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

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Available online 28 February 2016

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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Keywords: Liquid radioactive waste; Ion exchange; Complexation; Inorganic ligands.

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 nonradioactive 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 1×10^5 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.
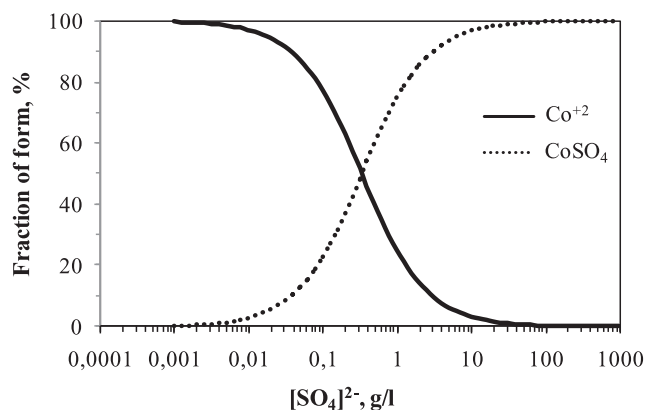
To verify the hypothesis about the effects of inorganic ligands on the capability of LRW deep treatment, studies were conducted on the effects of the ligand nature and concentrations on the ability of cation exchange resins to retain divalent cations, when these are eluted by solutions of different compositions.

A Dowex-50×8 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
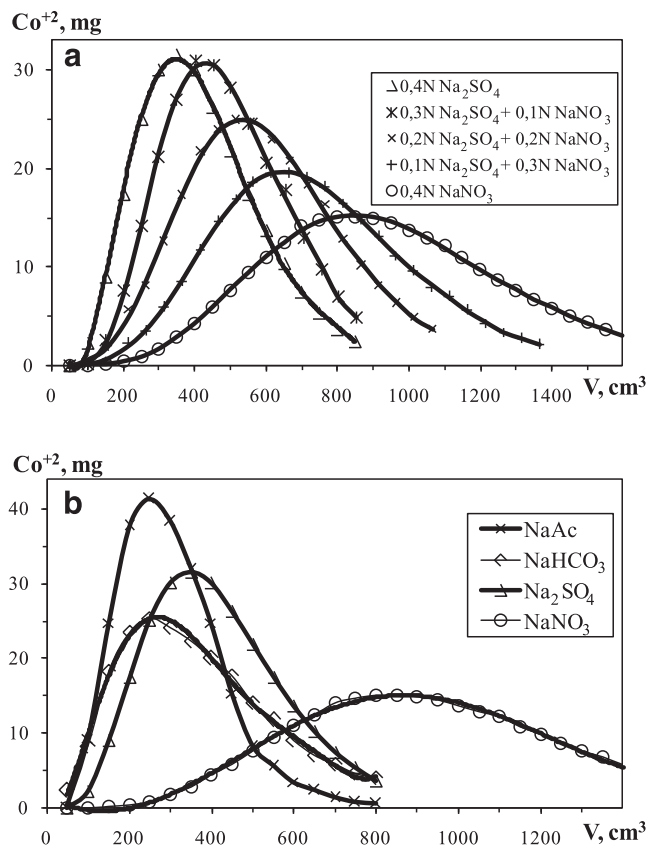
Fig. 1. Distribution of cobalt existence forms as a function of the sulfate anion concentration. Analytical concentration of Co^{+2} = 59 mg dm^{-3}.

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