage during the transition from aqueous solution to the phenolic phase rather than the stage of binding to the ionexchange groups. The phenolic ion exchangers have greater selectivity for caesium and rubidium ions than polystyrene-type sulphonic acid cation exchangers due to the fact that the former can bind much less water, and the ions in them are much more dehydrated. This is especially true for ion exchange on phenolic ion exchangers, which differ from other ion exchange resins and polyelectrolytes by considerably lower amounts of bound water (this can be seen, for example, from our data in [11]).

This conclusion is consistent with the explanation of the emergence of selectivity for the

potassium ion in the ion channels of a biological cell. It says when the ion binds in the narrowest part of the channel, called the ion filter, it is also in a partially or completely dehydrated state [65]. The mechanisms of the emergence of selectivity of the ion channel and phenolic sorbents seem to be similar. The data [11] indicate a greater differentiation of water in phenol-formaldehyde sorbents in terms of its binding energy as compared to polystyrene sulphocationites. In general, the amount of water in such sorbents is quite large and comparable with the amount of water in polystyrene sulphocationites. However, the amount of strongly bound water is several times less. This seems to indicate that weakly bound "free" water is located in large pores, and relatively small amounts of water strongly bound to exchange groups can be located in narrow pores, which are similar to the ion channels in cells.

This conclusion about the mechanism of ion selectivity also coincides with the conclusion obtained in [66, 67]. The studies analysed the reasons for the preferential binding of potassium ion to guanine complexes and complexes with 18-crown-6-ether compared to sodium ions.

### 5. Conclusions

The sorbent obtained by condensation of resorcinol with formaldehyde plays the key role in caesium extraction from highly mineralised alkaline radioactive solutions. The sorbent of this type is capable of exchanging ions on phenolic groups in alkaline solutions, while exhibiting high selectivity for caesium against large excesses of sodium and potassium ions. It also makes it possible to filter large flows of solution and to elute concentrated caesium quantitatively and quickly with a small volume of acid. We compared the ion selectivity of sorbents obtained by condensation of phenol and diatomic phenols with formaldehyde and of modern materials obtained by condensation of calixarenes and resorcinarenes with aldehydes. The study showed that the latter had no advantage in selectivity and had a lower chemical stability.

### Author contributions

All authors made an equivalent contribution to the preparation of the publication.

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### **Conflict of interests**

The authors declare that they have no conflict of interest.

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