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Ion exchange resin selection for concentration and purification of uranium leached by sulphuric acid solution

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Abstract: Ion exchange is one of the most popular techniques for recovery and purification of uranium from sulfuric acid leaching solution, especially for recovery of uranium from a low uranium containing solutions. Resins commonly used are strong base or weak base anion resins with amine functional group. The anionic form of resins may be NO_3^-, Cl^- , SO_4^{2-} or OH^-. The selection of a resin depends on the uranium total exchange capacity, selectivity and the cost. The previous studies often use Amberlite IRA-420 for concentration and purification of uranium solution from Pa Lua sandstone ores. This is a good and suitable resin but high price. To diversify the resins and reduce the costs, instead of IRA-420, the authors tested two commercial resins Indion GS300 (India) and Purolite A400 (UK) in the processing of uranium solution from sandstone ores. The results showed that the uranium total exchange capacity of these resins is only about 80 - 85% over Amberlite IRA-420, but these resins should be able to be used instead of Amberlite IRA-420 due to their low cost and availability in Vietnam.

Keywords: *ion exchange, resin, uranium, uranium ore processing*

I. INTRODUCTION [1]

The concentration and purification of uranium leaching solution is one of the most important steps to ensure high efficiency of uranium recovery and yellow cake quality. The methods for concentration and purification of uranium solution including direct precipitation (often used in case of carbonate leaching), solvent extraction, ion exchange or a combination of ion exchange - solvent extraction. Solvent extraction has high selectivity but ion exchange could be the best in the treatment of low concentration uranium solution.

Many types of resins such as cationic, anionic, etc. can be used for ion-exchange method, however anion resins are widely used in the production of uranium over the world.

Pa Lua sandstone belongs to low grader uranium ores (about 0.04 to 0.06% U_3O_8). To extract uranium from ore, sulfuric acid leaching is a common method. The concentration of uranium in the leaching solution is usually in the range of 0.5 - 0.7 g/l with a lot of other impurities. Therefore, many previous studies have focused on using strong base anion resin Amberlite IRA-400 and IRA-420. These resins have high uranium capacity with good selectivity. However, these resins are expensive.

Therefore, the trial of other ion exchange resins to avoid the dependence on one resin in the processing of solutions containing uranium is needed. In this work, the authors will present the test results on two commercial resins Indion GS300 and Purolite A400 and assessment of their applicability in the treatment of uranium solution.

II. THEORETICAL BASIS [4, 5]

Uranium ion-exchange process based on the formation of uranyl complexes. In sulphuric

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acid leaching solution, the dynamic equilibria between complexes of U(VI) can be described as follows:

$UO_2^{2+} \leftrightarrow UO_2(SO_4) \leftrightarrow [UO_2(SO_4)_2]^{2-} \leftrightarrow [UO_2(SO_4)_3]^{4-}$

In conventional conditions of uranium leaching by means of sulphuric acid, the formation of $[UO_2(SO_4)_3]^{4-}$ complex is favorable, concentration ratio $[UO_2(SO_4)_3]^{4-}/[UO_2(SO_4)_2]^{2-}$ is 7/1 and $[UO_2(SO_4)_3]^{4-}/UO_2(SO_4)$ is 50/1. The higher the concentration ratio SO_4^{2-}/U^{6+} in the solution the equilibrium will be fowarded to increasing the concentration of $[UO_2(SO_4)_3]^{4-}$ complex in the solution. The ion exchange reaction between resin and uranyl complexes occurs as follows:

$4RCl + [UO_2(SO_4)_3]^{4-} \leftrightarrow R_4UO_2(SO_4)_3 + 4Cl^-$

Additionally, the complex formation of some impurities in the solution (eg. iron) can be found, so the ion exchange reactions between those complexes and resin can be occurred depending on the impurity affinity and concentration. Some other impurities that can be adsorbed by resin under other mechanisms (eg. aluminum).

Nitrate, sulphate and chloride solution can be use for uranium elution.

III. ION EXCHANGE RESINS AND URANIUM SOLUTION

Two types of ion exchange resin Indion GS300 and Purolite A400 have been tested to selecting an appropriate resin for the concentration and purification of leaching solution containing uranium.

A. Indion GS300

Indion GS 300 is a strong base Type I anion exchange resin, containing quaternary ammonium groups. It is based on crosslinked polystyrene and has a gel structure with high mechanical strength. GS300 is a product of Ion Exchange Group, manufactured in India and exported to the United States, Britain, Japan, Russia, Thailand, Philippines, Malaysia and others. Indion GS300 has a high exchange-capacity, high mechanical strength and a good regeneration efficiency. With a uniform particle size, Indion GS300 is often used to high flow rate solution. When saturated exchange resins can be regenerated by means of sodium chloride solution.

Table I. Indion GS300 characteristics

Polymer structure	Crosslinked Polystyrene Divinylbenzene
Ionic form	Cl^-, OH^-
Total capacity	1.2 eq/l
Moisture retention	48 - 54%
Particle size range	16 - 50 mesh (0.3 - 1.2 mm)
Maximum temperature limit	70^{o}C
pH range	0-14
Shipping weight	640 g/l

B. Purolite A400

Purolite A400 (table II) is a strong base anion exchange resin, containing quaternary ammonium groups. It is based on crosslinked styren-divinylbenzene and has a gel structure. Purolite A400 is a product manufactured in England.

Table II. Purolite A400 characteristics

Polymer structure	Polystyrene crosslinked with DVB
Functional groups	Type 1 quaternary ammonium
Ionic form	Cl^-
Shipping weight	680 - 715 g/l
Specific gravity	Approx. 1.08
Particle size range	16 - 50 mesh (0.3 - 1.2 mm)
Moisture retention	48 - 54%
Total capacity	1.3 eq/l
Maximum temperature limit	100°C

According to the characteristics of the above resins (total sorption capacity 1.2 - 1.3 eq/l, particle size 0.3 - 1.2 mm, maximium temperature limit 60°C, etc.) the technical data of these resins are similar to Amberlite IRA-420 which has been used popularly for treatment of uranium leaching solution. Moreover, these resins are much cheaper (about 90,000 - 100,000 VND/kg) than Amberlite IRA-420.

C. Leaching solution

Uranium solution for resin test is Palua sandstone heap leach solution using sulphuric acid as leaching agent; The uranium concentration is 0.7 g/l, pH 1.3, Fe 6.4 g/l with some other impurities.

IV. EXPERIMENT

In addition to comparing resin characteristics, resin price, the authors have focused on investigating the sorption capacity of uranium and impurities (such as iron), the sorption curve and elution curve for Palua sandstone leaching solution.

The experiments to test the uranium sorption capacity, impurities sorption capacity and to establish sorption, elution curves have been carried out on a single column of 2 cm diameter, resin volume of 100 ml (bed volume (BV) 100 ml). The resin preconditioning has been made by using 2M sulfuric acid solution and then washed with distilled water. pH of the solution is adjusted to a predetermined value by using NaOH diluted solution.

During the sorption stage, uranium solution is pumped to the top of ion exchange column, through the resin layer and flows to the column bottom until the uranium concentration in effluent solution equals to the concentration of feeding solution. After the soption phase, the resin layer is washed with a solution of sulfuric acid 1/1000 (volume) for separating off the feeding solution in the column. Then uranium desorption was conducted by using a mixture of 1M of NaCl and 0.05M of H_2SO_4 [1, 2, 3]. Uranium, iron and other impurities containing in the eluate solution will be determined to calculate the resin sorption capacity of uranium, iron. For experiments to establish sorption and elution curves, the composition of eluate solution will be analysed just after a few of bed volumes.

Each experiment was conducted on both resins. From the data obtained, the appropriate conditions and the applicability of each type of resin have been identified.

V. RESULTS AND DISCUSSION

A. Effect of pH on the sorption capacity of the resin

First of all leached solution is adjusted to a pH value of 1.2 by NaOH solution. Then the solution is pumped through the resin bed at a rate corresponding to retention time of 8 minutes. Similar experiments were conducted with solutions of pH = 1.4, pH = 1.6 and pH = 1.8. From obtained results, the sorption capacity of the resins are calculated and given in the following table:

pH		1.2	1.4	1.6	1.8
Loading (g U/l of wet resin)	GS300	28.5	39.1	46.8	50.2
	A400	27.1	38.3	43.4	47.7

It can be seen that uranium loading of the two resins tends to increase with increasing pH of solution. Uranium loading of GS300 resin increases from 28.5 to 50.2 gU/l of wet resin when pH of solution increases from 1.2 to 1.8. Similarly, uranium loading of A400 resin increases from 27.1 to 47.7 gU/l. However, in the pH range from 1.6 to 1.8 uranium loading of the two resins does not increase significantly. In the same experimental conditions, uranium loading of GS300 resin is little higher than A400 resin.

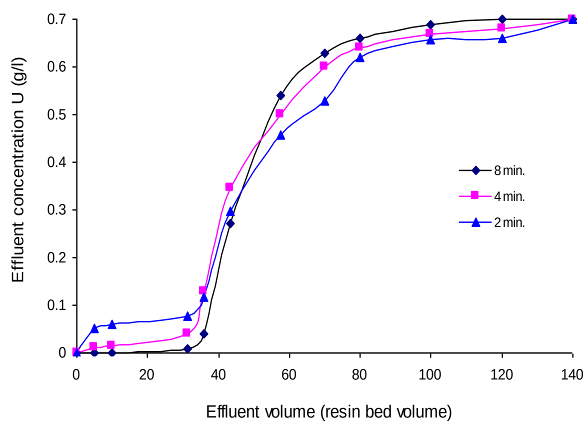
According to previous studies elsewhere, when pH increases to 1.8 or higher, some impurities will be precipitated within the resin bead in the sorption stage. So, in the sorption stage we should proceed with solution of pH = 1.6.

In the previous research results, for the similar solution uranium loading of IRA-420 resin reached 55 gU/l at pH of 1.6. Thus, the uranium loading of A400 resin is only equal to 80% of IRA-420 resin, while uranium loading of GS300 resin was 85%.

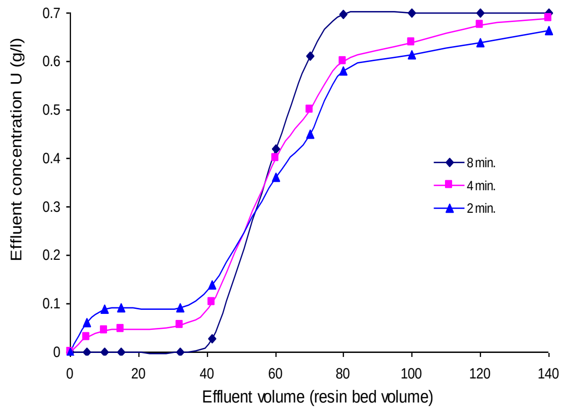
Because total capacity of IRA-420, GS300 and A400 resin is the same, so the difference in uranium loading of GS300 and A400 resin comparing to IRA-420 resin is of other impurities. This proves that GS300 and A400 resins has lower selectivity than IRA-420 resin.

B. Sorption curves

Leached solution adjusted to a pH value of 1.6 was pumped through resin bed at a rate corresponding to retention time of 2 minutes. Uranium concentrations in effluent at different bed volumes were analyzed. Similar experiments were conducted with retention time of 4 and 8 minutes. Relation of uranium concentrations in effluent and the volumes of effluent is shown in the following figures:



Uranium loading of A400 resin with different retention time



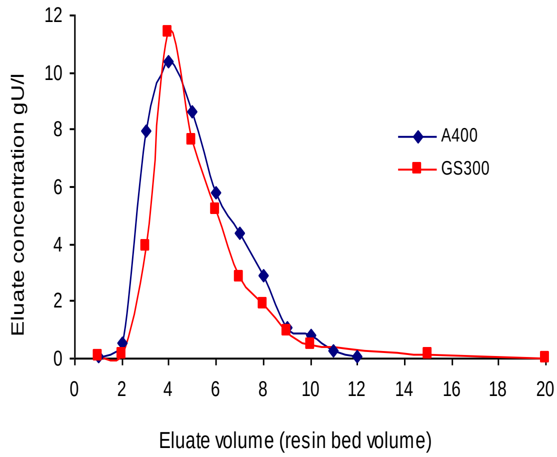
Uranium loading of GS300 resin with different retention time

Experimental results show that, similarly to IRA-420, the sorption curve of two resins can be divided into three parts: first, most of the uranium is sorbed in resin beads so uranium concentration in effluent is very low and changes slowly. In the next section (after breakthrough point), uranium concentration increase very fast. In the last section, uranium concentration varies slowly and resin beads reach state of uranium saturation.

When retention time increases, breakthrough volume increases: with retention time of 2 - 4 minutes, breakthrough point appears at about volume of 5- 10 resin bed volume (BV) for A400 and GS300 resins. However, when increasing the retention time of 8 minutes, for A400 resin breakthrough point appears at about 30 BV and for GS300 resin at about 40 BV. So with the two resins, retention time of 8 minutes is appropriate. Under this condition, GS300 resin will be saturated with uranium at volume of 80BV and A400 - 120 BV.

C. Elution curves

Saturated resin war washed by diluted H_2SO_4 solution (1/1000) to remove all leached solution from the resin bed. Then the resin was eluted by NaCl 1M + H_2SO_4 0.05M solution to recover uranium with retention time of 10 minutes. From uranium concentration in each bed volume of eluate, elution curve for each resin was plotted. The results are described in the following figure:



Uranium elution curves of A400 and GS300

Results show that in the same condition, elution curves of GS300 and A400 resin are divided into two stages. In the first one, most of the uranium is eluted from the resin in about first 10 BV. Later stage, to elute the entire uranium, relatively large volume of eluant is needed. Elution process can be completed in 15-20 BV of eluate.

VI. CONCLUSIONS

1. pH of solution effected significantly on the uranium loading of GS300 and A400 resin. Suitable pH of solution for these two resins is 1.6. Under this condition, uranium loading of GS300 resin was 46.8 g U/l and that of A400 resin was 43.4 g U/l, accounted for approximately 80-85% to the uranium loading of Amberlite IRA-420 resin. The shape of uranium loading curve is similar to that with Amberlite IRA-420 resin, retention time of solution was 8 minutes (while the IRA-420 resin Amberlite only 3.5 - 4 minutes).

2. By using conventional eluant, nearly all of the uranium can be eluted from the resin with 15 - 20 bed volumes of eluant.

3. Although the uranium loading is lower, we may still use GS300 and A400 resins for concentration and purification of leached solution because these resins are imported and sold popularly in Vietnam with cheaper price. However, due to the lower sorption capacity as well as slower kinetic sorption and eluation characteristics, the overal benefit must be evaluated carefully in term of the operation of the whole IX system before deciding to use these resins.

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