

Simultaneous ion-exchange sorption of uranium with concomitant impurities

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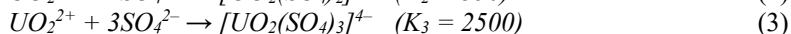
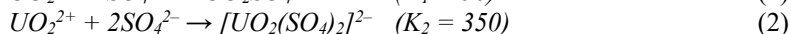
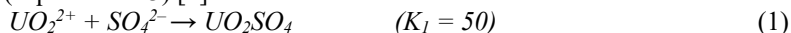
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Abstract. The aim of the study is to elucidate the effect of simultaneous sorption of uranium with different concomitant impurities that are contained in underground leaching solutions (sulfates, chlorides, nitrates, phosphates, silicates, iron, aluminum, and manganese) at pH = 1.2. Different sorption isotherms are studied for the uranium sorption by the strongly basic anion-exchange resin (BO020): (i) uranium and a number of concomitant impurities; (ii) uranium in the presence of the studied impurities. The negative effect of impurities is manifested at low uranium concentrations. With an increase in uranium concentration, the depressing effect of impurities (Al, Fe, Mn) becomes less. The most negative effect is exerted by nitrates in the amount of 0.4 g/L, silicates - 0.3 and 1 g/L, chloride - 1 g/L. The phosphorus contributes to better sorption of uranium in the low concentration range of 0.02 to 0.200 g/L but becomes a depressant at higher concentrations.

1 Introduction

The strongly basic anion-exchange resin (AER) can sorb uranium and some different elements (depressants) from solutions by ion-exchange mechanisms. The uranium anion ion exchange extraction is based on the high stability constants of the negatively charged uranium sulfate complexes (Equations 1-3) [1].



The high charge of the major sulfate complex in solution ($[UO_2(SO_4)_3]^{4-}$) causes great sorption capacity but poor desorption and stripping. Many different anionic sulfate metal complexes compete with uranium sulfate complexes during the sorption process.

As a result, the selectivity of the uranium sorption strongly depends on the chemical composition of the solution and the AER. Moreover, the efficient ion-exchange process requires a large amount of expensive nitric or hydrochloric acids for stripping.

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The uranium ore's chemical composition consists of a number of macrocomponents, including SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , uranium, and phosphate minerals. The acid dissolution leads to contamination of the uranium ore leaching liquor by different concomitant macrocomponents such as iron, aluminum, calcium, silicon, phosphates, chloride, and nitrate ions, as well as a number of minor components such as vanadium, arsenic, molybdenum, etc. [2–5]. Some of these anions and metal complexes are present in the process solutions of uranium extraction. In this case, the AER can form a strong association with the sum of all these different components in solutions, and, finally, the resin becomes less selective and hardly regenerates by desorption. For instance, the AER can adsorb silica, followed by its further accumulation in the resin. Therefore, it requires special treatment to remove silica from the resin because, usually, the uranium ores leaching sulfuric acid solutions contain silica in soluble low-polymer and colloidal forms. Apparently, the sorption of silica is limited mainly to low-polymer forms. It is assumed that silica is sorbed from the ores leaching solutions with fast polymerization in resin. In addition, it has been shown that sulfate ions better increase the sorption of silicates than chlorides and nitrates [6].

This work is aimed at studying the uranium sorption from a multicomponent solution to determine the influence of concomitant components of the Uch-Kuduk deposit ore leaching. The BO020 AER is applied for uranium extraction and processing in the Uch-Kuduk Factory, Navoi Mining and Metallurgical Complex (NMMC) [7]. Although uranium sorption has been widely studied [1–4], the interfering effect of the concomitant ions and speciation of trace elements in resin were not determined for the BO020 anionite, as well as the process solutions of Uch-Kuduk Factory. According to the salt composition of the Uch-Kuduk uranium solutions, different amounts of concomitant ions are able to be sorbed simultaneously with uranium. The chloride, phosphate, nitrate, sulfate, and silicate ions are the main interfering components. As mentioned above, manganese, aluminum, and calcium should not be sorbed by the AER. However, their presence together with other components can affect the uranium sorption by the BO020 AER.

This report highlights the novel results of the simultaneous sorption of different elements that are contained in the underground leaching solution of Uch-Kuduk, NMMC. Several possible major and minor concomitant impurities are leached from the ores into the solution and treated by the BO020 resin in sulfuric acid at pH 1.2. For the first time, different sorption isotherms are studied for the uranium sorption by the BO020 resin: (i) uranium and a number of concomitant impurities; (ii) uranium in the presence of one of the studied impurities. The negative and positive effects of concomitant ions were determined for the elucidation of the simultaneous ion-exchange sorption of uranium with concomitant impurities.

2 Experimental part

The BO020 AER (China) was sieved to a size of 0.4 mm, soaked in water, and converted into the sulfate form with a solution of sulfuric acid ($C(\text{H}_2\text{SO}_4) = 150 \text{ g/L}$).

The sorption capacity (Q_e) was determined according to Equation (4):

$$Q_e = \frac{(C_0 - C_e)}{m} V \quad (4)$$

where C_0 and C_e are the initial concentration of ions in mg/L and the concentration at equilibrium in mg/L, respectively; Q_e is the adsorption capacity in mg/g; V is the volume of ion solution (L) and m is the weight of AER (g).

The sorption of uranium and concomitant impurities is studied by the sorption isotherms (Q_e vs C_e) in static batch experiments. The metal ion concentration was determined in solutions using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP Pro, Thermo Fisher, USA), pH adjusted according to a pH meter (Mettler Toledo,

SevenEasy, China), and anions concentration measured by ion chromatography (IONUS, Membrapure, Germany).

The effect of each concomitant component and the sum of the components on uranium sorption were determined. The Uch-Kuduk leaching solution has the following chemical composition: U^{6+} - 0.1-0.5 g/L; Fe^{3+} - 0.07-0.7 g/L, Fe^{2+} - 0.07- 0.7 g/L; SO_4^{2-} - 7.0 - 13.0 g/L; P^{5+} - 0.08-0.2 g/L; Cl^- - 0.15 - 0.3 g/L; Si^{4+} - 0.085 - 0.3 g/L; Al^{3+} - 0.01 - 0.164 g/L, Ca^{2+} - 0.5 - 0.7 g/L. The simultaneous sorption of uranium and concomitant impurities was carried out using the BO020 AER in static conditions at varying concentrations of the main concomitant ions (sulfates, chlorides, nitrates, phosphates, silicates, iron, aluminum, and manganese) at pH = 1.2. All reagents were analytically graded. The sulfuric acid leaching solutions were treated by the BO020 AER (China) in Pachuca reactors with air stirring using the following conditions: pH=1.2, $t=24$ hours, $V_{AER}:V_{solution}=1:400$ (5 ml: 2000 ml), $C_{neutral\ sulfates} = 7$ g/L (10 g/L of sulfate ions, including 3 g/L of H_2SO_4). The sulfate ion concentration was maintained by adding sodium, aluminum, manganese, iron sulfates, and sulfuric acid, respectively.

3 Results and discussions

3.1 Effect of neutral sulfate, chloride, nitrate, phosphate on the sorption of uranium

The influence of neutral sulfates was studied by two sorption isotherms at pH = 1.2 in solution by application of the BO020 AER in static conditions (Figure 1). The first isotherm is related to uranium sorption in solution without any addition of sodium sulfate; the second isotherm is sorption in the presence of sodium sulfate (7 g/L of sulfate ions). As shown in Figure 1, sulfate ions (7 g/L) reduce the AER capacity for uranium. Thus, the BO020 AER capacity for uranium decreases by 25% at $C_U=0.005$ g/L and by 9% at $C_U=0.15$ g/L, respectively. It is confirmed by the strong competing ion exchange between sulfates and the uranium sulfate complex.

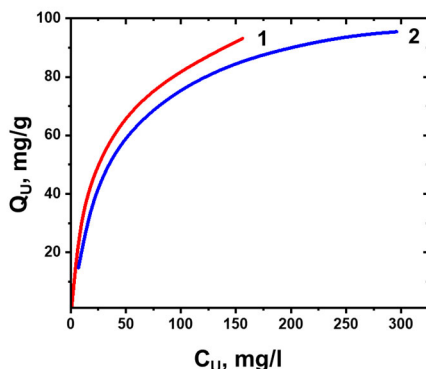


Fig. 1. Sorption isotherm of the uranium by the BO020 AER at neutral sulfate concentration in solution with $C(SO_4^{2-}) = 0$ g/L (1); 7 g/L (2).

The sorption of uranium in the presence of chloride ions is shown in Figure 2. The chloride ions were introduced into the system in the form of NaCl. As can be seen from Figure 2, an increase in the chloride-ions concentration from 0.1 g/L to 2.0 g/L reduces the equilibrium capacity of the BO020 AER for uranium.

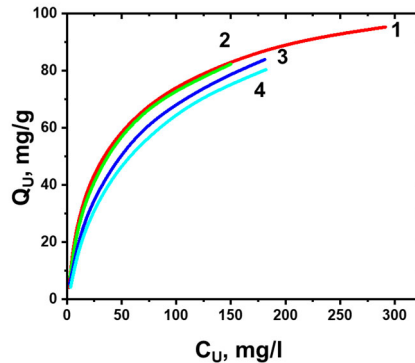


Fig. 2. Sorption isotherm of the uranium by the BO020 AER at chloride concentration in solution with $C(\text{Cl}^-) = 0 \text{ g/L}$ (1); 0.5 g/L (2); 1 g/L (3); 2 g/L (4).

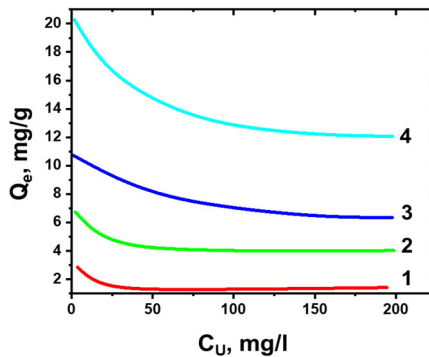


Fig. 3. Dependence of the BO020 AER capacity for the chloride ions vs the uranium concentration in solution with $C(\text{Cl}^-) = 0.1 \text{ g/L}$ (1); 0.5 g/L (2); 1.0 g/L (3); 2 g/L (4).

Figure 3 indicates that the chloride-ion capacity of the BO020 AER decreases with increased uranium concentration in the solution. Hence, the increase in uranium concentration ($C(\text{Cl}^-)=\text{const}$) confirms the fact that the chloride ions sorption is better at low uranium concentrations in solution and becomes less with increasing the uranium concentration in solution, whereas it tends to remain constant at higher uranium concentrations in solution. This regularity was observed at all investigated chloride-ion concentrations. It was determined that the BO020 AER capacity for chloride ions is equal to 6.3 mg/g at $C(\text{Cl}^-)=0.5 \text{ g/L}$ at a comparatively low uranium concentration ($C_U=0.005 \text{ g/L}$); however, the BO020 AER capacity for chloride ions is equal to 4 mg/g at a high uranium concentration ($C_U=0.2 \text{ g/L}$). Generally, with an increase in the concentration of chloride ions, the BO020 AER capacity for chloride ions increases, which leads to a decrease in the AER capacity for uranium.

Figure 4 shows the similar effect of the nitrate-ions concentration at the uranium sorption. The nitrate ions were introduced into the system as sodium nitrate. Figure 4 indicates that with an increase in the nitrate concentration from 0.1 to 0.4 g/L , the BO020 AER capacity for uranium decreases. The nitrate sorption decreases with increased uranium concentration in the solution (Figure 5), analogous to the identical trend observed for the chloride ions. The proportional increase of uranium in the solution led to less nitrate sorption by the resin.

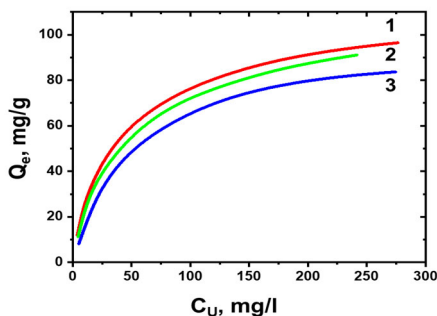


Fig. 4. Sorption isotherm of the uranium by BO020 AER at nitrate concentration in solution with $C(\text{NO}_3^-) = 0 \text{ g/L}$ (1); 0.1 g/L (1); 0.4 g/L (1).

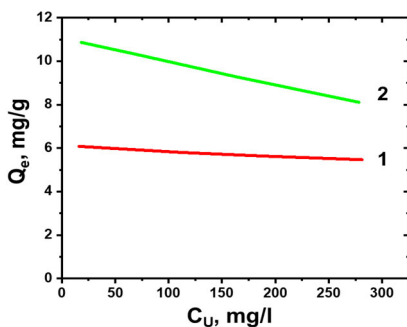


Fig. 5. Dependence of the BO020 AER capacity for the nitrate ions vs the uranium content in the solution with $C(\text{NO}_3^-) = 0.1 \text{ g/L}$ (1); 0.4 g/L (2).

The experimental results of the study on the effect of phosphate ions on the uranium sorption by the BO020 AER are given in Figures 6-9, the phosphates were introduced into the uranium-containing solution as phosphoric acid and/or trisubstituted sodium salt.

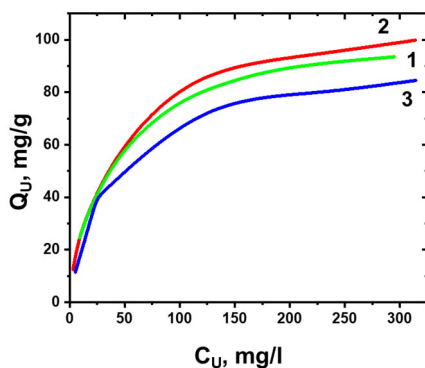


Fig. 6. Sorption isotherms of the BO020 AER for uranium at the phosphate acidic form concentrations in solution with $C(\text{P}) = 0 \text{ g/L}$ (1); 0.3 g/L (2); 0.5 g/L (3).

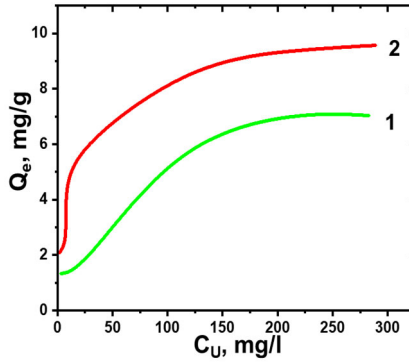


Fig. 7. Dependence of the BO020 AER capacity for phosphorus vs the uranium concentration in the solution with $C(P) = 0.3$ g/L (1); 0.5 g/L (2).

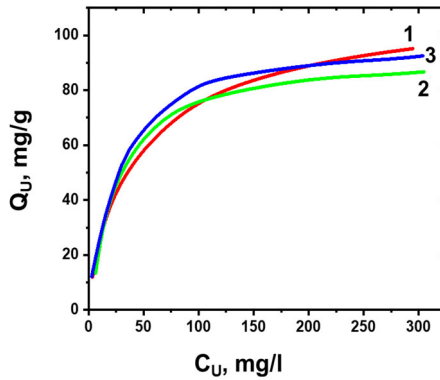


Fig. 8. Sorption isotherms of the BO020 AER for uranium at the phosphate salt form concentrations in solution with $C(P) = 0$ g/L (1); 0.3 g/L (2); 0.8 g/L (3).

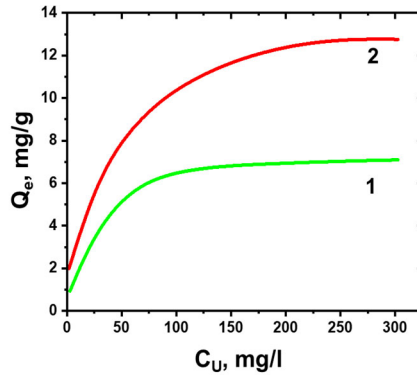


Fig. 9. Dependence of the BO020 AER capacity for the phosphorus vs the uranium content in the solution with $C(P) = 0.3$ g/L (1); 0.8 g/L (2).

Figure 6 indicates that the BO020 AER capacity for uranium is reduced at a concentration of phosphoric acid of 0.5 g/L (in terms of P). The BO020 AER equilibrium capacities for uranium increase with the increased uranium concentration in the solution to more than 0.04 g/L in the presence of 0.3 g/L of phosphate ions.

Figure 8 illustrates the impact of the concentration of various phosphate salt types. As can be seen from Figure 8, the equilibrium capacities for uranium increase from 0.005 g/L to 0.130 g/L with increased uranium concentration in the solution with a phosphate ions concentration of 0.3 g/L. The BO020 AER capacity for uranium decreases in the range of uranium concentrations of 0.005–0.015 g/L in the solution with a phosphate-ion concentration of 0.8 g/L. At the same time, the BO020 AER capacity for uranium increases and begins to decrease with a further increase of the uranium concentration from 0.015 g/L to 0.220 g/L in the solution. In this case, the sorption of phosphates by the BO020 AER is shown in Figures 7 and 9. As can be seen from these figures, the BO020 AER capacity for phosphate (in terms of phosphorus) increases with an increase in the uranium concentration in the solution, in contrast to the chloride and nitrate sorption in the uranium solutions. Thus, the capacities of the BO020 AER resin for phosphorus are the same as for acid and salt forms at uranium concentrations higher than 100 mg/L and phosphate at 0.3 g/L.

In the solution with a phosphate-ions concentration of 0.3 g/L, as shown in Figure 8, the equilibrium capacities for uranium rise from 0.005 g/L to 0.130 g/L with increased uranium concentration. As can be seen from Figure 8, the equilibrium capacities for uranium increase from 0.005 g/L to 0.130 g/L with increased uranium concentration in the solution with a phosphate-ions concentration of 0.3 g/L. The BO020 AER capacity for uranium decreases in the range of uranium concentrations of 0.005–0.015 g/L in the solution with a phosphate-ion concentration of 0.8 g/L. At the same time, the BO020 AER capacity for uranium increases and begins to decrease with a further increase of the uranium concentration from 0.015 g/L to 0.220 g/L in the solution.

In this case, the sorption of phosphates by the BO020 AER is shown in Figures 7 and 9. As can be seen from these figures, the BO020 AER capacity for phosphate (in terms of phosphorus) increases with an increase in the uranium concentration in the solution, in contrast to the chlorides and nitrates sorption in the uranium solutions. Thus, the capacities of the BO020 AER resin for phosphorus are the same as for acid and salt forms at uranium concentrations higher than 100 mg/L and phosphate at 0.3 g/L.

The BO020 AER phosphorus capacity becomes higher at lower uranium concentrations, less than 100 mg/L, and, especially, less than 30 mg/L if phosphates are added in the phosphate salt form.

Moreover, the BO020 AER capacity for phosphate increases in the presence of uranium compared with the sorption of the model phosphorus-containing solutions without uranium. For instance, the BO020 AER capacity for phosphorus is equal to 1.2–1.3 mg/g for model solutions with $C_U = 0$ mg/L and $C(P) = 0.3$ g/L. The BO020 AER capacity for phosphorus increases to 2.2 mg/g in the uranium solution with a concentration of $C_U = 0.03$ g/L and $C(P) = 0.3$ g/L if phosphate is added in salt form. Additionally, the BO020 AER capacity for phosphorus increases to 7 mg/g with an increase in the uranium concentration to 0.3 g/L.

3.2 Sorption of uranium in the presence of a manganese, aluminum, iron

The sorption isotherm of uranium in the presence of a manganese ion is shown in Figure 10. The manganese ions in an amount of 0.2 g/L do not affect the sorption of uranium in solutions. With an increase in the manganese-ions concentration to 0.8 g/L, the BO020 AER capacity for uranium slightly decreases by about 5% when the uranium concentration is higher than 50 mg/L in the solution.

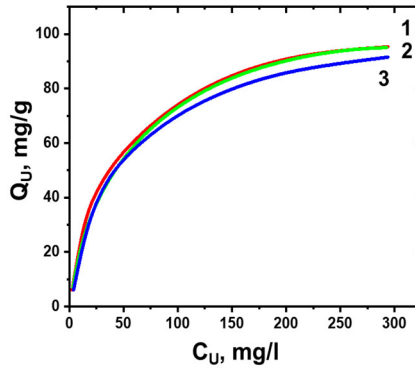


Fig. 10. Sorption isotherms of the BO020 AER for uranium at the manganese concentrations in solution with $C(Mn) = 0$ g/L (1); 0.2 g/L (2); 0.8 g/L (3).

The uranium sorption isotherms are shown in Figure 11 for solutions containing aluminum ions. As can be seen from Figure 11, the BO020 AER capacity for uranium reduces for the aluminum ion solutions at $C(Al)=0.3$ g/L. However, the BO020 AER capacity for uranium becomes higher with an increase in the aluminum ion concentration up to 1 g/L in the solution. The presence of uranium reduces the resin capacity for aluminum in the solution, so the resin capacity for aluminum decreases from 0.2 mg/g to 0.06 mg/g with an increased uranium concentration of 0.150 g/L in the solution.

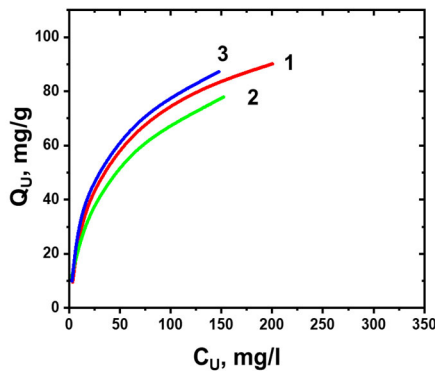


Fig. 11. Sorption isotherms of the BO020 AER for uranium at the aluminum concentrations in solution with $C(Al) = 0$ g/L (1); 0.3 g/L (2); 1 g/L (3).

The effect of iron on the sorption of uranium is shown in Figure 12. It indicates that the uranium sorption by the BO020 AER decreases with an increase in the iron concentration in the solution. The increase in the iron concentration from 0.3 to 0.8 g/L has almost no effect on the sorption of uranium. Thus, the BO020 AER capacity for uranium is 90 mg/g at $C(Fe)=0$, $C_U=0.200$ g/L in solution, and the AER capacity for uranium is equal to 83–84 mg/g in the presence of iron with $C(Fe)=0.3$ and 0.8 g/L. With an increase in the uranium concentration in the solution, the sorption of iron decreases. If the uranium content increases from 0.005 to 0.200 g/L, the iron concentration in resin reduces from 1.45 mg/g to 0.7 mg/g in solution with $C(Fe)=0.3$ g/L. Therefore, increasing the uranium concentration in solution prevents the sorption of iron by the BO020 AER.

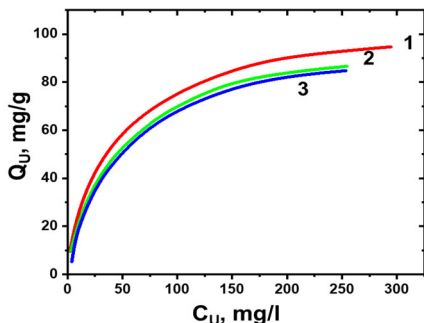


Fig. 12. Sorption isotherms of the BO020 AER for uranium at the iron concentrations in solution with $C(Fe) = 0$ g/L (1); 0.3 g/L (2); 0.8 g/L (3)

3.3 Sorption of uranium in the presence of silicates

The sorption isotherms of uranium in the presence of silicate ions in solution are shown in Figure 13. It can be observed that the increase of the silicate concentration from 0.3 to 1 g/L reduces the capacity of the BO020 AER for uranium in the solution. Thus, the BO020 AER capacity for uranium is 15 mg/g in the absence of silicate, and it decreases to 7-8 mg/g in the presence of silicate at a uranium concentration in a solution of 0.005 g/L.

At a concentration of uranium in the solution of 0.2 g/L, the BO020 AER capacity for uranium is 90 mg/g in the absence of silicate, and it decreases to 83–73 mg/g in the solution with a silicate concentration of 0.3–1 g/L, respectively. Silicate content in resin decreases from 9.1 to 4 mg/g with increased uranium concentration from 0.005 to 0.180 g/L in the initial solution with $C(Si) = 1$ g/L. Increasing the concentration of uranium reduces the silicate sorption by the BO020 AER; nevertheless, the presence of silicates in the solution depresses the sorption of uranium.

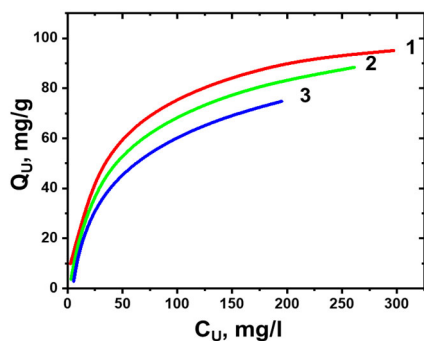


Fig. 13. Sorption isotherms of the BO020 AER for uranium at silicate concentrations in solution with $C(Si) = 0$ g/L (1); 0.3 g/L (2); 1 g/L (3).

4 Conclusions

The impurities affect the sorption of uranium by the BO020 AER in different ways.

The most negative effect is exerted by nitrates in the amount of 0.4 g/L, silicates - 0.3 and 1 g/L, and chloride - 1 g/L. The concentration of impurities by 2-4 times leads to a significant reduction of the BO020 AER capacity for uranium. The negative effect of impurities is manifested at low concentrations of uranium. With an increase in the concentration of uranium in the solution, the depressing effect of impurities becomes less. The silicate reduces the uranium sorption by 46-53.5%, nitrate ion by 46%, chloride - ion by 13% in a uranium solution with $C_U = 0.005$ g/L and $C(\text{impurities})=0.3-0.4$ g/L. However, if $C_U= 0.2$ g/L with the same concentrations of concomitant impurities, the silicates reduce the uranium sorption by 7%, nitrate by 11%, and chloride by 1%.

Some impurities have a positive effect on the sorption of BO020 AER. If the phosphate concentration is 0.3 g/L in the solution, it increases the uranium sorption by 12–13% in solutions with $C_U = 0.0051$ g/L. If $C(\text{P})=0.8$ g/L, the uranium sorption increases by 12–4% in solution with $C_U = 0.020-0.150$ g/L, respectively. Hence, the phosphorus content contributes to better sorption of uranium in the low concentration range of $C_U = 0.02.005-0.01$ g/L). The $C(\text{Al}) = 1$ g/L increases uranium sorption by 25–4% with an increased concentration of uranium from 0.01–1.050 g/L. The negative effect is manifested in solutions with $C_U = 0.005$ g/L. The aluminum depresses uranium sorption by 6–12% in solution with $C(\text{Al}) = 0.3$ g/L.

Therefore, the effect of impurities is mainly negatively reduced by 10–50% at low uranium concentrations, with the U:impurities ratio ranging from 1:20 to 1:200. With an increase in the U:impurities ratio in the range of 1:1 to 1:5, the negative effect is reduced, and the BO020 AER capacity for uranium is reduced by only 2-11%.

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