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# "THE PREVENTION OF SILICA CONTAMINATION OF ANION EXCHANGE RESINS DURING URANIUM RECOVERY BY CYCLIC WASHING WITH ACID-FLUORIDE SOLUTIONS"

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ABSTRACT

The use of dilute acid fluoride solution as a cyclic wash for the prevention of silica contamination in anion exchange resins is described. A cyclic wash employing 0.5 molar sulphuric acid and 0.05 molar ammonium bifluoride was found to be adequate in preventing the accumulation of more than one per cent of silica on a resin over a period of 13 cycles.

## 1. INTRODUCTION.

Acid leaching of some uranium ores may yield liquors containing silica. Such silica readily precipitates in the anion-exchange resin bed used to adsorb the uranium. The siliceous deposit accumulates in and around the resin beads, and cannot be completely removed physically by backwashing the resin bed. In time, the accumulated silica affects the resin efficiency, by slowing down the bead-diffusion-rate of the adsorbing ions, and may even seriously obstruct liquor flow.

Previous successful use in these laboratories of acid ammonium fluoride solutions to prevent the accumulation of precipitated titania on anionic resins, led to the present analogous application.

Experiments in which silica-contaminated resins were batch-washed with acid fluoride solutions have shown that, if time is allowed for equilibrium conditions to be achieved, dilute solutions can remove the silica with almost theoretical efficiency with respect to the fluorine content of the wash. It might thus be economically possible to prevent silica accumulation in a resin bed by washing an operating column each cycle with such a solution.

This procedure was investigated both in the laboratory and on small pilot scale.

In the laboratory, resins receiving various acid fluoride washes on cycle were compared with control resins receiving the usual acidified water wash.

For the pilot scale work only one acid fluoride wash solution was employed and the resin from this treatment was compared with a control resin receiving the normal washing with acidified water.

## A. LABORATORY INVESTIGATIONS.

### 2. MATERIALS EXAMINED.

#### 2.1 - Acid-fluoride Wash

The various acid fluoride washes used were made from analytical reagent grade sulphuric acid, technical grade ammonium bifluoride, and tap-water. The ammonium bifluoride contained 66 percent fluorine and 2 percent silica.

#### 2.2 - Exchange Resin

This was fresh "Deacidite FF" anion exchange resin, screened to eliminate minus 30 mesh material.

### 3. ANCILLARY MATERIALS AND EQUIPMENT.

#### 3.1 - Adsorption Liquors

Actual sulphuric acid leach liquors were used. These varied somewhat in uranium and silica content. The liquors used in the three runs reported contained the following concentrations of uranium and silica.

| Run No. | Liquor $U_3O_8$ g/l | Liquor $SiO_2$ g/l |
|---|---|---|
| 1 | (0.8 | 1.4 |
| | (1.7 | 1.7 |
| 2 | (1.0 | 3.0 |
| | (2.4 | 2.9 |
| 3 | 0.9 | 3.4 |

#### 3.2 - Eluent

The eluent was molar sodium chloride solution, acidified with sulphuric acid to pH 1.4.

3.3 - Wash (other than acid-fluoride)

Wash used for the control resins after adsorption and again after elution, and for the test resins after adsorption, was water acidified with sulphuric acid to pH 2.

3.4 - Equipment

The cyclic operations of the resin columns were controlled by a two channel resin life test unit. The operation of a similar unit is described by Audric, Bryant, and Long (1).

The apparatus automatically supplies four separate solutions in sequence to each of two separate columns, the sequence being repeated for as long as the reservoirs hold supplies of the solutions. The volume of each solution supplied in one sequence is pre-set, and controls the operation of the succeeding valve. The sequence for an ion exchange column, viz:

(1) Adsorption
(2) Wash
(3) Elution
(4) Wash

is thus operated automatically.

Columns for this unit were made of transparent, rigid, plastic tubing, 0.5 inch internal diameter and 6 inches in length. The resin bed was supported on a perforated porcelain disc, below which was a glass column-base tapered to connect to a capillary tube outlet. The column and base were connected by a sleeve of flexible plastic tube with the porcelain disc held in position between them.

Each set of valves was connected to the respective column through a four-way glass distributor piece, sealed into the column top through a rubber stopper. The liquors from the reservoirs above the valves were siphoned through the appropriate open valve and through the column, the siphon circuit being sealed from reservoir to column outlet. The capillary outlet of the column in conjunction with

adjustable constant-head-devices in the reservoirs controlled the flow-rate of liquor.

4. EXPERIMENTAL PROCEDURE.

Three runs were carried out with different acid fluoride washes. For each run the two columns were each charged with 10 ml. of fresh wet settled resin, giving bed depths of 3 inches. The columns were marked A and B, according to the respective channels A and B, of the resin test equipment.

Column A was in each case the test column, receiving the acid fluoride wash, whilst Column B was the control receiving an equivalent volume of wash with acidified water.

The reservoir and supply line for the acid fluoride wash were of plastic material, and the particular glass valve involved, and the glass adaptor leading from valve to column, were coated with "Bostikote". The acid fluoride wash thus did not contact any glass until it had passed through the resin.

The flow-rate for each column was adjusted to approximately 1.6 ml. per minute for adsorption (2.5 minutes retention time); 1 ml. per minute for elution (4 minutes retention time); and 3 ml. per minute for all washes (1.3 minutes retention time).

Each of the three runs was continued for 30 complete cycles. Details of the cycles in each particular case are given in Table 1.

TABLE 1.

| | Adsorption | Wash | Elution | Wash |
|---|---|---|---|---|
| Runs Nos. 1 and 2 | | | | |
| Channel A | 750 ml. | 30 ml. | 220 ml. | * 50 ml. |
| Channel B | 750 ml. | 30 ml. | 220 ml. | 50 ml. |
| Run No. 3 | | | | |
| Channel A | 750 ml. | 30 ml. | 220 ml. | * 20 ml. |
| Channel B | 750 ml. | 30 ml. | 220 ml. | 20 ml. |

* Acid fluoride wash. Other washes were with water acidified with $H_2SO_4$ to pH 2.0.

The time for a complete cycle was approximately 12 hours. The composition of the acid fluoride washes used in these runs is shown in Table 2.

TABLE 2.

| Run No. | Sulphuric Acid Normality. | Ammonium Bifluoride Molarity. |
|---|---|---|
| 1 | 1 | 0.05 |
| 2 | 0.5 | 0.025 |
| 3 | 0.5 | 0.025 |

At the completion of 30 cycles, immediately after the post-elution wash, the resin charges were removed from the columns. The resin was washed free of such solid impurities as could be removed by stirring in a beaker of water, allowing the resin to settle, and decanting the water and suspended matter. The resin was then filtered, dried at 110°C and analysed for silica.

5. RESULTS.

The silica content of the resin samples obtained from the above treatment is shown in Table 3.

TABLE 3.

| Run No. | Test Resin A | Control Resin B |
|---|---|---|
| 1 | 0.2% $SiO_2$ | 3.8% $SiO_2$ |
| 2 | 0.3 | 5.5 |
| 3 | 3.2 | 7.2 |

## B. PILOT SCALE INVESTIGATION.

6. MATERIALS.

6.1 - Acid fluoride wash

Technical grade reagents were used to prepare a solution 0.05 molar in ammonium bifluoride and 0.5 molar in sulphuric acid.

6.2 - Exchange Resin

As in the laboratory investigation the resin used was "Deacidite FF" anion exchange resin.

6.3 - Adsorption liquors

Two samples of a uranium ore were leached to provide two leach liquor samples, the compositions of which are shown in Table 4.

TABLE 4.

| | Liquor Composition | | | |
|---|---|---|---|---|
| | $U_3O_8$ g/l. | $SiO_2$ g/l. | $SO_4$ g/l | pH |
| Sample A | 0.78 | 2.21 | 14.0 | 2.03 |
| " B | 2.27 | 2.21 | 13.8 | 2.10 |

Sample A was used for the first seven cycles and Sample B for the last six cycles.

7. EQUIPMENT.

The resin columns were constructed from 3 inches internal diameter polythene tubes, with stainless steel end pieces.

The acid fluoride solution was pumped to the columns through plastic tubing by means of a rubber lined pump.

The columns each contained 6.3 litres of wet settled resin with a bed depth of 4.5 feet.

8. EXPERIMENTAL PROCEDURE.

Following backwash, one column was washed with 4 bed volumes of the acid fluoride solution at 190 ml. per minute or approximately 0.85 gal. per sq.ft. per minute. The control column received 4 bed volumes of water wash. This procedure was operated for a total of 13 cycles.

Samples of the fluoride wash solution were assayed for silica after each cycle and the resin in each column was sampled and assayed for silica at the end of the run.

9. RESULTS.

At the end of the run, the resin which had received the fluoride wash in each cycle appeared to be very much cleaner than that in the control column.

The silica contents of both resins at the end of the run are shown below. The resin samples were dried at 110°C and the silica content expressed as a percentage of the dry resin.

| Resin Sample | $SiO_2$ per cent |
|---|---|
| Control | 9.32 |
| Fluoride washed | 0.99 |

The silica content of the wash solutions after each cycle is shown in Table 5.

TABLE 5.

| Adsorption liquor | Fluoride Wash No. | $SiO_2$ in fluoride Wash g/l. |
|---|---|---|
| Sample A | 1 | 0.38 |
| " | 2 | - |
| " | 3 | 1.04 |
| " | 4 | 0.78 |
| " | 5 | 0.71 |
| " | 6 | 0.86 |
| " | 7 | 0.87 |
| Sample B | 8 | 0.74 |
| " | 9 | 0.70 |
| " | 10 | 0.55 |
| " | 11 | 0.72 |
| " | 12 | 0.53 |
| " | 13 | 0.41 |

From the results in Table 5 the total amount of silica removed from the resin by the fluoride wash was 226 g. Allowing for the approximation in assigning an average assay value to the unknown sample (number 2) and an assumed S.G. 0.344 for the dry resin, this total silica is in reasonable agreement with the amount of 202 g. calculated as being on the control resin. Moreover the 226 grams of silica obtained from the test resin was removed with approximately 90 per cent efficiency with respect to the fluoride used. The theoretical quantity of silica which could have been removed as $SiF_6^=$ is 252 grams.

10. DISCUSSION.

The results of the laboratory investigation indicate that a cyclic wash with five bed volumes of a solution 0.5

molar in sulphuric acid and 0.05 molar in ammonium bifluoride adequately prevented accumulation of silica on the resin.

This is substantiated by the pilot scale results and the procedure appears more attractive than resin regeneration by sodium hydroxide for the reason that the resin is maintained in an acid circuit, thereby eliminating possible resin contamination by insoluble hydroxides. The use of the fluoride wash did not significantly increase the fluoride content of the uranium products recovered from the eluates.

11. REFERENCES.

(1) **Audric**, B.N.; Bryant, J.W.; and Long, I.V.P. C.R.L./AE.107 D.S.I.R. England.