

Modeling of competitive sorption of uranium by the BO020 anion-exchange resin

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Abstract. The aim of this report is to focus on competitive sorption of strongly basic anion-exchange resin (BO020) in model solutions similar to on-site sulfuric acid solutions obtained by leaching the Uch-Kuduk deposit ores. The BO020 resin was applied to a modeling study of the uranium and competitive ions sorption in sulfuric acid solutions at pH = 1.2 and a concentration of 7 g/l of sulfate ions. The chemical composition of the salt solution after sulfuric acid ore leaching was as follows: 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 BO020 resin has fairly high uranium uptake and sorption capacities, but phosphorus, iron, aluminum, and manganese sorption capacities are very small. The nitrate and chloride ions have high sorption capacities only at high concentrations in solution. The results can be used to make the best choice of ion exchanger application for underground leaching of uranium.

1 Introduction

Ion-exchange methods have been widely used in underground leaching of uranium (U) to extract uranium from uranium-containing solutions and for possible remediation of the environment [1-4]. Efficient uranium removal showed anion-exchange and chelating resins, natural product-modified chelate resins, and impregnated and imprinted sorbents [2–3]. Since cation-exchange resins have a lower selectivity for uranium ions, anion-exchange resins (AER) are widely used in the technology of ion-exchange extraction of uranium. Among the different types of materials used for the sorption extraction of uranium, the ion-exchange resins functionalized with quaternary ammonium groups have the greatest practical importance.

The uranium ions can be sorbed from sulfate solution in the form of trisulfate complex anions ($[UO_2(SO_4)_3]^{4-}$), as well as disulfate complex ($[UO_2(SO_4)_2]^{2-}$) and, partially, uranyl

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sulfate $-\text{UO}_2\text{SO}_4$. In addition, uranium-containing sulfate solutions can contain complex ferric ions ($[\text{Fe}(\text{SO}_4)_2]^-$ and $[\text{Fe}(\text{SO}_4)_3]^{3-}$), vanadium, phosphorus, arsenic, molybdenum, chloride, nitrate ions, and etc. These ions are depressants for the ion-exchange sorbent. At the same time, sulfuric acid may be present in solution as sulfate (SO_4^{2-}) and bisulfate (HSO_4^-) ions. Almost all of the listed anions can be sorbed on a strongly basic AER; as a result, the degree of saturation of the anionite with uranium decreases due to contamination with competitive species [1]. For other ions, such as calcium, magnesium, sodium, potassium, aluminum, and cobalt ions, the formation of complex sulfates is unfavorable; therefore, they should not be sorbed by anion-exchange resins.

Some anions present in process solutions can form strong compounds with the AER and not be washed out during uranium desorption. For example, the AER can adsorb silica with further accumulation in the resin, and special treatment is required to remove silica from the resin. The solutions from sulfuric acid leaching of ores usually 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 sorbed from solutions after the leaching of ores with fast polymerization in the AER. In addition, it has been shown that sulfate ions better increase the sorption of silicate than chloride and nitrate ions [5].

Various studies consider the combination of physical, chemical, and biological methods applied to real on-site deposits and environmental factors in order to remove U from solution and a contaminated environment efficiently and thoroughly [4]. The strongly basic anion-exchange resin (BO020) is used for uranium sorption from solutions produced as a result of the leaching of the Uch-Kuduk deposit's uranium-containing ores by sulfuric acid. The BO020 resin is prepared from the product of the copolymerization of styrene and divinylbenzene via chloromethylation with further amination with pyridine. Previously, the saturation of the BO020 anionite by uranium from sulfuric acid solutions and desorption with sulfuric acid solutions were studied [6–7].

In this paper, we consider modeling the sorption of the BO020 anion-exchange resin to competing ions in sulfuric acid solutions obtained by leaching the Uch-Kuduk deposit ores. The chemical composition of the salt solutions after sulfuric acid ore leaching is: 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.

According to the salt composition of solutions, a number of ions are able to be sorbed together with uranium by the BO020 resin. The chloride, phosphate, nitrate, sulfate, and silicate ions are the main interfering and competing components. As mentioned above, manganese, aluminum, and calcium should not be sorbed on the BO020 anion-exchange resin. However, their presence together with other components can affect the uranium sorption by the BO020 resin.

This work aimed to study the sorption of uranium and competitive components by the BO020 anion-exchange resin in model solutions similar to the Uch-Kuduk deposit ore leaching process.

2 Experimental part

The sorption of uranium and competing ions (sulfate, nitrate, chloride, phosphate, silicate, iron, manganese, aluminum, and calcium) on the BO020 resin was carried out under static batch conditions. The sulfuric acid solutions of the studied components were contacted with the commercial anion-exchange resin (BO020, China) in pachuca reactors with air stirring at $\text{pH} = 1.2$. The contact time is equal to 24 hours, the ratio of the resin volume to the solution volume is 1:400 (5 ml of resin and 2000 ml of solution), and the concentration of neutral sulfates is equal to 7 g/L. The addition of neutral sulfates to the studied solutions was used for more adequate modeling of the tested solutions to the production solutions of the Uch-

Kuduk deposit ore leaching process, containing an average of 10 g/L of sulfate ions, including 3 g/L of free sulfuric acid. The sulfate ion concentration was maintained by adding sodium sulfate and sulfuric acid. With the addition of sulfate salts of aluminum, manganese, and iron, the proportion of sodium sulfate decreased on the assumption that the concentration of neutral sulfates remained constant at 7 g/L.

The BO020 resin was used for the sorption of the studied components. Before the experiment, the anionite was sieved to a size of 0.4 mm, after which the resin was soaked in water and converted into the sulfate form with a solution of sulfuric acid with a concentration of 150 g/L. The AER sulfate form was used in all experiments except the experiment where the capacity of the AER was studied for sulfate ions depending on the concentration of sulfuric acid in the initial solution. For this experiment, the AER was used in chloride form [5–6].

The sorption of uranium and competitive ions on the BO020 resin was studied by the sorption of each individual component. A series of solutions with different contents of the studied components were prepared, and the sorption isotherms were calculated.

The sorption capacity (Q_e) was determined according to the following equation (1): The sorption capacity (Q_e) was determined according to the following equation (1):

$$Q_e = \frac{(C_0 - C_e)}{m} V \tag{1}$$

where C_0 and C_e are the initial concentration of ions in mg/L and the concentration at equilibrium in mg/L; Q_e is the adsorption capacity in mg/g; V is the volume of ion solution in liters (L) and m is the weight of the prepared adsorbent used in grams.

The concentration of metal ions in the solution was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP Pro, Thermo Fisher, USA); pH was adjusted according to a pH meter (Mettler Toledo, SevenEasy, China); and anions concentration was measured by ion chromatography (IONUS, Membrapure, Germany).

3 Results and discussions

3.1 Sorption of sulfate ion on the BO020 anion-exchange resin

Experiential results of the sorption capacity of the BO020 resin related to sulfate ions ($Q_{H_2SO_4}$, mg/g) vs the equilibrium concentration of sulfuric acid in the solution ($C_{H_2SO_4}$, g/L) are given in Table 1 and Figure 1.

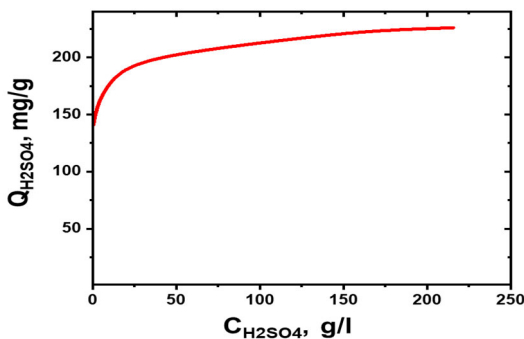


Fig. 1. Sorption isotherms of sulfate ions by BO020 resin.

Table 1. Dependence of the sulfate ions sorption capacity of the BO020 resin on the concentration of sulfuric acid in the solution.

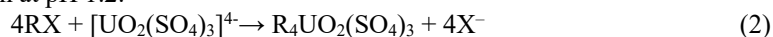
No.	Equilibrium concentration of sulfuric acid, g/L	AER capacity for SO ₄ ²⁻ ion, mg/L
1	0.005	108.1
2	0.24	116.0
3	1.22	146.0
4	7.1	187.0
5	11.52	178.0
6	19.1	194.0
7	51.8	206.0
8	84.5	218.0
9	105.0	218.0
10	143.0	206.0
11	181.0	234.0
12	224.0	227.0

As seen from Table 1 and Figure 1 the AER has a high affinity for sulfate ions. The sulfate-ion sorption capacity is equal to 230 mg/g at a sulfuric acid concentration of 180-200 g/L. The capacity for sulfate ions is also high, up to 140 mg/g at a low concentration of sulfuric acid in the solution (equal to 1.2 g/L).

3.2 Sorption of chloride, nitrate and phosphate ions

The saturation of the BO020 resin in sulfate form at pH 1.2 by chloride ions is presented in Table 2 and in Figure 2, and depends on their concentration in the solution. The chloride ions were added to the systems in the form of sodium salt. As can be seen from Table 2 and Figure 2, the higher chloride ion concentration increases the AER capacity for chlorides in the solution, and the AER sulfate-ion capacity decreases at the same time.

Thus, the maximal chloride sorption capacity of the BO020 resin is 119 mg/g at an equilibrium concentration of chloride ions of 99.4 g/L, and the sulfate ions sorption capacity is 5 mg/g. It seemed that an increase in the chloride ion concentration would obviously depress the sorption of the sulfates and sulfate complexes of uranium by the BO020 resin in sulfuric acid solution at pH 1.2.



where R = resin; X = HSO₄⁻; Cl⁻; NO₃⁻; H₂PO₄⁻; HPO₄²⁻; PO₄³⁻.

It is expected to follow the same trend for the sorption of chloride, nitrate, and phosphate ions by the BO020 resin.

The saturation of the BO020 resin by nitrate ions was studied in sulfuric acid at pH = 1.2 at a sulfate concentration of 7 g/L. The nitrate was added to the solution in the form of sodium nitrate. The results of the experiment are given in Table 3 and Figure 2. It indicates that the

nitrate capacity increases with the concentration of the nitrate ions in the solution. Figure 2 shows that the AER has higher capacities for nitrates than for chlorides. In this experiment, the capacity for sulfate was not checked, but since the chloride ions with an increase in their concentration can displace the sulfate ions from the AIR surface into the solution, it characterizes the exchange nature of the sorption of these anions. It should be concluded that with an increase in the concentration of nitrate ions in the solution, the AER capacity for sulfate will decrease.

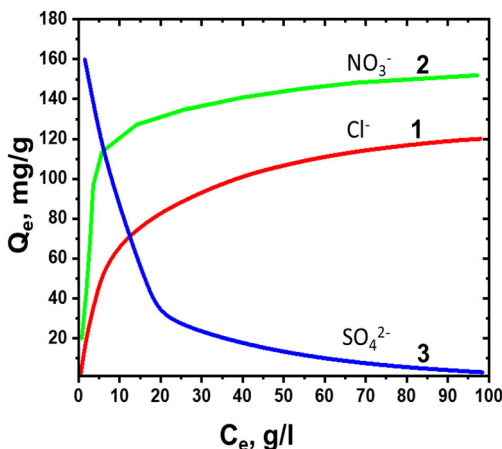


Fig. 2. Sorption isotherm of chloride (1), nitrate (2) ions and displacement of sulfate (3) from the resin by chloride ion.

Table 2. Dependence of the sorption capacity of the BO020 resin in the sulfate form vs the chloride ions equilibrium concentration in solution.

No.	Equilibrium concentration Cl ⁻ in solution, g/L	Equilibrium capacity of the AER for Cl ⁻ , mg/g	SO ₄ ²⁻ content in resin, mg/g	pH
1	0.355	4.26	168.0	1.22
7	0.497	7.1	168.0	1.22
3	0.734	11.0	163.0	1.22
4	3.08	30.0	131.0	1.2
5	6.0	43.0	102.0	1.2
6	10.8	65.0	65.0	12
7	14.9	81.0	15.0	1.2
8	20.9	83.0	20.0	1.25
9	50.4	104.0	10.0	1.2
10	99.4	119.0	5.0	1.25

The sorption of phosphate ions by the BO020 resin in the sulfate form was studied in sulfuric acid media at pH 1.2, the concentration of sulfate ions was 7 g/L. The sorption isotherms of phosphates in solutions were plotted as for phosphoric acid and phosphate salts. The equilibrium sorption capacity of the phosphate ions (in terms of phosphorus) is given in Table 4. It shows that the BO020 resin sorbs the phosphates contained in the solution in the form of acids and salts. The AER capacity for phosphorus increases from 0.48–0.8 mg/g to 3.5–4.12 mg/g with an increase in its concentration in solution from 0.06 to 1.2 g/l. Phosphorus is sorbed by the AER in a smaller amount than the chloride and nitrate ions.

Table 3. Dependence of the sorption capacity of the BO020 resin in sulfate form vs the nitrate ions equilibrium concentration in solution.

No.	Equilibrium concentration of NO ₃ ⁻ in solution, g/L	Equilibrium capacity of the AER for NO ₃ ⁻ mg/g	pH
1	0.14	7.0	1.24
2	0.36	17.4	1.2
3	0.9	32.0	1.2
4	3.77	68.0	1.23
5	4.34	104.0	1.2
6	5.16	120.0	1.16
7	44.37	140.0	1.27
8	98.2	150.0	1.20

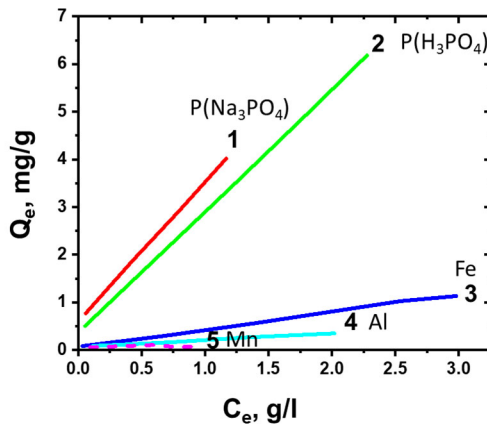


Fig. 3. Sorption isotherms of phosphorus (1, 2), iron (3), aluminum (4), and manganese (5) by the BO020 resin.

Thus, the AER sorption capacity of chloride is 20 mg/g, nitrate is 25 mg/g, and phosphorus is 2.9 mg/g, determined at a low ion concentration, which is approximately equal to 1 g/l in solution. Figure 3 and Table 4 show the initial section of the complete phosphorus sorption isotherms in comparison with other minor components with low concentrations (Fe,

Al, and Mn). It is possible to conclude that, it is not possible to achieve the complete saturation of all functional groups of the sorbent with phosphorus at the studied concentrations due to its low content in solution obtained by leaching the Uch-Kuduk deposit ores.

Table 4. The dependence of the sorption capacity of the BO020 resin in the sulfate form for phosphorus vs the equilibrium concentration of phosphorus in the solution.

No.	H ₃ PO ₄			Na ₃ (PO ₄) ₃		
	Equilibrium concentration of P		pH	Equilibrium concentration of P		pH
	In solution, g/L	In AER, mg/g		In solution, g/L	In AER, mg/g	
1	0.060	0.48	1.15	0.060	0.84	1.22
2	0.212	1.05	1.15	0.350	1.66	1.27
3	0.660	2.10	1.17	0.620	2.23	1.27
4	0.970	2.9	1.17	0.940	2.7	1.27
5	1.3	3.5	1.17	1.19	4.12	1.27
6	2.3	6.3	1.15	-	-	-

3.3 Sorption of iron, manganese, aluminium, ions

The sorption of iron sulfate complexes by the BO020 resin has particular interest since the iron concentration usually significantly exceeds the uranium concentration during sulfuric acid leaching. The AER saturation by iron was studied in sulfuric acid solutions (pH = 1.2, sulfate ions of 7 g/l). The Fe ions were added to the solution in the form of iron ammonium sulfate (Fe(NH₄)(SO₄)₂*12H₂O). The results of the experiments are given in Table 5 and Figure 3. As can be seen from Table 5, the BO020 resin showed low capacities for iron in the studied system. Even when the iron content in the solution is 18 g/l, the AER capacity for iron is only 4 mg/g.

Table 5. Dependence of the sorption capacity of the BO020 resin vs equilibrium iron concentration in solution.

No.	Equilibrium concentrations of Fe		pH
	In solution, g/L	In AER, mg/g	
1	0.112	0.010	1.20
2	0.186	0.040	1.20
3	0.440	0.280	1.20
4	0.90	0.520	1.20
5	1.79	0.690	1.2

6	4.52	2.02	1.15
7	8.8	2.89	1.15
8	18.14	4.04	1.15

The sorption of manganese by the AER was also studied in sulfuric acid solutions at pH 1.2 and a sulfate concentration of 7 g/l. Manganese was added into the system either as pyrolusite (MnO₂) or as manganese sulfate. The equilibrium capacity of the AER for manganese is given in Table 6 and Figure 3. As can be seen from Table 6, the AER sorption capacities are negligible within the studied manganese concentrations in the solution. The manganese concentrations in the model solutions are close to the manganese concentrations in the production solutions. When manganese is added in the form of pyrolusite, the concentration of manganese in the solution is not exceeded by 0.025 g/L due to the poor solubility of pyrolusite.

Table 6. Dependence of the sorption capacity of the B0020 resin vs the manganese equilibrium concentration in solution.

No.	MnO ₂			MnSO ₄		
	Mn concentration in solution, g/L	AER capacity for Mn, mg/g	pH	Mn concentration in solution, g/L	AER capacity for Mn, mg/g	pH
1	0.005	0.045	1.12	0.063	0.022	1.20
2	0.0095	0.06	1.17	0.22	0.02	1.18
3	0.013	0.06	1.15	0.34	0.02	1.18
4	0.020	0.07	1.15	0.43	0.02	1.18
5	0.025	0.07	1.15	0.77	0.06	1.18

As can be seen from Table 7, the BO020 resin rather weakly sorbs aluminum, and the resin capacity is only 0.47 mg/g even at its rather high aluminum equilibrium concentration in solution - 2 g/L.

Table 7. Dependence of the sorption capacity of the BO020 resin on the aluminum equilibrium concentration in the solution.

No.	Equilibrium concentrations of Al		pH
	In solution, g/L	In AER, mg/g	
1	0.106	0.075	1.70
2	0.307	0.112	1.20
3	0.520	0.12	1.22
4	0.763	0.2	1.20
5	1.07	0.21	1.15

6	1.58	0.35	1.18
7	2.02	0.47	1.22

3.4 Sorption of uranium

Sorption of uranium by anionite was studied in equilibrium systems with sulfuric acid solutions at pH = 12 and a sulfate ion concentration of 7 g/L. The uranium was introduced into the system in the form of uranyl sulfate. Data on the uranium sorption by the BO020 resin are given in Table 8 and Figure 4.

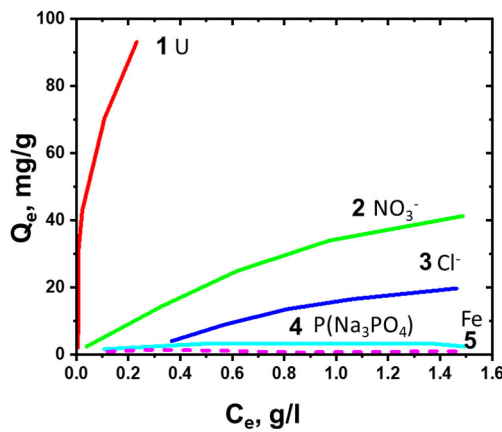


Fig. 4. Sorption isotherms of uranium (1), nitrate (2), chloride (3), phosphorus (4), and iron (5) by the BO020 resin.

Table 8. Dependence of the uranium capacity of the BO020 resin on the concentration of uranium in the solution.

No.	Equilibrium concentrations of uranium		pH
	In solution, g/L	In AER, mg/g	
1	0.005	15	1.27
2	0.010	25	1.25
3	0.020	37	1.25
4	0.050	60	1.28
5	0.100	77	1.25
6	0.150	84	1.25
7	0.200	90	1.27
8	0.300	95	1.28

Figure 4 shows sorption isotherms of uranium and different species for a comparative assessment of the sorption properties of the BO020 resin with respect to uranium and the main competitive species in the solution's component concentration ranges, which vary from 0.1 to 1.5 g/L. As can be seen from Table 8, the AER has large capacities for uranium. Thus, with a uranium concentration in the solution of 0.233 g/l, the AER capacity for uranium reaches 95 mg/g.

4 Conclusions

The modeling of sorption was carried out to determine the effect of the competing species on the sorption of uranium by the BO020 anion-exchange resin in sulfate form for sulfuric acid solutions at pH = 1.2 and a concentration of sulfate ions of 7 g/L.

Based on the sorption isotherms of competing species, the influence of the equilibrium concentrations (sulfate, nitrate, chloride, phosphate, iron, aluminum, manganese, and uranium) on the BO020 resin capacities was determined.

The BO020 resin has remarkable high uranium uptake capacities in sulfuric acid solutions at pH 1.2 and a constant sulfate concentration of 7 g/L. The phosphorus, iron, aluminum, and manganese sorption capacities are insignificant. The nitrate and chloride ions have high sorption capacities only at high concentrations in solution (10–100 g/L).

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