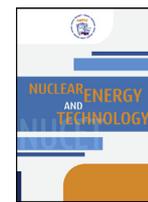


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Effects of inorganic ligands on the efficiency of ion-exchange treatment of radioactive waste

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Abstract

Normally, liquid radioactive waste contains salts of mineral acids, the concentration of which may exceed the concentration of polyvalent ions of radioactive metals by several orders of magnitude. This, however, does not make improbable the formation of metal cation complexes with acid anions. The effects of inorganic ligands on the sorption characteristics of cations were evaluated by eluting milliquantities of metal (cobalt, magnesium) ions from the sulfocationite phase using sodium salts. The dependences of the time of retention of polyvalent metal ions by the Dowex-50×8 sulfocationate on Leden's function have been studied. It has been proved that ligands of mineral acids are capable to have a pronounced effect on the efficiency of the cation-exchange treatment of solutions. It has been found that the charged complexes formed have a greater effect on the ion exchanger sorption behavior than neutral complexes, despite the fact that the stability constant value of charged complexes is at least an order of magnitude as less as that of neutral complexes.

Practical methods have been proposed to minimize the effects of inorganic ligands on the radioactive solution ion-exchange decontamination factor.

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The requirement for minimizing the amount of radioactive waste is dictated by the considerations of radiation safety and economy. The significance of the latter has increased greatly after the adoption in 2011 of Federal Law No. 190-FZ and respective bylaws [1]. Currently, in the given context, of a special importance are the tasks of increasing the efficiency of liquid radioactive waste (LRW) treatment, and, accordingly, of reducing the amount of secondary waste to be disposed.

One of the most attractive solutions to the above tasks is to use ion-exchange technologies, since, theoretically, ion exchange helps reaching any, whatever low, level of residual concentration of the substance in the filtrate of ion-exchange facilities. Practically, the efficiency of ion-exchange treatment is critically dependent on the chemical composition of liquid radioactive

waste, and, specifically, on the presence of ligands in solutions, such ligands being capable to convert target elements (radionuclides) from a cationic form to a sorption-inactive molecular form.

With respect to such organic ligands “typical” of LRW (EDTAs, oxalates, synthetic surfactants), this fact is taken into account in the development of waste treatment facilities [2–6]. However, even when such aggressive methods as ozone oxidation of organic compounds are used, quality indicators of “decontaminated” solutions do not always and fully conform to the regulatory LRW exemption levels.

It should be noted that LRW invariably contains nonradioactive products of corrosion of structural materials, mostly iron, chromium, manganese and nickel. Ions of these metals, the concentration of which is incommensurably higher than that of radionuclides, are capable to bind into complex forms practically all organic ligands. Moreover, complexones enter LRWs of NPPs with VVER-type reactors already in the form of non-radioactive solutions of nonferrous metal complexonates [7], which are much more stable than CoEDTA and CoCit [8].

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During long-term LRW storage, oxalate ions are nearly totally oxidized by atmospheric oxygen, and, if present in stillage residues, even EDTAs may be oxidized by nitrate and nitrite ions, with iron and manganese ions acting as the oxidation catalysts [9].

All this, as well as an analysis of the complex compound stability data [8] suggests that the constraints of the LWR deep ion-exchange treatment technology may be caused by the processes of cation sorption inactivation by inorganic ligands generally neglected until quite recently.

Meanwhile, compounds capable to bind polyvalent metal ions (^{60}Co , ^{90}Sr - ^{90}Y and others) into complex forms with different degrees of stability, are nearly invariably present in LRW. These ligands can enter radioactive solutions in the following ways:

- with service water (sulfate and hydrocarbonate ions);
- with spent decontamination compositions (ortho- and polyphosphates, carbonate ions);
- through the contact of alkaline LRW with air (carbonate and sulfide ions);
- as components of process solutions (boron oxygen compounds), etc.

The validity of the hypothesis about the effects of inorganic ligands is illustrated by the relationships among the forms of the cobalt (II) existence in sulfate solutions (Fig. 1) calculated by us using reference data [8]. As can be seen, notable quantities of complex forms are generated even with the sulfate ion concentrations in the solution being about 5–10 mg dm^{-3} , which is below the permissible sulfate concentration in service water [10, 11].

The specific activity of LRW formed at an NPP is generally about $1 \times 10^5 \text{ Bq dm}^{-3}$. The intervention level for drinking water prescribed by federal regulations is 10–100 Bq dm^{-3} (depending on the radionuclide composition [12]). Therefore, the share of radionuclides in the form of complex sorption-inactive compounds may not exceed 10^{-1} to $10^{-2}\%$. This conditional criterion is what defines the set of technological measures aimed at ensuring the required efficiency of the LRW ion-exchange treatment method.

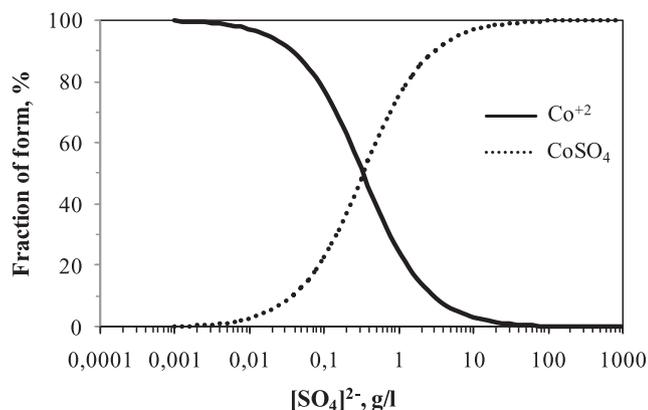


Fig. 1. Distribution of cobalt existence forms as a function of the sulfate anion concentration. Analytical concentration of $\text{Co}^{+2} = 59 \text{ mg dm}^{-3}$.

To verify the hypothesis about the effects of inorganic ligands on the capability of LRW deep treatment, studies were conducted on the effects of the ligand nature and concentrations on the ability of cation exchange resins to retain divalent cations, when these are eluted by solutions of different compositions.

A Dowex-50 \times 8 ionite specimen with a volume of 25 cm^3 was placed in a glass column with a height of 500 mm and a diameter of 11 mm, conditioned using a commonly known procedure [13] and converted to a working form by being washed with sodium chloride solution with a concentration of 58.5 g dm^{-3} . Prior to the sample introduction, the overlayer water was drained down to the upper sorbent level. An amount of the solution (20 cm^3) containing 273.3 mg of cobalt nitrate or 112.7 mg of magnesium nitrate was introduced into the upper section of the column by means of a measuring pipette. The introduced solution was then drained down to the upper ionite layer, after which the sorbent was washed off the reaction products with 30 cm^3 of demineralized water.

The metal was eluted using a solution of individual or mixed sodium salts prepared such that the total sodium concentration in each solution was 9.2 g dm^{-3} . The mixed solutions contained different proportions of NaL as the complexing agent and sodium nitrate. The metal ion analysis was performed using a standard procedure [14].

Fig. 2 shows representative dependences of cobalt desorption by a mixed solution of sodium nitrate and sulfate with a constant

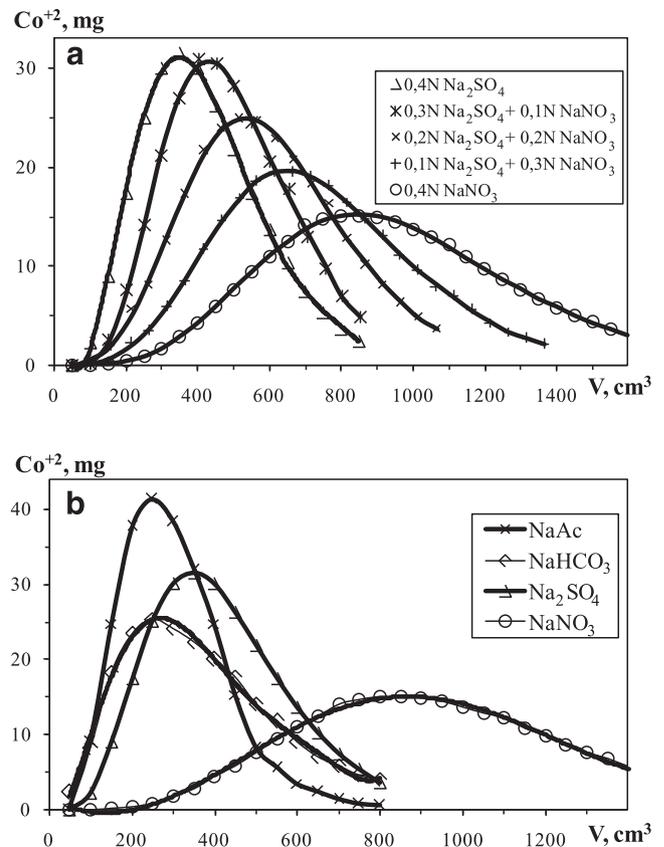


Fig. 2. Curves of the Co^{+2} elution from Dowex-50 \times 8 sulfocationite by mixed (a) and individual (b) sodium salts.

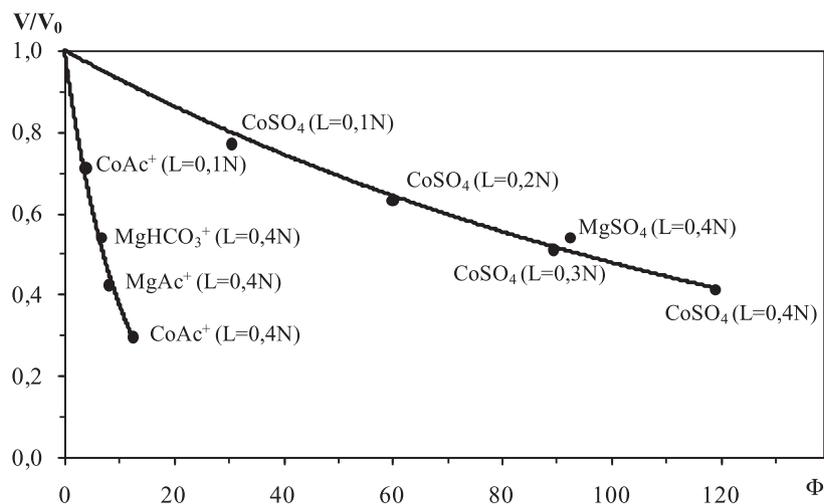


Fig. 3. Dependence of the relative positions of concentration peaks (V and V_0 are the chromatographic peak maximum positions for the ligands L and NO_3^- respectively): $K_{st}(\text{CoSO}_4) = 10^{2.47}$; $K_{st}(\text{MgSO}_4) = 10^{2.23}$; $K_{st}(\text{CoAc}^+) = 10^{1.46}$; $K_{st}(\text{MgAc}^+) = 10^{1.27}$; $K_{st}(\text{MgHCO}_3^+) = 10^{1.16}$ [8].

sodium concentration and with different sulfate ion concentrations in the eluent.

Fig. 3 presents data on the variation in the time of the metal ion retention by the Dowex-50 \times 8 sulfocationite as a function of Φ values for the corresponding forms, as calculated using reference data, where Φ is the function of complexity defined as [15].

$$\Phi = 1 + \sum \beta_i [L]^i,$$

where β is the stepwise stability constant and $[L]$ is the ligand equilibrium concentration.

The obtained data show that the time of ion retention by sorbent depends primarily on the ligand nature and on the composition of the complex forms generated. Thus, divalent sulfate ions forming molecular forms with cations of metals have a smaller effect on the cation exchanger selective properties than monovalent anions, the complex forms with which only reduce the charge of the ion present in the solution, as compared to the charge of the central atom.

This phenomenon may be explained in terms of the general laws of ion exchange processes. We shall assume that all components existing in the solution are involved in the interfacial distribution. Neither the Nikolsky equation nor the Donnan effect applies to nonionic forms, and the concentration thereof in the ionite phase is nearly equal to the concentration in the intergranular solution. When entering a cation-poor internal solution, these compounds dissociate producing a divalent cation, which is subjected to the electroselectivity effect, resulting in the fixation of many of the divalent cations in ionic groups. Desorption from this layer is possible only with fresh batches of eluate, free of these cations. Therefore, the combination of the processes involved in the distribution of nonionic components and in the dissociation of the fairly weak complex forms thereof leads to a slowdown of the front movement.

The distribution of charged forms takes place in accordance with selectivity sequences, in which the positions of ions are defined by the ionic radius of the component. Decisive to sulfocationites during the exchange of equally charged ions is the

size of the hydrated ion, which is larger in the complex form. Besides, the ionic fraction of the complex form in the solution is much smaller than that of the eluting component (sodium ions). The combination of these factors is what leads to a drastic reduction in the time of the divalent cation retention by ion-exchange resin.

In practice, the major LRW macrocomponents are nearly invariably represented by alkali metal ions, and it is their competitive influence that will define the sorbent performance. Therefore, the LRW composition correction using sodium and, moreover, potassium salts, most commonly used in technologies, shall be as small as possible.

It should be noted that all considered and potential ligands capable to form complex forms with polyvalent metal ions may be divided into two groups: those inactivated through a change of the existence form and the ones inactivated due to degradation (elimination).

The latter group includes anions of amino carboxylic acids (except for NTAs), amino phosphonic acids, and sulfate ions, anions of which exist in moderately acid solutions.

Complexing abilities of most of the other inorganic ligands, as well as of organic acids, can be suppressed through the protonation of these. The acid inactivation degree depends on the dissociation constant of the corresponding acid. Ligand protonation (with $pK > 3$) results in a loss of the complexing ability of acetate, oxalate, citrate, hydrocarbonate and phosphate ions. Ligands can be inactivated:

- via moderate acidification of solutions with nitric acid;
- in the process of the LRW treatment using hydrogen forms of some cation exchanger types.

The prospects of the second approach are illustrated by experimental data on the ion-exchange treatment of low-salt radioactive waste containing predominantly hydrocarbonate and phosphate ions (Fig. 4). The presented data show an approximately 1.5-fold increase in the cationite protective action time with respect to cesium radionuclides not capable of complex-

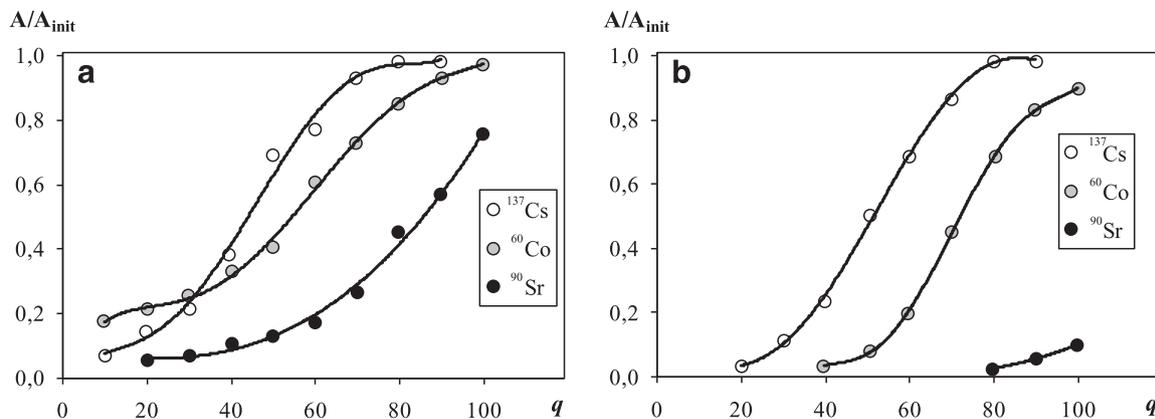


Fig. 4. A variation in the filtrate specific activity during LRW filtration: (a) via Na^+ form; (b) via M^+ form of KU-2 cationite; q —specific flow rate, $\text{dm}^3 (\text{dm}^{-3} \text{ of resin})$.

ing, when sodium cationization is changed for sorption on a hydrogen form, this being consistent with the variation in the constant of the cesium ion exchange for counterions [16]. As to strontium radionuclides, a change of the ionite working form for that protonated leads to approximately a fourfold increase in the cationite protective action time (Fig. 4), which cannot be explained only by the variation in the exchange constant value of $k^{1/2}_{\text{Sr,Na}}$. With ^{60}Co , the sodium form of the cationite does not provide for the required level of purification (Fig. 4a). When using a cationite in the M^+ form, the filtration cycle duration and the LRW decontamination factor for ^{60}Co increase dramatically, which may be caused only by the inactivation of ligands due to monohydrophosphate ions passing into dihydrophosphate ions, and carbonate ions passing into hydrocarbonates.

Conclusions

The results of a phenomenological analysis of operating data and of experimental studies have shown that the presence of inorganic ligands, of both natural and technogenic origin, in solutions may be a critical factor limiting the efficiency (purification factor) of the ion-exchange radioactive waste treatment technology. By forming molecular compounds with radionuclides (metal cations), anions of inorganic acids reduce the concentration of particles able to participate in ion exchange and, accordingly, the radioactive media decontamination factor. With formation of the low-charged cationic complexes, the ion-exchange treatment factor also decreases, but due to the competitive effects of the alkali metals present in the solution.

To suppress the complexation processes, it is proposed to use protonized forms of cation exchange resins as filtering materials, which leads to the ligand denticity reduction through the pH correction, and as a consequence, to an increase in the mass exchange efficiency in the solution–ionite system.

The same result may be obtained with the ion-exchange treatment of solutions diluted as much as it is technologically and economically reasonable.

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References

- [1] A.F. Nechaev, A.S. Chugunov, *At. Energy* 115 (6) (2014) 386–390.
- [2] M.R. Stakhiv, *Sbornik Tezisev MNTK-2010* [Book of Abstracts IRTC-2010], Moscow, 2010, pp. 287–289 (in Russian).
- [3] A.S. Chugunov, A.F. Nechaev, S.A. Dmitriev, F.A. Lifanov, S.N. Shibkov, *Vopr. Materialovedeniya* 5 (11) (1997) 15–21 (in Russian).
- [4] A.S. Chugunov, A.F. Nechaev, Proceedings of the 8th International Conference (ICEM'01), NY, 2001, p. 34.
- [5] A.S. Chugunov, A.F. Nechaev, S.N. Shibkov, S.A. Dmitriev, F.A. Lifanov, Proceedings of International Conference on Radioactive Waste Management and Environmental Remediation (ICEM'97), NY, 1997, pp. 503–505.
- [6] A.S. Chugunov, A.F. Nechaev, *Sb. trudov NTK "Nauchno-innovacionnoe sotrudnichestvo"* [Collection of STC Proceedings of "Scientific Innovation Cooperation"], Moscow, 2002, pp. 32–33. (in Russian).
- [7] O.P. Arkhipov, S.I. Brykov, L.A. Siryapina, R.A. Kashirin, A.Yu. Petrov, A.A. Salnikov, E.V. Khromovskikh, A.G. Zhukov, G.A. Vaver, Yu.F. Kutdyusov, I.O. Budko, A.N. Makartsev, M.V. Rusakova, V.Ya., Kozlov, *Sbornik Trudov VII Mezhdunarodnogo Seminara po Gorizontalnym Parogeneratoram* [Collection of Proceedings of 7th International Workshop on Horizontal Steam Generators], Podolsk, 2006 (in Russian).
- [8] A.E. Martell, R.M. Smith, *Critical Stability Constants*, 4–6, Plenum, New York, 1976/1982/1989.
- [9] A.S. Chugunov, A.F. Nechaev, *Izvestiya SPbGTI(TU)* 36 (10) (2011) 32–38 (in Russian).
- [10] Yu.M. Kostrikin, N.A. Meshcherskiy, O.V. Korovina, *Vodopodgotovka i Vodny Rezhim Energo-obyektov Nizkogo i Srednego Davleniya, Spravochnik* [Water and Water Regime of Power Facilities Low and Medium Pressure, Directory], Energoatomizdat, Moscow, 1990, p. 248.
- [11] I.T. Goronovskiy, Yu.P. Nazarenko, E.F. Nekryach, *Kratkiy Spravochnik po Khimii* [A Brief Guide to Chemistry], Kiev. Naukova Dumka Publ., 1987, p. 828. (in Russian).
- [12] SanPiN 2.6.1.2523-09, *Normy radiatsionnoy bezopasnosti (NRB-99/2009)* [Radiation Safety Standards (RSS-99/2009)].
- [13] N.G. Polyanskiy, G.V. Gorbunov, N.L., Polyanskaya, *Metody Issledovaniya Ionitov, Izvestiya Vuzov—Yadernaya Energetika*, no. 1, 2015, p. 127 [Methods of Investigation of Ion Exchangers], Chemistry Publ., Moscow, 1976, p. 208. (in Russian).
- [14] GOST 10398-76, *Reagents and Super Pure Substances. Complexometric Method for Determination of Basic Matter Content*, Standartinform Publ., Moscow, 2008 (in Russian).
- [15] V.P. Vasilyev, *Termodinamicheskiye Svoystva Rastvorov Elektrolitov* [Thermodynamic Properties of Electrolyte Solutions], Vysshaya shkola Publ., Moscow, 1982, p. 320. (in Russian).
- [16] M. Markhol, *Ionoobmenniki v Analiticheskoy Khimii* [Ion Exchangers in Analytical Chemistry], Mir Publ., Moscow, 1985 (in Russian).