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THE REMOVAL OF SILICA FROM PLUTONIUM
PROCESSING ANION EXCHANGE RESIN
BY CAUSTIC WASH

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
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U.S. ATOMIC ENERGY COMMISSION
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Robert P. DeGrazio

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ADDENDUM

The Removal of Silica from Plutonium Processing Anion Exchange Resin by Caustic Wash

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The following additions should be made as indicated:

Page 3: Column 2, after 2nd paragraph add the following section:

Potential Hazards for Large Scale Operations:

In converting the resin to the nitrate form from the hydroxyl form on laboratory-scale quantities (i.e., 158 grams resin), no increase in column temperature was detected. However, on large scale quantities (i.e., 4-inch-diameter columns) exothermic reactions could occur that could lead to column pressurization.⁸⁻¹⁰ Care should be taken to ensure complete nitration of the resin with 0.35M HNO₃ before reconditioning the resin with 7M HNO₃. The time required for complete nitration of the resin is based on the reaction of the particular type of anion exchange used.¹¹

Page 3: Column 2, 3rd paragraph, include the following references:

8. W. J. Van Slyke, G. Jansen, Jr., and W. H. Swift, "Thermal Effects in Anion Exchange Resin-Nitric Acid Systems," BNWL-114, August 1968.
9. H. T. Fullam, "Thermal Stability of Nitrate Form Anion Resins in a Vented System," RL-SEP-826, December, 1965.
10. F. Helfferich, "Ion-Exchange," McGraw-Hill Book Company, Inc., New York, pp 488-489, 1962.
11. W. J. Van Slyke, "Final Report of Chemical Safety for Technetium-99 Recovery by Anion Exchange," BNWL-476, January, 1967.

The Removal of Silica from Plutonium Processing Anion Exchange Resin by Caustic Wash

Robert P. DeGrazio

Abstract. DOWEX® 1 anion exchange resin is used for the recovery and purification of plutonium from nitrate solutions. The resin is plugged with silica (SiO_2) preventing efficient processing of the plutonium. An experiment is described for the removal of silicon dioxide from the anion exchange resin.

SUMMARY AND CONCLUSIONS

Ion exchange is routinely used at Rocky Flats in the recovery and purification of plutonium. Silica (SiO_2) is present in certain plutonium recovery streams and is adsorbed rapidly on anion resin columns. Consequently, the resin columns are plugged, preventing efficient processing of the plutonium. Replacement of the resin is usually required every 1 to 3 months.

Experiments were conducted on a laboratory scale to determine the feasibility and effectiveness of removing silica from anion exchange resins with a sodium hydroxide wash.

The results indicate that the procedure developed will effectively remove the silica and considerably increase the operational lifetime of the resin. The washing procedure is simple, safe and effective. Data show that approximately 99% of the adsorbed silica is removed. The concentration of plutonium in the caustic waste solution was below discard level, and therefore, did not require additional processing.

INTRODUCTION

Ion exchange is used at Rocky Flats in the recovery and purification of plutonium from nitrate solutions. Plutonium nitrate feed contains many impurities. Silica (SiO_2) is a major impurity in the feed and will rapidly plug columns containing DOWEX® 1 anion exchange resin, resulting in a decrease in feed throughput. Consequently, the resin must be replaced every 1 to 3 months. This condition is economically undesirable. The lifetime of the resin will be increased and column downtime decreased if silica can be removed from the resin bed without destroying the ion-exchange properties.

To prevent silica and other impurities from reaching the ion columns, the feed solutions are filtered using both gravity and pressure type filters. These filters are rated to remove particles greater than 3 microns. Silica, however, is found in process lines, process tanks, and the ion-exchange columns located downstream of the filters. This indicates that the filters are not stopping the silica impurity. Two reasons are suggested: (1) silica (at least in part) is in the sub-micron range, and (2) the silica is present in the feed solutions as a species other than SiO_2 . Investigations have shown that both hypotheses are valid. Infrared spectrophotometric analyses of plutonium feed solutions show the presence of the hydrofluosilicic acid ion (SiF_6^-).¹ A microscopic analysis of the feed used in this study showed that silica is present in sub-micron size particles.

During the acid leaching of plutonium-containing residues, the SiF_6^- ion is probably converted to silicon tetrafluoride gas and hydrofluosilicic acid² which is carried downstream and hydrolyzed elsewhere in the system, forming colloidal, sub-micron silica particles. This form of silica probably accumulates and grows into large silica polymers on the ion-exchange resins and thus eventually plugs them.

Ion column experiments were performed on a laboratory scale to develop a procedure for the removal of silica from DOWEX® 1 Resin. The procedure is similar to that used in the uranium ore processing industry,³ but was modified to plutonium production conditions.

Initial investigations were performed using synthetic feed solutions which contained no plutonium. This was to determine if degradation of the resin occurs when it is in contact with caustic solution under pressure. Other experiments were carried out with feed solutions containing plutonium.

EXPERIMENTAL

Non-Plutonium Experiments

Initially, the ion-column experiments were conducted with silica solutions which did not contain plutonium.

The purpose of these experiments was to determine the effects of caustic on the resin when the resin was subjected to pressure.

A glass column having dimensions of 12 in. by 1 in. and a sintered glass frit at the base to contain the resin was used. The column contained DOWEX® 1-X4, 50-80 mesh Resin in nitrate form except when treated with caustic solution. Pressurizing the system was accomplished by pumping the feed solution through a closed system. Pressures were regulated with a valving system and measured with pressure gages. The operating parameters used in this system are listed in Table I.

TABLE I. Operating Parameters of Pressurized System.

Resin: 158 grams dry DOWEX® 1-X4, 50-80 mesh Resin, nitrate form
 Temperature of Resin: 50°C
 Inlet Pressure: 35 psig
 Flow Rate: 100 liters/hour
 Feed: 7M HNO₃ containing silica, aluminum nitrate, and calcium fluoride

FIGURE 1. Ion-Exchange System.

Silica Preparation

Solutions of silica were prepared by dissolving sodium silicate in water and adjusting to 7M HNO₃. At this acid molarity, silicon dioxide is precipitated. The total silica concentration, reported as SiO₂, was determined by a modified emission spectroscopic method.⁴ The size of the silica particles was measured by diffraction microscopy and averaged between 1 and 5 microns.

Plutonium Experiments

Production plutonium feed solutions consisting of leached incinerator ash were used as a source for both silica and plutonium. One ash-feed assayed at 18 g/l Pu per liter with a silica content of greater than 20 mg/l. In these experiments a nonpressurized system was used. The feed solution was circulated through a column containing DOWEX® 1 Resin using a tube pump as shown in Figure 1. The feed was pumped from a beaker to the top of the resin column at a rate of 12 liters/hour.

It was allowed to circulate through the resin column for 30 minutes and at the completion of this loading cycle, the column effluent was analyzed for silica and plutonium. In another experiment, 400 ml of plutonium

feed, assaying at 18 g/l Pu in 7M HNO₃, 4 g/l fluoride ion and 20 mg/l SiO₂ were circulated through the resin bed for 30 minutes at a flow rate of 12 liters per hour. The feed was then allowed to remain in contact with the resin for 48 hours to promote silica growth (polymer formation) in the crosslinked polystyrene matrix. The resin was then washed with several column volumes of 7M HNO₃ until the SiO₂ in the effluent was at background level. The resin was then analyzed for silica.

Column Washing Procedure

After loading the resin column with silica, it was washed with caustic. The stepwise caustic wash procedure used is shown in Table II. This procedure was used for both the nonplutonium and plutonium containing experiments.

Analytical

After washing the columns, samples were taken of the untreated resin, the washed resin, and the feed and wash solutions. Silica content was determined by emission spectroscopy.

TABLE II. Procedure for Silica Removal from DOWEX® 1 Anion Exchange Resin.

1. Elute the plutonium from the resin with 0.35M HNO₃.
2. Air sparge the resin to remove any solid material that may likely cement the resin together when the caustic solution is added.
3. Neutralize the acid in the column by passing 3/4 column volume of 1 w/o NaOH through the resin bed.
4. Pass 3/4 column volume of 10 w/o NaOH through the bed to remove the silica contamination.
5. Neutralize the caustic by passing 3/4 column volume of 0.35M HNO₃ through the resin.
6. Recondition the resin to its nitrate form using 7M HNO₃.
7. Air sparge the column to remove any solids that may have been formed during acidification.
8. The column is now ready for the next plutonium loading cycle.

RESULTS AND DISCUSSION

Results from the non-plutonium, caustic wash experiments showed that: (1) no significant gassing occurred when converting the resin from an acidic to a basic form, (2) there was no temperature increase during this conversion, (3) there was no significant resin swelling when the resin was treated with caustic, and (4) there was no decrease in flow rate after repeating the caustic-acid cycle several times. However, degradation of the resin beads will occur if the temperature exceeds 50°C.⁵ These results indicate that no degradation of the resin occurs during the washing treatment. The washed resin should be nearly as effective for plutonium purification as new, unused resin.

Solutions from the dissolution of plutonium-containing incinerator ash originally contained 18 g/l Pu and greater than 20 mg/l silica. The solution, after circulation through the resin, contained 0.04 mg/l SiO₂ and 0.31 mg/l Pu indicating that the resin had retained both silica and plutonium.

Microscopic examinations of plugged resin clearly show that the beads are covered with a white substance identified as amorphous silica, and that the spaces between the packed beads were also filled with this same substance. Other investigators have determined that silica will also aggregate and precipitate within the resin bead itself.⁶

The results of the caustic wash are shown in Table III.

TABLE III. Silica Removal by Caustic Wash.

Exp. No.	Total SiO ₂ on Resin (g)	Total SiO ₂ on Resin after Caustic Wash (g)	SiO ₂ Removed (%)
1	2.447	0.024	98
2	0.895	0.009	99
3	0.480	0.010	98

After the caustic wash, the resin was analyzed for silica and found to be 0.01 mg/g resin. This amount was the same as the silica content in new resin. Microscopic examination showed that most of the amorphous silica had been removed. These results indicate that silica can be removed from the resin with the proposed wash treatment. Also, the plutonium concentrations in the caustic wash will be below the permissible discard level, and therefore, need not be reprocessed. The removal of approximately 98% of the silica will allow the previously plugged and non-adsorptive resin to be reused.

The method outlined for washing the resin columns and demonstrated with laboratory tests does not present any hazards. Others who have used similar washing treatments on anion resins also report no hazardous effects.⁷

ACKNOWLEDGMENTS

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