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## STUDY OF SORPTION OF URANIUM FROM PULPS OF LOW ACIDITY

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### SUMMARY

The sorption of uranium on anion-exchange resins is usually carried out from solutions or pulps at pH 1.5-2. The possibility of the sorption of uranium from solutions and pulps of higher pH using Varion AP anion exchanger is discussed. Data concerning the dependence of the distribution coefficients of uranium and iron(III), the variation of capacity with pH and losses of uranium during neutralization are presented.

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### INTRODUCTION

Ion-exchange resins are widely applied in hydrometallurgy. Arden<sup>1</sup> was the first to refer to the high selectivity of anion exchangers with respect to uranium. Subsequently anion-exchange resins have been used in the uranium industry<sup>2</sup>. Valuable work has been carried out to develop the technology of sorption from pulps<sup>3,4</sup>.

Using anion-exchange resins for sorption, one of the most important parameters is pH. It has been found that the capacity of anion exchangers increases with increasing pH of solution, because instead of  $[\text{UO}_2(\text{SO}_4)_2]^{2-}$  and  $[\text{UO}_2(\text{SO}_4)_3]^{4-}$  complexes the  $[\text{U}_2\text{O}_5(\text{SO}_4)_3]^{4-}$  complex is sorbed mainly on the exchanger. However, this advantage of higher pH cannot be realized in practice because of the slower diffusion of  $[\text{U}_2\text{O}_5(\text{SO}_4)_3]^{4-}$  anions and the hydrolysis of contaminating ions<sup>5</sup>, which is why the optimal pH is 1.5-2.0. Consequently, the sorption of uranium is carried out from pulps or solutions of pH 1.5-2.0 when using anion-exchange resins.

However, in some instances the processing of uranium ores may result in pulps of higher pH (for example, on mixing acidic and alkaline leaching pulps or leaching at low acidity) and it is therefore important to know all the advantages and disadvantages of the sorption process at higher pH.

In addition to the above-mentioned, the study of sorption of uranium over a wide pH range is desirable as this process has not been investigated sufficiently in the presence of iron(III) hydroxide, which precipitates at higher pH.

The present investigations included the study of the dependence of the distribution coefficient of uranium and the main contaminating ion, iron(III), on the pH of pulps and the losses of uranium during neutralization of pulps. The anion exchanger used was a Hungarian-made pyridine basic resin, Varion AP; pulps contained about 300 g/l solid material.

## EXPERIMENTAL AND RESULTS

*Dependence of sorption of uranium and iron(III) on pH*

Some experiments were carried out to determine the dependence of the sorption of uranium and iron(III) on the pH of solution. Model solutions containing 0.25 mol/dm<sup>3</sup> of sodium sulphate, 0.08 g/dm<sup>3</sup> of uranium and 0.1 g/dm<sup>3</sup> of iron(III) were used. Dry ion exchanger in the chloride form (0.6 g, equal to 1 ml of swollen resin) was added to 100 ml of solution, the mixture was shaken for 24 h and, after separation, the two phases were analysed for uranium and iron(III).

Distribution coefficients calculated from the experimental data are presented in Fig. 1:

$$D = \frac{\text{mol/dm}^3 \text{ in resin phase}}{\text{mol/dm}^3 \text{ in aqueous phase}}$$

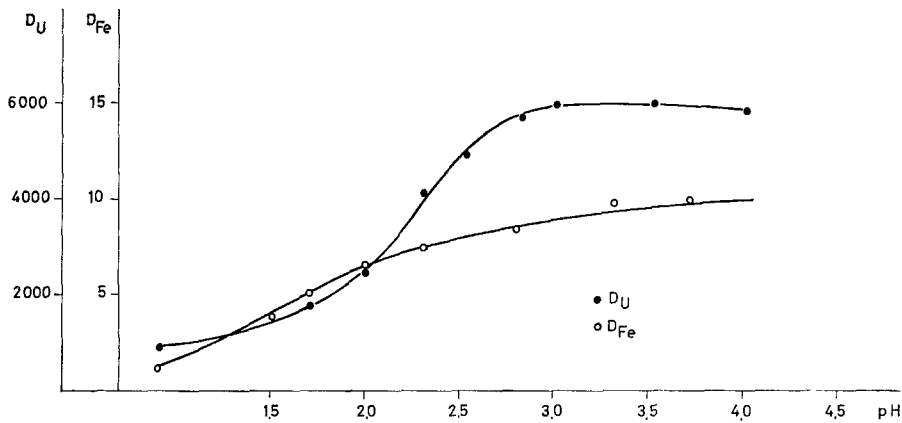
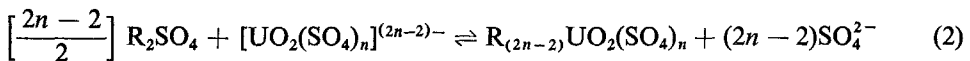
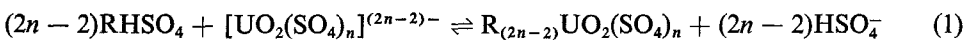


Fig. 1. Dependence of distribution coefficients of uranium and iron(III) on the pH of solution.

As with other anion exchangers, Varion AP shows increasing sorption with increase in the pH of solutions. This fact may be explained by the equilibria existing between two phases and in solution.

Obviously, the sorption of anionic complexes proceeds according to the following equations:



At higher pH of the solution, process 2 prevails over process 1.

As the selectivity of Varion AP towards  $\text{HSO}_4^-$  is higher than that towards  $\text{SO}_4^{2-}$ , an increase in the pH of solution leads to an increase in the distribution coefficients. In addition, the formation of polynuclear complexes and their sorption also have an important role, as was mentioned earlier<sup>5</sup>.

If the uranium and iron(III) are present simultaneously and, in addition, iron(III) is present at a high concentration ( $>2 \text{ g/dm}^3$ ), the effect of pH is more complicated. To determine the variation of the capacity ( $Q$ ) of Varion AP, experiments were carried out using industrial solutions containing  $33 \text{ g/dm}^3$  of sulphate,  $0.4 \text{ g/dm}^3$  of uranium,  $2.8 \text{ g/dm}^3$  of iron(III) and other, mainly divalent, ions (this solution was used in all experiments). The ratio of the volumes of solution and ion exchanger was chosen so that the equilibrium concentration of uranium in solution was about  $15 \text{ g/dm}^3$ . The data obtained are presented in Fig. 2.

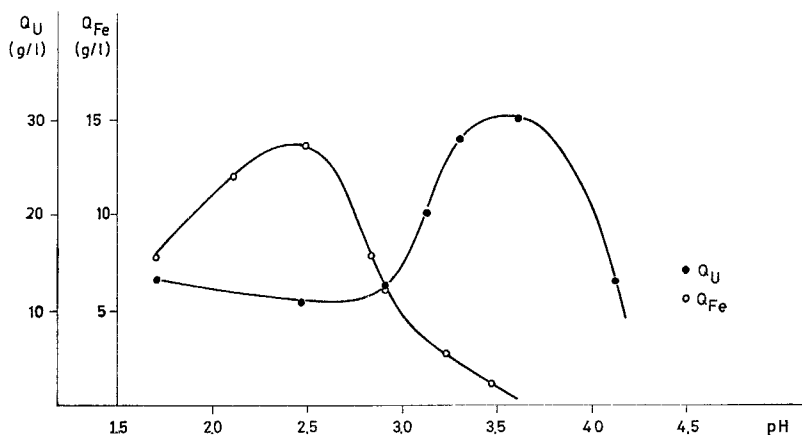


Fig. 2. Dependence of capacity of Varion AP resin for uranium and iron(III) on the pH of the pulps.

It is important to note that the maximum capacity for iron(III) is at pH 2–2.7 and for uranium at pH 3–3.5. The capacity for iron(III) decreases sharply at pH 2.8. The above data can be explained by reactions proceeding simultaneously: hydrolysis of ions, sorption of their different anionic complexes, changes in the concentration of  $\text{HSO}_4^-$ , etc. The sorption of iron(III) decreases significantly at the pH where iron(III) is hydrolysed; at these pH values the sorption of uranium increases, reaching a maximum. At pH 3.7 sorption of uranium also decreases, presumably owing to hydrolysis. Of course, the actual capacity of the ion exchanger is a function of the equilibrium concentration of the ion investigated. For this reason, the curves in Fig. 2 show only the general picture of the simultaneous sorption of uranium and iron(III); the actual values of the capacity for uranium and iron(III) depend on the concentration of the two ions.

#### *Equilibrium curves for the sorption of uranium*

Equilibrium curves for the sorption of uranium at two different pH values are shown in Fig. 3. One can conclude that the sorption process for uranium at pH 3.2 has an advantage over sorption at pH 1.7 from the point of view of the distribution of uranium: the capacity at pH 3.2 exceeds that of at pH 1.7 by about 20%, and the losses of uranium in waste liquor have to be smaller than those at pH 1.8 because of the higher distribution coefficient of uranium at pH 3.2.

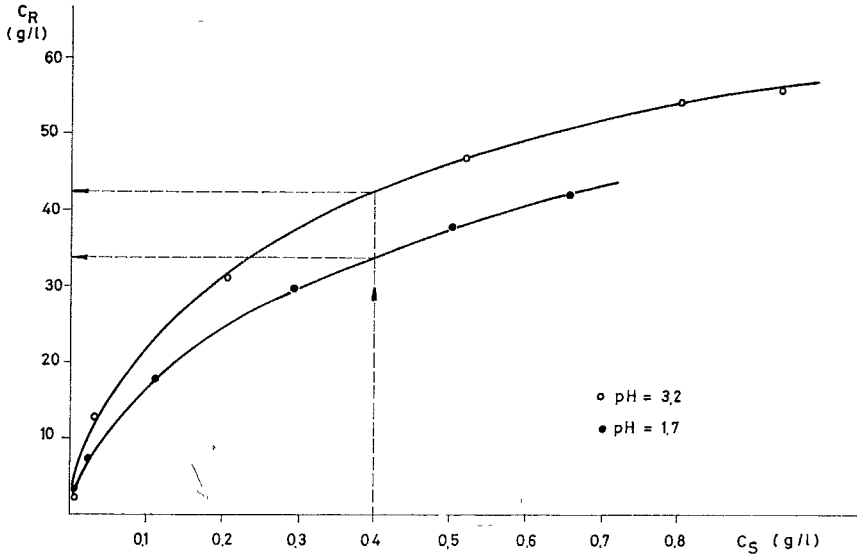


Fig. 3. Sorption equilibrium of uranium at different pH of solution.

#### *Losses of uranium during neutralization of pulps*

The losses of uranium during neutralization of acidic pulps are important from the practical point of view and special investigations were therefore carried out.

The losses were determined by analysing for uranium the initial solution, neutralized solution and solutions after the sorption process. The remaining coprecipitated uranium was determined by adding concentrated hydrochloric acid to the pulp after sorption (uranium from precipitate was redissolved in this way), after which the solution was analysed for uranium. The results in Fig. 4 show that the losses of uranium during the neutralization of pulps with slaked lime to pH  $3.3 \pm 0.1$  vary

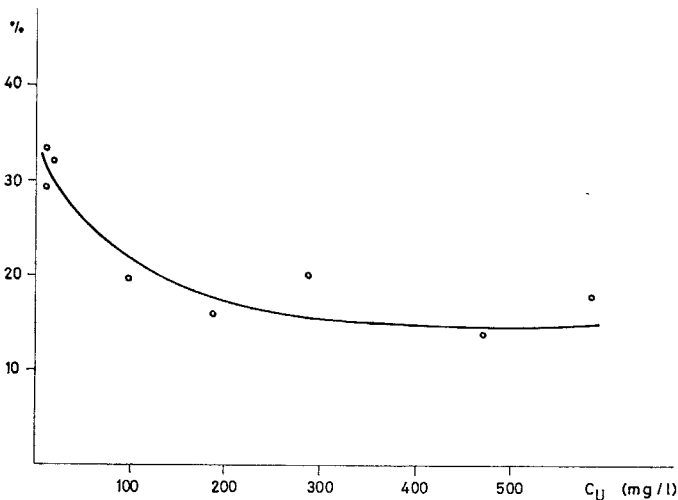


Fig. 4. Dependence of losses of uranium on its concentration during neutralization.

with the concentration of uranium in the solutions to be neutralized and reached 12–30% when the concentration of uranium varied in the range 800–1 mg/dm<sup>3</sup>. However, the main part of these losses was removed from the precipitate during the sorption of uranium. On addition of Varion AP to pulps neutralized to a high pH, the losses did not exceed 2–3 mg/dm<sup>3</sup> (see Table I). It can be expected that the losses in a countercurrent process will be lower (about 1 mg/dm<sup>3</sup>).

TABLE I

## LOSSES OF URANIUM DURING NEUTRALIZATION OF ACIDIC PULPS

The pH of the pulp was 3.7.

Volume of neutralized pulp (ml)	Volume of Varion AP added to pulp (ml)	Concentration of uranium (mg/dm <sup>3</sup> )		Losses (mg/dm <sup>3</sup> )
		In solution at pH 3.7	In solution after acidifying to pH = 1.0	
700	10	160	187	27
500	10	68	89	21
200	10	8	12.6	4.6
100	10	3.4	6.2	2.8

TABLE II

## COMPOSITION OF ION EXCHANGER SATURATED AT DIFFERENT pH OF PULP

pH of pulp	Component (relative concentration)			
	U	Fe	SO <sub>4</sub>	Cl
1.7	1	1	1	1
2.1	0.9	1.8	1	1
3.2	1.25	0.15	0.78	1.8

*Composition of saturated ion exchanger*

The relative concentrations of some components are given in Table II for Varion AP saturated in pulps at two different pH values. In accordance with the results discussed above, the composition of the ion exchanger saturated at pH 3.2 is more favourable for further technological operations. It has a higher capacity for uranium and a substantially lower capacity for iron(III) and also for sulphate.

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