



**KINETICS OF URANIUM (VI) ELUTION FROM  
CATIONIC EXCHANGE RESIN, AMMONIUM  
SULPHATE AS ELUENT**

*ALMIR AUGUSTO LARANJA*

**Publicação IEA — N.º 61**  
September — 1963

**INSTITUTO DE ENERGIA ATÔMICA**  
Caixa Postal 11049 (Pinheiros)  
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"  
SÃO PAULO — BRASIL

"KINETICS OF URANIUM (VI) ELUTION FROM CATIONIC EXCHANGE RESIN  
AMMONIUM SULPHATE AS ELUENT."

by

Almir Augusto Laranja

INSTITUTO DE ENERGIA ATÔMICA

Radiochemistry Division

São Paulo - Brasil

Publicação IEA nº 61  
September 1963

"KINETICS OF URANIUM (VI) ELUTION FROM CATIONIC EXCHANGE RESIN  
AMMONIUM SULPHATE AS ELUENT."

Almir Augusto Laranja

Radiochemistry Division  
Instituto de Energia Atômica  
São Paulo - Brasil

SUMÁRIO

O presente trabalho estuda a cinética da eluição de Urânio (VI) de resina catiônica com sulfato de Amônio. Apresenta resultados relativos à variação do uranyl na fase sólida com o tempo, mostrando tratar-se de uma reação de 2ª ordem da forma:

$$- \frac{dC}{dt} = KC^2$$

Estabelece ainda o valor da constante de velocidade, K, como função da concentração de sulfato no eluente.

São também estudadas as condições de equilíbrio da reação e a influência da relação massa de resina - volume de eluente sobre o andamento do processo.

RESUMÉ

Dans ce travail on étudie la cinétique d'élution de l'uranium (VI) d'une résine cationique avec sulphate d'ammo-

2.  
nium.

On présente quelques résultats relatives à la variation de la concentration de l'uranil dans la phase solide en fonction du temps, ce qui a permis de vérifier qu'il s'agit d'une réaction de seconde-ordre suivant l'équation:

$$- \frac{dC}{dt} = KC^2$$

On montre aussi les valeurs de la constant de vitesse K obtenues en fonction de la concentration du sulfate d'ammonium.

Les conditions d'équilibre et les effets de la masse de la résine-volume d'éluant sont aussi étudiés.

#### SUMMARY

This paper describes the kinetics of the Uranium(VI) elution with ammonium sulphate from a cationic exchanger resin. Some results on the concentration of uranyl in the solid phase as a function of time are shown allowing the conclusion that a second-order reaction takes place, according to the equation:

$$- \frac{dC}{dt} = KC^2$$

The values of the rate-constants, in several concentrations of ammonium sulphate are found, and are plotted as function of the composition of eluent.

The equilibrium conditions and the effects of the mass of resin - volume of eluent were also studied.

## I - INTRODUCTION

This paper describes the extraction of Uranium (VI), from cationic exchange resin, in order to illustrate the mechanism of the final step of elution, in the process of purification by ion-exchange. The use of sulphates as a means of extracting uranyl, is based on the formation of complexes, the structure of which have been represented by the general formula  $UO_2(SO_4)_n^{2-2n}$ .

The processes of dissociation of uranyl sulphate and hidrolisis of  $UO_2^{++}$  may occur simultaneously. In general, the mechanism of extraction may be showed by ionics equilibria and the respective constants, seen in Table I.

TABLE -I-

Reaction	Constant
$UO_2^{++} + SO_4^{=} \rightleftharpoons UO_2SO_4$	900 (1)
$UO_2^{++} + 2SO_4^{=} \rightleftharpoons UO_2(SO_4)_2^{=}$	7700 (2)
$UO_2^{++} + 3SO_4^{=} \rightleftharpoons UO_2(SO_4)_3^{-4}$	100 (3)
$2UO_2^{++} + H_2O \rightleftharpoons (UO_2)_2OH^{+3} + H^+$	$2 \times 10^{-5}$ (4)
$2UO_2^{++} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{+2} + 2H^+$	$4,9 \times 10^{-7}$ (5)
$HSO_4^{-} \rightleftharpoons SO_4^{=} + H^+$	$1,02 \times 10^{-2}$ (6)

4.

The value of the constants for the formation of amiopic complexes uranyl-sulphate guarantee the high level of extraction, since within large concentration limits of total sulphate, the ionic species  $UO_2(SO_4)_2^-$  is predominant. The conditions of pH, though more sensitive, will not be difficult to establish, since it has already been determined in experiments that the optimum is placed in a range from 1,8 to 2,0.

## II - EQUIPMENT AND REAGENTS

In the present work the Amberlit-IR-120 resin was used, with granulometry of 30-50 mesh.

The ion exchanger was conditioned as  $R-NH_4$ , washed and loaded with the feed-solution of uranyl nitrate 150 g/l, in  $U_3O_8$ , ph=2. After the water-washing, the exchanger was left to dry for 24 hours at 70-80°C.

### Reagents

1. Sulphuric Acid, PA, "Colombina", 96%, d=1,84.
2. Ammonium Sulphate, "Merck", PA.
3. Ammonium Diuranate, nuclearly pure, produced in the Pilot-Plant at the I.E.A., in São Paulo.

## III - EXPERIMENTAL PART

### A - Procedure

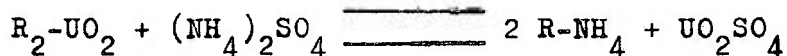
In order to determine equilibrium-conditions, portions of 2g dry resin in the form of uranyl were put in con-

tact with 25 ml of ammonium sulphate solution, in several concentrations, during an interval of one and a half hour, sufficient to attain equilibrium. Afterwards, the phases were separated by filtration in order to determine uranium in liquid phase, gravimetrically.

For the study of extraction-kinetics, 20g of dry cationic resin, in form of uranyl, were put in contact with 150ml of eluent, a constant stir being maintained. After several intervals, an aliquot of 1 ml in the liquid phase was taken.

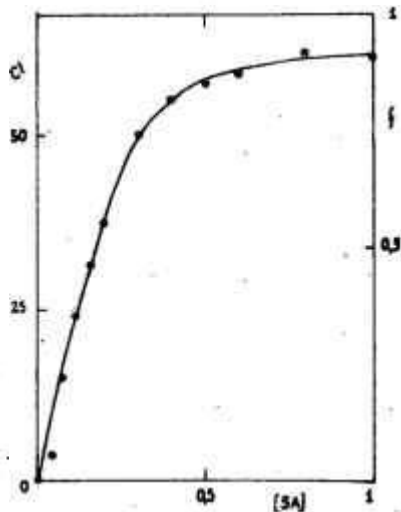
## B - Results and Conclusions

1. Equilibrium Conditions - The equilibrium conditions between uranium and ammonium sulphate, both in solid and liquid phases, which are plainly represented by the equation



depend basically upon the ionic species present in the liquid phase. The capacity of extraction, speaking of cationic resin, is directly linked to the formation of anionic complex  $UO_2(SO_4)_2^{=}$ , which appears as a predominant species, whatever is the total concentration of uranium (VI) and sulphate.

The experimental data obtained by us has made the correspondence between the formation of di-sulphuric complex and the capacity of eluent-extraction evident, as function of ammonium sulphate concentration.

**FIGURE I**

**CL** - Uranium (VI) Concentration  
in mMol/l

**AS** - Initial Ammonium Sulphate  
in Mol/l

**f** - Extracted Fraction.

The Equilibrium Concentration in the Liquid Phase, as a Function of the Ammonium Sulphate.

The variation of the extracted fraction  $f$ , with the concentration of sulphate, is practically linear up to the value  $f=0.6$ . However, the general aspect of the curve is very similar to an adsorption-isotherm, chiefly in conditions closer to the saturation of the liquid phase.

2. Kinetics of the Process - Through the procedure described above, the analysis of the decrease of uranium concentration in the solid phase was made.

Ammonium sulphate 1.0M - 0.5M - 0.25M and 0.10M solutions

tions were used for elution.

Based on these values, it was possible to relate the concentration of the solid phase,  $C$ , with the extraction period,  $t$ , through a second-order mechanism. Thus, the reaction rate,  $r$ , is shown by:

$$r = - \frac{dC}{dt} = KC^2 \quad (1)$$

Table II presents a synthesis of our results, where  $C_1$  is the uranyl-concentration in the liquid phase,  $C$  is the uranyl concentration in the solid phase and  $t$  is the time of extraction in minutes.

The integrated form of equation (1) as follows

$$1/C = 1/C_0 + Kt$$

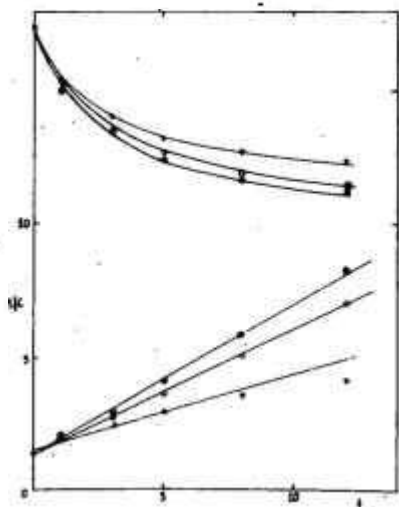
was plotted;  $C_0$  represents the initial concentration of the solid phase. The sulphate-concentration, as appears in Fig. 2 does not change the course of the process; it only modifies the values of  $K$ , characterized by the slope when  $1/C = f(t)$  is plotted.

The positive effect of the eluent concentration over the reaction-rate is evident in the increase on the value of  $K$ . One should notice that this influence is larger when the eluent concentration varies from 0 to 0.25M, as shown by the slope of Fig. 3.

TABLE - II -

(AS)*	t	Cl	C	1/C	K	
1,0 M	0	0	0,724	-	-	
	1	29,22	0,498	2,01	0,612	
	3	49,70	0,350	2,86	0,489	
	5	65,20	0,242	4,14	0,549	
	8	75,89	0,171	5,85	0,556	
	12	83,91	0,122	8,21	0,568	0,555 (Av.)
0,5 M	0	0	0,701	-	-	
	1	21,38	0,541	1,85	0,423	
	3	45,25	0,366	2,73	0,435	
	5	58,61	0,273	3,66	0,447	
	8	70,01	0,197	5,08	0,406	
	12	78,56	0,143	6,99	0,464	0,435 (Av.)
0,25 M	0	0	0,712	-	-	
	1	22,63	0,542	1,84	0,440	
	3	41,51	0,405	2,47	0,356	
	5	51,84	0,333	3,00	0,319	
	8	60,04	0,279	3,58	0,272	
	12	66,63	0,239	4,19	0,232	0,324 (Av.)
0,1 M	0	0	0,690	-	-	
	1	16,75	0,564	1,77	0,323	
	3	25,65	0,500	2,00	0,184	
	5	29,93	0,471	2,12	0,133	0,213 (Av.)

\* AS - Ammonium Sulphate.

FIGURE II

- C - Concentration in mMol/g  
 t - Time in minutes.  
 ● - AS-1M  
 ○ - AS-0,5 M  
 ▲ - AS-0,25 M

Variation of the Uranium (VI) Concentration in the Solid Phase.

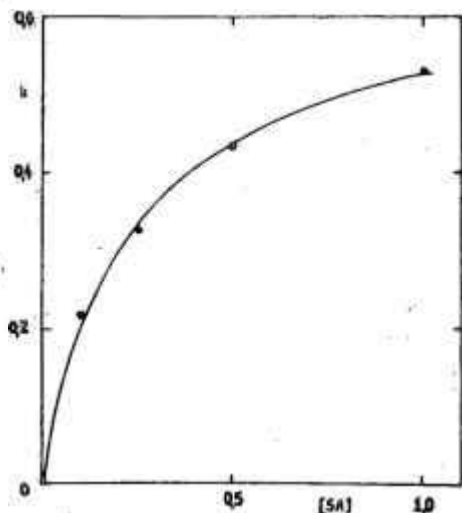
On the other hand, in the case of a column-process, admitted as a series of consecutive equilibria, eluents concentration from 0.5M to 1.0M being used, the extraction-rate will only depend upon the concentration of the solid phase, since in this range the rate-constant is less sensitive to the eluent composition, with regard to the concentration of ammonium sulphate.

Going back to the equilibrium equation of mono-sulphuric complex, the constant of which is 7700, we might say that the influence becomes evident up to the point where the system attains sufficiency, related to the formation of ion

10.

$UO_2(SO_4)_2$ . From then onwards, the increase of sulphate will also contribute, both for the formation of undissociated  $UO_2SO_4$  and for the tetravalent complex.

FIGURE III



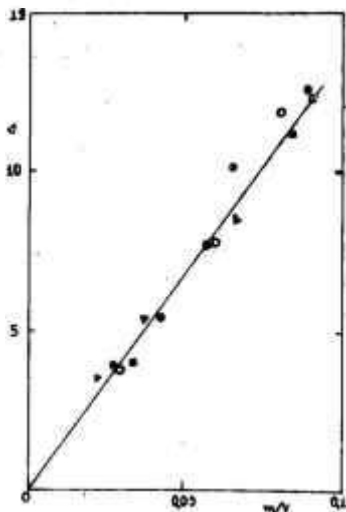
Rate-Const.in (g/mMol. min.)

Rate-Constant as a Function of SA in the eluent.

3. Influence of Relation  $m/V$ . - Another important point is the proportion between the mass of the solid phase and the volume of the eluent. In the case of column-reactions the influence of relation  $m/V$  is connected with the elution flow itself.

In this paper, the determination of the increase of uranyl in the liquid phase was carried out, with several values of  $m/V$ , this determination being made at the beginning of the process (3 minutes).

FIGURE IV



v - Reaction Rate in  
(mMol/1.min.)

R - Mass of resin -  
Volume of eluent  
Relation (g/ml).

- ● - AS - 1 M

- ○ - AS - 0,5 M

- ▲ - AS - 0,75 M

- ■ - AS - 0,25 M

Reaction Rate as a Function  
of  $m/V=R$ .

On the other hand, the graphic representation of  $v$  as a function of  $m/V$  has shown itself to be of a linear nature, and although a certain slope for each concentration of ammonium sulphate was obtained, an average slope may be admitted, in order to fulfill at a time all the concentrations of the eluent. Such a value, obtained through the graph in plate 4, is  $K=136$ .

#### IV - FINAL CONSIDERATIONS

The kinetics of elution of uranium (VI) fixed in cationic resin, depends rather on a physical factor (diffusion), than on any chemical factor. The intensity of the formation

12.

of anionic complexes with sulphates, shown by the high values of the stability-constants, does not allow of a sudden fall in the reaction-rate, in function of chemical factors. The decrease of rate in the final phase of the process and its inter-dependence to the concentration of the solid phase also lead us to this conclusion. In this way, the kinetics of the process depends on the ion-speed, not only in the liquid phase up to the surface of the resin, but also within the resin itself, meaning that diffusion within the ion-exchanger is the rate determining step, since stirring of the liquid phase will make in the liquid phase diffusion an unimportant factor to be considered.

Other sulphates will behave in a similar fashion with variations depending on the cation used. On the case of monovalent cations only different degree of cation-hydration should affect the exchange.

#### REFERENCES

1. J.A.Kitchener - "Ion-Exchange Equilibria and Kinetics", Ion-Exchange and its Applications, Society of Chemical Industry, (1955);
2. P.E.Stein - "Ionic Equilibria and Anion Exchange of Uranyl Sulphate Solutions", Report Number Y-1398, (1962);
3. H.G.Cassidy - "Adsorption And Chromatography", Technique of Organic Chemistry, vol. V, Inters. Public. Inc., N.Y. (1951).