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Synthesis of Strong Basic Resins for Uranium Recovery (Part II)

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SUMMARY

Ion exchange resins were synthesized by a crosslinking reaction and a subsequent alkylation of the branched polyethylenimine. In general, all the resins have a good retention behaviour for uranium at the pH range tested, besides of an adequate selectivity for uranium compaired to copper.

INTRODUCTION

Ion exchange materials are widely used for the hydrometallurgical recovery of uranium from sulphuric acid leached ore bodies. Anion exchange resins are usually used for this purpose and type I strong base quaternary ammonium resins have been preferred. (1-2).

Liquid-liquid extraction offers very high chemical versatility. However, one disvantages in the loss of reagent due to dissolution in the large volumes of aqueous solution from which the extraction of uranium is desired. Solid-liquid extraction on the other hand offer technological simplicity and the loss of reagent is minimized.

We reported the shynthesis and analytical properties of strong base resins from a lineal polyethylenimine in a previous work (3).

We did use a crosslinked polyethylenimine(4)which is N-alkylated with dimethylsulfate. These polymers were studied in relation to the pH influence for uranium, maximum capacity for uranium and copper, acid and basic elution assays for the resins loaded with uranium and copper. Besides for the resins PZM-2, PZM-4 and PZM-5 their thermal stability was studied.

EXPERIMENTAL

Materials: Dimethylsulphate was distilled (b.p.188°C)

Measurements: Uranium was analyzed on a PMQ II Carl Zeiss spectrophotometer. The thermal stability was recorded on a Thermical Gravimetric Scanning Perkin Elmer TGS-1.

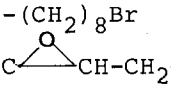
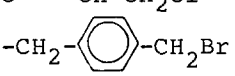
RESULTS AND DISCUSSION

Alkylation of Crosslinked Polyethylenimine

A suspention of 0.1 eq/g of crosslinked polyethylenimine in 50 ml acetonitrile, 0.24 mol of dimethylsulphate were added. The mixture was stirred by 6h to 50°C. Then the resin was filtered-out and dried under vacumm up to constant weight.

The resins obtained are shown in Table 1.

TABLE 1.- Crosslinked derivatives and polymers obtained.

Crosslinker derivative	Polymer
$Br-(CH_2CH_2O)_2-CH_2CH_2Br$	PZM - 1
$Br-(CH_2)_3-Br$	PZM - 2
$Br-(CH_2)_8Br$	PZM - 3
	PZM - 4
	PZM - 5
$BrCH_2-C\equiv C-CH_2Br$	PZM - 6
$Cl-CH_2-C\equiv C-CH_2Cl$	PZM - 7

Polymer chelation procedure.-

1.- pH dependence

The ion solution was prepared dissolving 2.0 g per litre of uranium from uranylacetate in water at the corresponding pH. Ten ml of the solution were mixed with 0.25 g of dry resin over 2 hours with constant stirring. Uranium analysis was perfomed by a spectrophotometric method (5).

TABLE 2.- Percent adsorption of uranium.

RESINS	Initial pH					
	0	1	2	3	4	4.5
PZM-1	58.3	78.4	78.4	80.7	81.8	82.5
PZM-2	64.1	77.8	82.9	82.9	82.9	82.5
PZM-3	39.8	66.4	66.4	69.9	69.9	70.4
PZM-4	63.5	78.4	80.7	80.7	83.5	83.5
PZM-5	65.9	84.3	84.8	86.3	86.3	86.3
PZM-6	51.8	72.7	82.9	81.2	78.4	81.2
PZM-7	21.3	62.3	72.7	72.2	71.6	71.6

The resins show a percent adsorption of 21 to 86% of uranium.

The resins PZM-2, PZM-4 y PZM-5 show an uranium adsorption higher than 63% between pH 0 and 4.5. All the resins present very significant uranium retention percentages at pH=2. This is very important as this is the normal pH for copper solution containing uranium.

2.- Determination of the maximum capacities.

A 250 ml beaker containing dry resins (1.0g) and uranylacetate pentahydrated aqueous solution (50 ml)(equivalent to 4 g of uranium per litre) was placed in a thermostatically controlled bath at 25°C. The mixture was stirred for 2h at 200 cycles per minute. The aqueous solution was separated by decanting and washed several times with water. This process was repeated twice using an uranium solution (50 ml) of the same initial concentration. Uranium was analized by spectrophotometry and the uranium fixed in the resins is determined from the difference.

A solution of copper II (pH=2.0, containing 20.0g/l in copper from copper sulphate p.a) was placed in thermostatically controlled bath at 25°C. The procedure is similar to the uranium one. Copper was determined on the filtrates by the Iodometric method (6) and the copper fixed in the resins is determined from the difference.

The results are shown in Table 3.-

TABLE 3.- Determination of the maximum capacity for copper and uranium.

RESINS	PZM-1	PZM-2	PZM-3	PZM-4	PZM-5	PZM-6	PZM-7
Copper(meq/g)	1.3	0.6	0.4	0.6	0.8	1.3	1.1
Uranium(meq/g)	5.9	7.0	6.0	9.1	6.0	5.0	6.8

Commercial Amberlite IRA-400 was used as standard in order to evaluate the extractive properties of the resins with respect to the pH of the solution.

All the resins present a load capacity for uranium higher than for copper. The best resin is PZM-4 that shows a maximum uranium capacity of 9.1 meq/g per dry resin. Most of the synthesized resins have a load capacity which is not only similar to the resin on the market (IRA-400 4.6 meq/g dry resins);but in some cases, even higher.

3.- Uranium and copper elution.

One tenth of a gram of each of the resins(loaded with uranium or copper to maximum capacity, at pH=2.0) were contacted in one stage separately with 10 ml of solution of 1M-4M H_2SO_4 and 0.25 M-1M solutions of Na_2CO_3, with stirring for 1 hour.

TABLE 4.- Percentage of acid elution of uranium.

RESINS	% Uranium			
	$[H_2SO_4]$ 1M	2M	3M	4M
PZM-1	63.3	72.8	76.1	77.9
PZM-2	46.0	52.7	54.5	55.6
PZM-3	57.3	59.9	65.3	66.5
PZM-4	29.4	32.0	32.2	32.2
PZM-5	40.9	47.0	50.2	54.0
PZM-6	72.5	67.3	66.2	67.5
PZM-7	59.7	60.4	61.0	61.0

TABLE 5.- Percentage of uranium eluted with molar salt solution

RESINS	% Uranium			
	$[Na_2CO_3]$ 0.25M	0.50M	0.75M	1.0M
PZM-1	55.4	60.4	62.9	63.9
PZM-2	55.1	57.4	60.3	61.2
PZM-3	48.9	48.4	50.6	50.1
PZM-4	38.3	43.6	44.3	46.0
PZM-5	47.8	53.3	53.6	55.1
PZM-6	72.5	67.3	66.2	67.5
PZM-7	59.7	60.4	61.0	61.0

Most of the resins (in a basic medium) increase the uranium elution, when the concentration of the Na_2CO_3 increases. The percentages of elution for uranium is between 29,4 and 82.6 % and between 38.3 and 72.5% in basic medium. The elution assays for copper with H_2SO_4 is nearly cuantitative in all the concentration range studied. The selective separation of uranium is possible, since low percentages of copper was obtained by basic elution.

Ion exchange chemistry uranium.

The reactions are greatly dependent on pH value and sulphate concentration in aqueous solution (7).

It is the di and tri-sulphate complexes that can exchange with the functional groups in either a strong or weak base resins. However, at pH values between 1.5-2.0 the typical ion exchange reaction are shown below. Uranium forms an adduct with the ligand atom of nitrogen from the resins.

a) Weak base resins

$$2(R_3N) + H_2SO_4 \rightleftharpoons (R_3\overset{+}{N}H)_2SO_4^{=}$$

$$(R_3\overset{+}{N}H)SO_4^{=} + UO_2(SO_4)_2 \rightleftharpoons (R_3\overset{+}{N}H)_2UO_2(SO_4)_2^{=} + SO_4^{=}$$

b) Strong base resin

$$(R_4\overset{+}{N})_2SO_4^{=} + UO_2(SO_4)_2^{=} \rightleftharpoons (R_4\overset{+}{N})_2UO_2(SO_4)_2^{=} + SO_4^{=}$$

Thermal Stability

A resin must show a right-thermal stability(8). The resins PZM-2, PZM-4 and PZM-5, that show the best retention properties for uranium, were studied by thermogravimetry. The results are shown in the Figure 1.

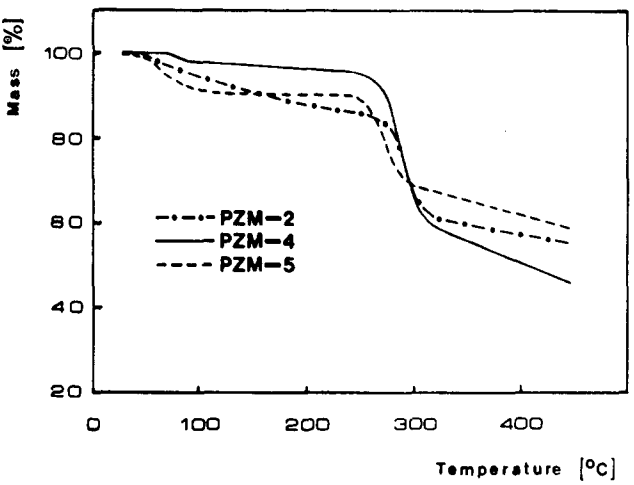


Figure 1.- Thermal behaviour for resins PZM-2, PZM-4 and PZM-5

All the resins loose weight due to absorbed water up to 120°C. Three resins loose up to 260, 250 and 230°C respectively. The recovery of the resins is 46%, 56% and 59% respectively at 450°C.

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