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Pacific Northwest Laboratories
Richland, Washington 99352

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SCAVENGING OF PROTACTINIUM
FROM THORIUM SOLUTION
WITH SILICA GEL
AND UNFIRED VYCOR GLASS

MASTER

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BY

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J. A. Partridge

Chemical Systems Technology Section
Chemical Technology Department

Supported by
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SCAVENGING OF PROTACTINIUM FROM THORIUM SOLUTION
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J. A. Partridge

INTRODUCTION

In solvent extraction processing of thorium fuels, formation of objectionable solids has been observed. It is believed that these solids result from thermal and radiolytic degradation of the tributyl phosphate (TBP) solvent. Most of the radiolytic heat in irradiated thorium results from decay of protactinium-233. Thus, a practical system for protactinium removal from dissolver solution prior to Purex processing is desirable.

This report describes laboratory and shielded cell studies of protactinium removal from dissolved thorium solution by batch contact adsorption on silica gel and pulverized unfired Vycor glass. The laboratory studies were performed with synthetic thorium dissolver solution containing tracer Pa-233. Shielded cell tests were made on two thorium dissolver solutions (0.71M Th and 1.34M Th) prepared by dissolving recently irradiated thorium wafers. Process variables that were examined included contact time, adsorbent particle size, contact temperature, leaching solution, leaching contact time and temperature. Adsorption by normal and low density silica gel was compared. Previously reported studies have not examined protactinium adsorption by low density silica gel.

It was not the purpose of this investigation to examine the effects on Pa adsorption of the dissolver solution composition. For such data the reader is referred to the work of Moore and others at Oak Ridge National Laboratory.¹⁻⁴ They report data obtained from adsorption column tests and, to a lesser extent, from batch contact tests with silica gel and unfired Vycor.

A co-precipitation process⁵ and a solvent extraction process⁶ for removal of protactinium from thorium dissolver solution have also been proposed and investigated by workers at Hanford.

SUMMARY

Protactinium adsorption from thorium dissolver solution by batch contact with silica gel and pulverized unfired Vycor glass was investigated. Laboratory and shielded cell tests demonstrated that Pa is removed from a thorium solution by either adsorbent, that the Pa can be leached from either adsorbent, and that the adsorbents can be recycled with no apparent decrease in sorption efficiency.

Laboratory studies were performed with synthetic dissolved thorium solution (0.71M Th) containing tracer Pa-233. Low density silica gel was found to be superior to normal density silica gel in adsorption of Pa from the thorium solution. With a given weight of both silica gel and unfired Vycor, Pa adsorption increased as particle size decreased.

At a given adsorbent mesh-size, Pa adsorption was greater with low density silica gel than with an equal weight of unfired Vycor.

Adsorption of Pa on silica gel was found to be temperature independent.

A sodium tartrate solution was found to be effective in leaching Pa from silica gel and unfired Vycor. Elevated temperature increased the leaching rate.

Shielded cell tests were made on two solutions (0.71M Th and 1.34M Th) which were prepared by dissolving some recently irradiated thorium wafers. Adsorption contacts were 1 hour at ambient temperature. Leaching contacts were 30 minutes at 80°C. Tests in which each adsorbent (3-8 mesh low density silica gel and 8-20 mesh unfired Vycor) was put through six sorption-leach cycles demonstrated that either adsorbent should be usable for many sorption-leach cycles without degradation of its sorption efficiency.

EXPERIMENTAL WORK AND DISCUSSION

Laboratory Investigation

For the laboratory tests, a synthetic thorium dissolver solution was prepared having the composition: 0.71M Th-7.3M HNO_3 -0.15M $\text{Al}(\text{NO}_3)_3$ -0.039M KF-0.17M NaNO_3 .

All chemicals were reagent grade. Protactinium-233 was added at tracer concentrations.

The silica gels tested included: (1) Grade 12, 60-100 mesh and 28-60 mesh, normal density; (2) Grade 407, 8-20 mesh, normal density; (3) Grade 01, 3-8 mesh, normal density; (4) Grade 58, 35-60 mesh, low density and (5) Grade 59, 3-8 mesh, low density - all obtained from Davison Chemical. The Grade 58, 35-60 mesh silica gel is no longer produced by Davison, but was included in this study for comparison.

Two mesh sizes (35-60 and 8-20) of pulverized unfired Vycor glass were tested. Each was glass No. 7930 (Corning Glass Works).

The experimental procedure for the adsorption tests was to add a given amount of adsorbent to 10 ml of synthetic dissolver solution which was being stirred with a stainless steel stirring bar. Samples (100 λ) were taken as a function of time, diluted to 3 ml, and analyzed for Pa-233 with a well-counter and a 400-channel gamma energy analyzer.

The effects of the type and amount of adsorbent, the mesh size, the solution temperature, and contact time were examined.

The results displayed in Figure 1 show a comparison of performance of normal and low density silica gel at various mesh sizes. The smaller mesh silica gel was more efficient at removing Pa from the solution, and for a given mesh size the low density gel was superior to the normal density silica gel. Figures 2 and 3 show the results as the amount of normal density and low density silica gel was varied in a constant volume of solution.

*Normal density silica gel has a bulk density of 44-48 lbs/cu ft. Other properties include a surface area of 600-800 m²/gm, a pore-volume of 0.40-0.43 cm³/gm, and a maximum pore radius of about 9 Å. Low density silica gel has a bulk density of 24-28 lbs/cu.ft., a surface area of 300-350 m²/gm, a pore volume of 1.0-1.5 cm³/gm, and a maximum pore radius of about 47 Å.

The adsorption of Pa on silica gel was essentially temperature independent between 20 and 80°C as shown by the data in Figure 4.

At a given mesh size, the low density silica gel was also more efficient (in terms of amount of Pa adsorbed per gram of adsorbent) than unfired Vycor, as shown by the results in Figure 5.

Vycor adsorption of Pa as a function of amount of Vycor and contact time is shown in Figure 6.

For a batch contact adsorption process to be economically feasible, the adsorbent must be used a number of times. Thus, a method of leaching the Pa from the adsorbent is necessary. Scouting experiments with several possible leaching solutions were performed, and some of the results are listed in Table I. The procedure was to sorb Pa from the synthetic solution onto silica gel for a given length of time, remove the silica gel and rinse the Th solution from it with a minimum amount of water, and then put the gel in a leach solution which was being stirred with a stainless steel stirring bar. Solutions of 0.5M and 0.25M citrate, 0.5M and 0.25M oxalate, and 0.5M diethylenetriaminepentacetic acid (Na^+ form) formed precipitates (presumably with interstitial thorium) when put in contact with the gel and were eliminated from further investigation.

TABLE I
Leaching of Sorbed Pa from 3-8 Mesh Low Density Silica Gel, Percent Removed

Contact Time, Min.	Leaching Solution					
	Na_2HNTA 0.20M	H_3NTA^* (sat'd)	HNO_3 1M	1M HNO_3 3M NaNO_3	HEDTA** 0.20M	Hydroxyacetic Acid, 0.25M, Init. pH 4
5			6	2		
10	4.7	2.6			3.4	1.6
15			9	4		
30	8.2	5.2			5.3	3.6
50			7	5		
60						6.6
90	16	16			6.5	

* Nitrilotriacetic acid

**Hydroxyethylenediaminetriacetic acid

Tartrate at an initial pH of 4 to 6 gave the best results, as seen by comparing the data at pH 5 (Figures 7 and 8) with the data in Table I. Tartrate solutions at an initial pH higher than 6 were not investigated since both acidic protons of tartaric acid have been neutralized at pH 6 and the solution has no buffering action at higher pH values.

The leaching temperature was found to be important and the data in Figures 7 and 8 show the improved results at 80°C over those at room temperature.

Two tests were made in which unfired Vycor was put through 3 sorption-leach cycles. The results are shown in Table II:

TABLE II

Successive Sorption-Leach Cycles with Unfired Vycor

Sorption Cycle: 1 hour
10 ml Th solution
8-20 mesh Vycor

Leach Cycle: 1 hour
5 ml 0.50M tartrate,
Initial pH 5
80°C

<u>Cycle</u>	<u>Sorption of Pa From Th Solution, %</u>		<u>Elution of the Pa Sorbed in This Cycle, %</u>	
	<u>1.0g Vycor</u>	<u>0.50g Vycor</u>	<u>1.0g Vycor</u>	<u>0.50g Vycor</u>
1	78	62	79	83
2	76	62	93	92
3	76	60	95	94

The data in Table II demonstrate that there is no breakdown in the sorption characteristics of the Vycor for at least 3 cycles and suggest that one should be able to put it through several such cycles. These laboratory results agree well with results from similar tests in the shielded cell with actual dissolver solution, reported in the next section of this report.

Shielded Cell Investigation

Shielded cell tests were made with two solutions which were prepared by dissolving some recently irradiated thoria wafers. The solution compositions were: (1) 0.71M Th-7.3M HNO_3 -0.15M $\text{Al}(\text{NO}_3)_3$ -0.17M NaNO_3 -0.039M KF, and (2) 1.34M Th-5.4M HNO_3 -0.15M $\text{Al}(\text{NO}_3)_3$ -0.08M NaNO_3 -0.039M KF.

The effectiveness of protactinium adsorption from each of these solutions by batch contact with unfired Vycor glass (8-20 mesh) and low density silica gel (3-8 mesh) was investigated.

Tests were made with both adsorbents in which the adsorbent was put through 6 sorption leach cycles to check for possible degradation in the ability of the adsorbent to remove Pa from the solution. The 0.71M Th solution was used for these tests. The procedure was to lower the adsorbent in a stainless steel screen basket into the thoria solution which was being stirred. The basket allowed the solution to flow through the adsorbent, but prevented any abrasive action on the adsorbent by the magnetic stirring bar which would tend to produce fines (especially with the silica gel). After 1 hour of adsorption, the basket was removed from the solution, the excess thoria solution was rinsed from the adsorbent with water, and the basket was placed in a tartrate (0.25M or 0.5M, initial pH 5) solution at 80°C for 30 minutes to leach the protactinium from the adsorbent. The tartrate solution was stirred with a Teflon coated magnetic stirrer. Since thorium will precipitate with tartrate it was necessary to rinse the thoria solution and 50 ml of tartrate solution were used in each run. After the 30 minute leach, the adsorbent and basket were rinsed with water and placed in another 50 ml of the thorium solution and the procedure repeated. Fresh tartrate solution was used with each leach cycle.

The results with unfired Vycor are listed in Table III. There was no indication in 6 cycles of any degradation or "poisoning" of the Vycor. The precipitate which formed in the leach phase of the second cycle was apparently due to insufficient rinsing of the thorium solution from the Vycor prior to putting it in the tartrate solution. Even though the precipitate decreased the amount of

protactinium leached from the Vycor during that cycle, it did not damage the Vycor for future use.

TABLE III

Successive Sorption-Leach Cycles with Unfired Vycor

Adsorption Cycle: 50 ml 0.71M Th solution
10 gms unfired Vycor, 8-20 mesh
Ambient temperature
1 hour contact

Leach Cycle: 50 ml 0.25M Tartrate, Initial pH 5
80°C
30 minute contact

<u>Cycle</u>	<u>Pa Adsorbed, %</u>	<u>Elution of the Pa Sorbed in This Cycle, %</u>
1	86	75
2	86	14*
3	81	133
4	87	73
5	86	122
6	86	99

*Precipitate formed

The results of a similar test with low density silica gel are listed in Table IV. As with the Vycor, there was no indication in 6 cycles of any degradation or "poisoning" of the silica gel. Based on these results, it appears that both adsorbents would be capable of being used for many such sorption leach cycles.

TABLE IV

Successive Sorption Leach Cycles with Low Density Silica Gel

Adsorption Cycle: 50 ml 0.71M Th solution
 5.0 grams Low density silica gel, 3-8 mesh
 Ambient temperature
 1 hour contact

Leach Cycle: 50 ml 0.50M tartrate, Initial pH 5
 80°C
 30 minute contact

<u>Cycle</u>	<u>Pa Adsorbed, %</u>	<u>Elution of the Pa Sorbed in This Cycle, %</u>
1	83	87
2	84	92
3	85	117
4	84	103
5	84	102
6	85	90

Figures 9 and 10 show the results of protactinium adsorption tests as a function of the amount of adsorbent. These results make it possible to make an estimate of the amount of adsorbent required to remove a given percentage of the protactinium from either solution with 1 hour batch contact. Based on the laboratory results, the amount required would be less with a longer contact time.

Fresh tartrate leach solution was used each time in the above tests. However, one leach solution could probably be used for 2 or more batch leaches. An experiment was done in which the same 0.25M tartrate solution was used twice to leach the Pa from 10 grams of Vycor. Fresh 1.34M thoria solution was contacted with the Vycor both times. Seventy percent of the adsorbed protactinium was leached both times by the one tartrate solution.

An experiment was conducted which shows that the Vycor after a single 1 hour batch contact was probably far from being "loaded" with protactinium. The

procedure was to contact three 50 ml solutions (1.34M Th) in succession with the same 2.5 grams of Vycor. Each contact was for 1 hour. The Vycor was rinsed with water but not contacted with tartrate solution between each adsorption contact. The percent Pa adsorbed was 58, 50, and 59 from the first, second, and third solution, respectively. The results indicate that a batch of Vycor could be used for more than one batch contact with thorium solution between each tartrate leach, thus reducing the cost of the process associated with the tartrate. The number of effective adsorption batch contacts between tartrate leaches would be determined by the concentration of protactinium in the thorium solution and the capacity of the adsorbent.

REFERENCES

1. J. G. Moore and R. H. Rainey, "Separation of Protactinium from Thorium in Nitric Acid Solutions by Solvent Extraction with Tributyl Phosphate or by Adsorption on Pulverized Unfired Vycor Glass or Silica Gel," ORNL-TM-543, April 1963.
2. J. G. Moore, "The Effect of Nitric Acid, Thorium, Fluoride, and Aluminum on Protactinium Adsorption by Unfired Vycor Glass," ORNL-3599, April 1964.
3. J. G. Moore, et al., "Adsorption of Protactinium on Unfired Vycor: Initial Hot Cell Experiments," ORNL-3773, April 1965.
4. J. H. Goode and J. G. Moore, "Adsorption of Protactinium on Unfired Vycor: Final Hot Cell Experiments," ORNL-3950, June 1967.
5. L. L. Humphreys, "Hot Cell Studies on the Separation of Protactinium-233 from Irradiated Thoria by Co-precipitation with Manganese Dioxide," BNWL-78, July 1965.
6. W. W. Schulz, Atlantic Richfield Hanford Company, unpublished results.

FIGURE 1. ADSORPTION OF Pa BY SILICA GEL. COMPARISON OF NORMAL- AND LOW-DENSITY SILICA GELS WITH VARIOUS MESH SIZES.

FIGURE 2. ADSORPTION OF Pa BY VARIOUS AMOUNTS OF NORMAL-DENSITY SILICA GEL.

FIGURE 3. ADSORPTION OF Pa BY LOW-DENSITY SILICA GEL.

FIGURE 4. ADSORPTION OF Pa BY LOW-DENSITY SILICA GEL.
EFFECT OF TEMPERATURE.

FIGURE 5. ADSORPTION OF Pa BY LOW-DENSITY SILICA GEL AND VYCOR. EFFECT OF MESH SIZE.

FIGURE 6. ADSORPTION OF Pa BY UNFIRED VYCOR.

FIGURE 7. TARTRATE LEACH OF Pa FROM SILICA GEL.
EFFECT OF TEMPERATURE.

FIGURE 8. TARTRATE LEACH OF Pa FROM UNFIRED VYCOR.
EFFECT OF TEMPERATURE.

FIGURE 9. PERCENT Pa REMAINING IN 50 ml OF Th SOLUTIONS AS A FUNCTION OF AMOUNT OF 8-20 MESH UNFIRED VYCOR. ONE-HOUR CONTACT.

FIGURE 10. PERCENT Pa REMAINING IN 50 ml OF THE SOLUTION AS A FUNCTION OF AMOUNT OF 3-8 MESH LOW-DENSITY SILICA GEL. ONE-HOUR CONTACT.

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