SEPARATION OF DAUGHTERS OF ^{232}U FROM ^{233}U BY ION EXCHANGE

Robert H. Rainey and Ralph G. Nicol

We have developed an ion exchange process which has been used to remove the daughters of ^{232}U from a solution of ^{233}U , thereby decreasing the gamma activity to a sufficiently low level that kilogram amounts of ^{233}U may be further processed in glove boxes without additional shielding. This process takes advantage of the fact that, under suitable conditions, the longer-lived daughters of ^{232}U are more strongly absorbed by Dowex 50W than is uranium. We are, therefore, able to pass a large amount of uranium through the resin bed before the ^{228}Th and ^{224}Ra can be detected in the effluent stream.

When thorium is irradiated in a nuclear reactor to produce ^{233}U , it becomes highly radioactive because of both ^{233}U fission products and ^{232}U daughters.

SLIDE 1

The ^{232}U results from an $(n, 2n)$ reaction of high-energy neutrons with the thorium. Since the reacting neutron must have an energy of at least 6.37 MeV, the amount of ^{232}U that is produced depends strongly on the irradiation conditions. The ^{233}U we are processing contains about 8 ppm of ^{232}U .

SLIDE 2

Uranium-233 is recovered from irradiated thorium by solvent extraction and is initially extremely pure, but the ^{232}U daughters grow back to an objectionable extent after a few weeks. As a result, the uranium must be reprocessed again shortly before fuel fabrication, to remove these gamma-emitting daughters of ^{232}U . The basis of the ion exchange separation for separating the ^{232}U daughters from ^{233}U may be seen by examining the decay scheme

of ^{232}U . The longer-lived members, 1.9-year ^{228}Th and 3.64-day ^{224}Ra , are first in the chain; whereas the sources of the penetrating radiation are the ^{212}Pb and especially the 2.6-MeV gamma from the ^{208}Tl . When thorium and radium are removed, the gamma-emitting daughters decay rapidly.

SLIDE 3

This slide shows the effect on the gamma activity level from the chain when all of the thorium and varying amounts of radium are removed from ^{232}U in equilibrium with its daughters. Our control point is at 2% of the activity that ^{233}U containing 8 ppm of ^{232}U would have at equilibrium with its daughters. Experience at ORNL has shown that, at this level, operators processing kilogram quantities of ^{233}U receive exposures that are low in comparison with current guidelines for occupational exposure. Our practice is to maintain exposures as low as is practical. This slide shows that these conditions can be met if, and only if, essentially all of both the thorium and radium are removed.

SLIDE 4

It has been known for a long time that thorium is strongly absorbed on cation exchange resin whereas the uranyl ion is relatively weakly held. The distribution coefficient of radium has not been reported in the literature; however, for preliminary planning, we assumed that it would be twice that of barium. On this slide you can see that the distribution coefficients of thorium and radium are much greater than that of uranyl ion and also that this difference increases with decreasing acidity. The numbers in parenthesis are the slopes of the lines. The separation of uranium from thorium increases by about a factor of 40 when the acid concentration is decreased from 1 M to 0.2 M.

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The literature indicates that there should also be an increase in separation as the cross-linkage of the resin is increased.

SLIDE 5

Our data have shown that radium is held more strongly on the resin and that there is a larger increase in the separation with increasing cross-linkage than had been estimated from the information in the literature. Under our operating conditions, the separation factors of radium and thorium from uranium have been about 75 and 650 respectively. These data were obtained by equilibrating different quantities of resin with our feed solution and measuring the decrease in concentrations of the various daughters. These distribution coefficients are for 50% adsorption of the isotopes on the resin.

SLIDE 6

This simplified flowsheet shows the process as it has been carried out in our plant. We use two resin columns in order to simplify the control of thorium. We are restricting the thorium to the first column (I), which is equipped with a radiation scanner to measure how far the thorium has progressed through the column. This column was designed for easy replacement if there is any indication that the thorium is nearing breakthrough or if failure occurs for other reasons. Part of the radium also absorbs on the first column. The second column (II) absorbs additional radium and is also a backup for thorium in case of unforeseen difficulty. The feed solution consists of 175 liters of dilute nitric acid containing about 120 g of uranium and less than 0.1 g of thorium per liter. The solution is filtered and then passed via an upflow mode through the first column and downflow through the second. The flow of solution is continued until the radium just starts to break through the second column. The resin is then reconditioned by eluting nearly all of the uranium and radium and about half of the thorium. The elution is carried out via downflow

through each column. The eluate contains about 7% of the total uranium and is recycled to the solvent extraction plant for recovery.

The adsorption and elution times of the process are decreased by using 200- to 400-mesh resin and a rapid flow rate. The pressure drops across the columns are directly proportional to the volumetric flow rate and the length of the column, and inversely proportional to the cross-sectional area. The pressure of 100 psi, which is required to give a feed flow of 1 liter/min also has advantages in that it prevents an accumulation of gas in the resin and almost completely eliminates channeling through the bed. The rate of removal of the thorium was improved by eluting at 60°C. An elution procedure which gives much more complete removal of the thorium by using an acetate eluent has been developed. However, this process was not included in the routine operation because of concern that an accidental mixing of acetate with the feed would result in process failure. We have, nevertheless, demonstrated the acetate elution by removing 99% of the thorium remaining on the columns in the plant after completion of the processing to be described later.

A new column design has been used to simplify the backflow elution. In this design, the column is nearly completely filled with resin and is equipped with stainless steel frits at each end. At the high pressure drops we are using, the bed slides up and down the column as a cylinder and there is no mixing of the resin.

SLIDE 7

We have now made three plant runs using the equipment shown on this slide. The resin columns are 18 and 24 in. long. Except for the tankage, this is all of the equipment required to process 17.5 kg of uranium in about 17 hr. Those of you who are familiar with the size and complexity of an equivalent solvent extraction plant will appreciate the difference.

The three runs were increasingly severe tests of the flowsheet. In the first run, we processed 17.5 kg of ^{233}U containing 10 ppm of thorium. In the second, we processed 15 kg of uranium containing 1000 ppm of thorium; the third run consisted of 17.5 kg of uranium containing 1000 ppm of thorium. The age of the feed solutions varied from 9 months to 1-1/2 years. The conditions for the third run were the maximum required for our program. Operations went smoothly, and the operators were pleased with the process.

SLIDE 8

The products from the three runs were essentially identical. Each product was collected in two tanks. The first solution contained less ^{212}Pb ; therefore, it was initially somewhat less radioactive than the later material. During the first 3 days the activity of each product batch decayed with about the 10-hr half-life of the ^{212}Pb until it reached a level of about 0.1% of the activity that it would have at equilibrium with the daughters of ^{232}U . After the third day, the activity was not appreciably different from what it would have been if all of the daughters of ^{232}U had been removed, e.g., by solvent extraction. The activity then starts increasing due to the regrowth of the whole chain. The activity of the product was less than the 2% value required from the 2nd to the 25th day. Our schedule calls for converting the nitrate to the oxide during the 3rd to the 10th day. During this period, the activity was less than 0.5% of the equilibrium value.

The development of this ion exchange process adds additional flexibility to our processing of thorium and ^{233}U . The Thorex Process is used to recover both thorium and uranium from irradiated thorium fuels. Solvent extraction with di-sec-butylphenyl phosphonate is used to extract uranium from large amounts of thorium, leaving the thorium in the aqueous phase. Previously, whenever ^{233}U needed to be separated from its daughters, it was reprocessed by one of these methods. Now we have a much more simple ion exchange process for separating uranium from these daughters as well as certain other impurities.

SLIDE #1

SLIDE #2

DECAY SCHEME OF URANIUM-232

multiplied by year $mg-2.32 \times 10^{-11}$
 Radiation dose rate of 1 Foot (multiplied by $mg-2.32 \times 10^{-11}$)

ORNL DWG 71-3080 RI

Figure 3

#7

Sheet 5

Figure 5

ORNL-DWG 70-4366

#-8

- FEED 5.5%
- FIRST 10 kg ACCUM. ^{233}U PRODUCT
- x FINAL 7.5 kg ACCUM. ^{233}U PRODUCT
- + CALCULATED GROWTH CURVE WITH ALL DAUGHTERS REMOVED
- SAFE GLOVE-BOX OPERATION, MAXIMUM LIMIT.

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