LABORATORY DEVELOPMENT OF THE GRIND-LEACH PROCESS FOR THE H.T.G.C.R. FUEL CYCLE

PART 4. LEACHING AND DISSOLUTION OF BERYLLIA BASED FUELS

by

M. E. SHYING
E. J. LEE
M. S. FARRELL

July 1967
LABORATORY DEVELOPMENT OF THE GRIND–LEACH PROCESS
FOR THE H.T.G.C.R. FUEL CYCLE

PART 4. LEACHING AND DISSOLUTION OF BERYLLIA BASED FUELS

by

M. E. SHYING
E. J. LEE
M. S. FARRELL

ABSTRACT

This report covers the chemical development of an acid-leach head-end process for the separation of (U,Th)O₂ from a beryllia matrix. The work is related to a feasibility study of the H.G.T.C.R. fuel cycle.

Although more than 99 per cent of the actinides can be recovered in a single batch nitric acid leach, more than 30 per cent of the beryllia is dissolved. When it was found that sulphuric acid selectively dissolved the beryllia, a two-step process using nitric and sulphuric acids in sequence was developed, with recycling of the actinide-rich heap to the next batch. Preliminary results from multi-batch experiments indicate that it might be possible to decrease the beryllia loss to the nitrate stream to 10 per cent and still recover 99 per cent of the actinides. Further development of the process would involve the use of proven reactor material irradiated to high burn-up. Suggestions for further research are given.
PREFACE

The following list details a series of reports dealing with the fuel cycle of the High Temperature Gas Cooled Reactor. This report (AAEC/E180) is the fourth of the first group of reports dealing with the Laboratory Development of the Grind-Leach Process for the H.T.G.C.R. Fuel Cycle.

Laboratory Development of the Grind-Leach Process for the H.T.G.C.R. Fuel Cycle


Part 4. Leaching and Dissolution of Beryllia-Based Fuels, by M.E. Shying, E.J. Lee and M.S. Farrell. AAEC/E180.

Development of Solvent Extraction Processes for the H.T.G.C.R. Fuel Cycle


Economics of the H.T.G.C.R. Fuel Cycle


CONTENTS

1. INTRODUCTION

2. EXPERIMENTAL
   2.1 Materials and Reagents
   2.2 Apparatus
   2.3 Procedure
      2.3.1 Leaching
      2.3.2 Residue dissolution
      2.3.3 Mass balances
      2.3.4 Multi-batch Processing

3. RESULTS AND DISCUSSION
   3.1 Single Batch Leaching
      3.1.1 Mass balances and recoveries
      3.1.2 Effect of leaching time
      3.1.3 Effect of reagent concentrations
      3.1.4 Effect of silica
      3.1.5 Effect of particle size
   3.2 Beryllia Residue Dissolution
   3.3 Multi-batch Processing
      3.3.1 Chemical flow sheet for a composite leaching process
      3.3.2 Multi-batch processing of unirradiated oxides
      3.3.3 Multi-batch processing of irradiated oxides

4. CONCLUSIONS

5. RECOMMENDATIONS

6. ACKNOWLEDGEMENTS

7. REFERENCES

Table 1 Sieve Analysis for Comminuted 1:20:2000 (U, Th)O₂ Fuelled Beryllia
Table 2 Single Batch Leaching of 1:20:450 Fuel – Mass Balances and Recoveries
Table 3 Single Batch Leaching of 1:20:2000 Fuel – Effect of Leaching Conditions on Recoveries
Table 4 Single Batch Leaching of 1:20:2000 Fuel – Mass Balances
Table 5 Effect of Extreme Leaching Times on Recoveries
Table 6 Effect of Maximum Particle Size on Leaching
Table 7 Sulphuric Acid Dissolution of 1:20:2000 Fuel – Effect of Average Particle Size on Recoveries
Table 8 Sulphuric Acid Dissolution of Leach Residues
Table 9 Multi-batch Processing of Unirradiated 1:20:2000 Fuel – The Distribution of Elements for Each Cycle

(continued)

Table 11 Decontamination of Beryllium Sulphate from Uranium and Thorium by Crystallisation of the Tetrahydrate

Table 12 Multi-batch Processing of Irradiated 1:20:2000 Fuel – Distribution of Elements in Each Cycle

Table 13 Multi-batch Processing of Irradiated 1:20:2000 Fuel – Mass Balances and Final Distribution in Each Stream

Table 14 Relative Release of Fission Products During Nitric Acid Leaching

Table 15 Distribution of Fission Products in Nitrate and Sulphate Streams

Figure 1 Fuel Cycle for the H.T.G.C. Reactor Using a Beryllia-based Dispersion-type Fuel.

Figure 2 Dissolution Curves for (U,Th)O₂ and BeO in Single Batch Leach. Penalty of Beryllia Dissolution as Actinides are Released.

Figure 3 Dissolution Curves for (U,Th)O₂ and BeO in Single Batch Leach. Effect of Low Nitric Acid and Fluoride Concentrations.

Figure 4 Dissolution Curves for (U,Th)O₂ and BeO in Single Batch Leach. Effect of High Nitric Acid Concentration.

Figure 5 Dissolution Curves for (U,Th)O₂ and BeO in Single Batch Leach. Effect of Silica.

Figure 6 Dissolution Curves for (U,Th)O₂ and BeO in Single Batch Leach. Effect of Removal of Fines Less than 53μ.

Figure 7 Dissolution Rates of Thoria and Beryllia in Nitric Acid Leach Solutions. Effect of Acid and Fluoride Concentrations.

Figure 8 Photomicrographs of Comminuted 1:20:450 Composition Fuel.

Figure 9 Tentative Flow Sheet for a Multi-batch Process Using both Nitric and Sulphuric Acids as Selective Leachants: The Composite Process.
1. **INTRODUCTION**

Smith (1964) has described the fuel used by the A.A.E.C. in its feasibility study of the H.T.G.C.R. system. This fuel consists of a mixture of actinide oxides in a beryllia matrix, fuel particle size being 150–200 μ.

The reprocessing of this beryllia matrix fuel has been discussed by Cairns (1964). He suggested an aqueous fuel cycle using a grind-leach head-end process to obtain dissolution of the actinide oxides with maximum separation of the less readily dissolved beryllia. Figure 1 illustrates the conceptual fuel cycle proposed. A more general description of the head-end process is given in the first report of this series (Farrell and Isaacs 1965) which deals with the dissolution of (U, Th)O₂ fuel particles in nitric acid solutions. A second report concerns the dissolution of comminuted sintered beryllia in nitric acid solutions (Farrell, Isaacs and Shying 1966), while a third report (Baillie and Hubery 1966) outlines the results of a study of the comminution of the fuelled beryllia.

This report, the fourth in the series, summarises the results of a laboratory development of the leaching process whereby the fissile and fertile components are selectively dissolved from the comminuted fuelled beryllia with nitric acid fluoride leachants. Preliminary results on the dissolution of the beryllia residue in sulphuric acid indicate that sulphuric acid will preferentially dissolve the beryllia from the thorium-based fuel.

Unirradiated material was used throughout except for a few experiments with irradiated fuel to determine fission product behaviour.

2. **EXPERIMENTAL**

2.1 **Materials and Reagents**

Brush UOX-grade beryllia, mixed with (U, Th)O₂ fuel particles and ethyl alcohol, was pressed hydrostatically at 20 t.s.i.; the compacts were then sintered at 1500°C for either 2 hours under vacuum or 4 hours in nitrogen. The fuel particles were prepared as described by Farrell and Isaacs (1965) and had an average particle size of 180 μ, with a U:Th atomic ratio of 1:20, the UO₂ being in solid solution in the ThO₂.

The fuelled beryllia used had U:Th:Be atomic ratios of 1:20:450 and 1:20:2000 and respective bulk densities of 3.62 to 3.71 g cm⁻³ and 3.02 to 3.08 g cm⁻³. The more concentrated fuel was used only in preliminary experiments. The fuelled beryllia was in the form of bars (0.25 x 1.0 x 6.0 inch), except for the experiments with irradiated material in which rods 0.375 in. diameter and 4 in. long were used. In these rods U235 replaced the natural uranium used in the bars. The rods were irradiated in the A.A.E.C. high flux materials-test reactor, HIFAR. Irradiation was taken to 1 per cent fission burn-up in thermal neutron fluxes of 1.5 x 10¹⁸ n cm⁻² sec⁻¹ and the rods were subsequently cooled for 18 months.

Both unirradiated and irradiated * oxides were manually crushed in a percussion mortar until all material was less than the chosen maximum sieve size for the leaching experiment. A high load was used in the mortar and the mortar frequently recycled through the sieve to minimise the production of fines. Care was taken to avoid differential losses of the oxides present, but there was a tendency for electrostatic forces to cause the preferential removal of the lighter beryllia.

For some of the leaching experiments (Section 3.3), fuelled beryllia was comminuted using a vibratory stainless steel ball-mill, after preliminary hand-crushing. It was then sieved through a three-deck gyratory unit, the oversized material being recycled to the mill. The details of this procedure and the equipment are contained in the report by Baillie and Hubery (1966) on the development of the comminution process for this fuel. Typical sieve analyses are given in Table 1.

Reagents used in the leaching and dissolution processes were of analytical grade except for the aluminium nitrate which was of laboratory grade.

* Using manipulators in a hot-cell.
2.2 Apparatus

In the single batch nitric acid leaching experiments a stainless steel dissolver was normally used. It was of the same design as that previously used by Ekstrom et al. (1962) but larger (500 ml capacity), and since powdered samples were used, it was fitted with a four-bladed agitator. The residue was transferred to Pyrex glass equipment for dissolution in sulphuric acid.

Electrical resistance heating was used and the temperature controlled to within ±1°C.

The multi-batch leaching and dissolution experiments used all-purpose glass equipment. Experiments with irradiated material were performed behind 4-inch thick lead walls in a glove box, tongs being used only for the essential manipulative tasks as wherever possible all operations were made automatic. For example, all liquid transfers were by vacuum and product solutions could be accurately made-up to volume, agitated and sampled remotely for analysis.

2.3 Procedure

2.3.1 Leaching

The known mass of comminuted mixed oxide sample was added to a chosen volume of nitric acid fluoride solution of known concentration, and the slurry preheated to the required temperature and stirred at a constant speed (400 rev/min).

When reaction rates were being determined, the agitator was stopped and one minute allowed for the solids to settle before samples of the solution were withdrawn at time intervals chosen according to the expected dissolution rates. The samples were centrifuged to remove any fine solids and the supernate was analysed for beryllium, thorium and uranium, using colorimetric methods, with chrome-azurol-S (Cerrai and Testa 1962), thoronol (Thomason et al. 1949) and P.A.R. (Florence and Farrar 1963), respectively.

At the end of the leach, the reaction was stopped by turning off the heater and adding chilled distilled water. After the solids had settled the supernate was removed by suction through a filter-stick and the residue washed several times with distilled water. The washings were removed with the filter-stick and combined with the original supernate. The combined and known volume was equilibrated to 25°C and samples taken for analysis. To obtain accurate mass balances the beryllium was determined to ±1 per cent, the thorium to ±0.5 per cent, and the uranium to ±0.1 per cent. For beryllium and thorium a colorimetric method was sufficiently accurate, but for the uranium it was necessary to use a differential cathode ray polarographic method. Stainless steel sieves were used in place of the usual brass ones because copper interferes with this analysis.

Rates were calculated for each component by determining the mass dissolved (corrected for sample losses) per unit time interval. A plot of mass dissolved versus time gave a dissolution curve for each component oxide. As previously shown by Farrell and Isaacs (1965) the rate of dissolution of the thorium controlled the rate of dissolution of the urania, so that generally the thorium dissolution curve was accepted as the fuel particle dissolution curve.

2.3.2 Residue dissolution

When a stainless steel vessel had been used for leaching, the beryllia residue was transferred to glass equipment and was dissolved in sulphuric acid solution. The resulting beryllium sulphate sulphuric acid solution was diluted carefully with distilled water at the end of the reaction period. Dilution is necessary to prevent crystallisation of the dihydrate(\(\text{BeSO}_4\cdot2\text{H}_2\text{O}\)) which will set and is then very difficult to dissolve.

The beryllium sulphate solution made up to a known volume and containing small quantities of uranium, thorium and fission product sulphates was then sampled for analysis at 25°C.

For mass balances the analytical control for beryllium in the sulphate solution was required to ±1 per cent, but for the minor components ±5 per cent normally sufficed. Fission products were determined using a 256 channel gamma pulse height analyser.
Often after dissolution of the beryllia there remained a heel of (U,Th)O₂ rich oxides. This heel was dissolved by repeated contact with nitric acid fluoride solutions. The resulting solutions were also made up to volume and analysed.

2.3.3 Mass balances

Mass balances for the grind-leach process were calculated on the component analyses and volumes of the final bulk solutions, allowing when necessary for volumes and component concentrations of samples removed during rate experiments. The total mass of each component in the nitrate and sulphate stream was calculated and became the output figure for the component in the overall process. The input figure was taken as the actual mass of each oxide precision-weighed into each piece of fuel during its manufacture after correcting the mass for fabrication and comminution losses. A proportional loss was assumed for each component. The mass balance was expressed as a percentage output over input.

2.3.4 Multi-batch processing

In these experiments the above procedures were applied to a sequence of several batches of material. To do this, comminuted material was produced, and by use of a splitter the powder was divided up into either 4 or 8 equal sized batches.

After leaching of the first of these batches with nitric acid, the residue was washed and then leached with sulphuric acid. After washing the sulphuric acid leach residue, the second batch of comminuted oxide was added and the process repeated.

A complete mass balance can be obtained only over the whole multi-batch experiment, after a final exhaustive heel dissolution.

3. RESULTS AND DISCUSSION

3.1 Single Batch Leaching

3.1.1 Mass balances and recoveries

Six batches of 1:20:450 composition material, after comminution to various maximum particle sizes, were leached in 13.0M nitric acid containing 0.05M fluoride and 0.1M aluminium, the mixture being agitated for six hours in a stainless steel vessel at 115°C. The results (Table 2) show that in all cases the mass balances for UO₂, ThO₂ and BeO were acceptable and the dissolution of UO₂ and ThO₂ was almost complete. The apparent loss of beryllia is probably caused by the selective electrostatic removal of light beryllia ultra-fines during comminution (Section 2.1) above. In this set of experiments it became obvious that the (U,Th)O₂ component could be readily dissolved, and provided that sufficient exposure of the (U,Th)O₂ could be obtained during comminution, this could be done quantitatively. However, the loss of BeO to the nitric acid was high, ranging from 50 to 90 per cent, the greatest losses occurring with the material of finer particle sizes.

Similarly, from Tables 3 and 4, it is evident that with the more dilute fuel (1:20:2000) mass balances are acceptable and that the amount of (U,Th)O₂ dissolved is high, provided suitable leaching conditions are used. However, for practical recoveries of (U,Th)O₂ (> 90 per cent) under optimum conditions, more than 20 per cent of beryllia was lost to the nitric acid.

3.1.2 Effect of leaching time

A series of leaching experiments to determine the effect and interaction of each variable (reagent concentration, increasing product concentration, temperature, agitation, particle size and particle size distribution) appeared impracticable. Hence a series of leaching experiments to test only selected variables was devised. Initially dissolution conditions were chosen from basic data on the dissolution of (U,Th)O₂ (Farrell and Isaacs 1965) and BeO (Farrell, Isaacs and Shying 1966) in nitric acid. The consequent separation (Figure 2) was used for comparison to determine the effects of acid concentrations (Figures 3 and 4), silica (Figure 5) and fines (Figure 6).
Figure 7 shows the dissolution rates for (U,Th)O₂ and BeO in each run. These rates were calculated by comparing the mass of each component dissolved with the average mass present over the time interval considered. Under all conditions investigated the difference between the dissolution rates decreased as the leach proceeded.

Run 9 (Figure 5) was found to give optimum separation of (U,Th)O₂ from the matrix. Here 95 per cent of the (U,Th)O₂ was dissolved in approximately 100 minutes and at least 200 minutes was required to dissolve 99 per cent. In the time interval 100 to 200 minutes the amount of beryllia dissolved increased from 12 to 20 per cent. Leaching time must therefore be a compromise, so that actinide extraction and beryllia loss are kept at acceptable levels.

The results of long and short leach times (Table 5) illustrate the limits of the separations that can be achieved under the selected leaching conditions. For an exhaustive removal of the actinides (360 minute leach), 32 per cent of the beryllia dissolved, while for a 15 minute leach there was an 88 per cent dissolution of the (U,Th)O₂ with only an 11 per cent dissolution of beryllia.

These results suggest that 10 per cent beryllia is the smallest possible loss if there is to be a reasonable actinide separation, whereas for a complete recovery of the (U,Th)O₂, beryllia loss will be approximately 30 per cent. The conditions used in the nitric acid leaching were otherwise identical except for time and were the optimum conditions based on the results of Run 9.

3.1.3 Effect of reagent concentrations

The major reagents are nitric acid and hydrogen fluoride which is necessary to catalyse the dissolution of the thorium (Bond 1958). Aluminium is added to decrease the corrosion of the stainless steel equipment, but as shown by Farrell and Isaacs (1965) aluminium will also complex with the fluoride and tend to partially inhibit dissolution of the thorium. Beryllium and thorium going into solution will also complex with the fluoride and inhibit dissolution but this effect is relatively minor early in the leaching (Farrell and Isaacs 1965).

The results, Table 3, and Figures 2 to 6 inclusive, demonstrate that optimum conditions for leaching are obtained with the highest practical mole ratio of acid to total oxide used. This is obtained with a high acid concentration (15M), high acid volume to oxide mass ratio, and a fixed maximum fluoride concentration of 0.05M (Bond 1958). The larger reagent volumes also permit a higher initial total amount of fluoride, which will prevent an early "complexing-out" of the fluoride catalyst.

The inference from the data obtained is that a continuous leaching process may achieve a significantly greater separation of the actinides from the beryllia, by keeping the (U,Th)O₂ dissolution curve more linear. Nevertheless the dissolution rate curves (Figure 7) show that the BeO rate tends also to decrease with time. This is possibly caused more by the effect of decreasing fluoride activity than by a depletion of surface area. (The effect of particle size is discussed below).

3.1.4 Effect of silica

To avoid transfers it would be convenient to use Pyrex glass vessels for leaching. The effect of silica on the fluoride-catalysed dissolution of the thorium was therefore investigated. Silica reacts with hydrofluoric acid to form fluorosilicic acid which exists as a mixture of ions in solution (Rys 1956) as follows:

$$2HF \rightleftharpoons 2H^+ + 2F^-,$$

$$2F^- + SiF_4(s) \rightleftharpoons SiF_6^{2-},$$

$$2HF + SiF_4(s) \rightleftharpoons 2H^+ + SiF_6^{2-}.$$  

In the strong acid solution (15M) at high temperature (115 °C) it is possible that some or all of the fluoride could be displaced from the solution as volatile SiF₆. Babko and Shimadina (1959) have shown that silica forms weaker complexes than does aluminium or thorium.
With nitrogen gas agitation being used to enhance any loss of this type, a batch was leached in glass under conditions similar to a leach performed in a stainless steel vessel with mechanical agitation and 0.1M aluminium present. The results of the two leachings (Figures 4 and 5) indicate that the presence of silica dissolved from the Pyrex glass causes no deterioration in leaching behaviour.

### 3.1.5 Effect of particle size

As the maximum particle size of the comminuted fuel increases, there is a decrease in the amount of each component (BeO and (U,Th)O₂) dissolved in a given leaching time (Table 6). This is caused by the decrease in specific surface area. Comminuted beryllia has been shown by Farrell, Isaacs and Shing (1966) to have a proportionally increasing surface area (as determined by B.E.T.-K.R.a) for decreasing particle size. The same effect could be expected of the (U,Th)O₂ component. However the ratio of (U,Th)O₂ to dissolved BeO was highest with the batch of largest maximum particle size (500μ). Although finer particles give higher absolute dissolution rates they do not give greater separation under these conditions. Also leaching times become too short to be controlled and therefore impracticable.

Another important effect is the degree of fuel particle exposure. If beryllia has to be dissolved before the (U,Th)O₂ fuel particles become exposed to the leachant, this will tend to prevent a good separation by leaching. Photo-micrographs (Figure 8) illustrate the degree of fuel particle exposure attained, and show that there is very little evidence of fuel particle inclusion in the beryllia fragments. It appears from the photo-micrographs that the fuel particles preferentially break. Baillie and Hubery (1966) have shown that vibratory-milled fuelled beryllia, when sieved into fractions, contains a higher concentration of (U,Th)O₂ in the finer fractions, confirming that the fuel particles are more readily abraded.

During nitric acid leaching the ratio of (U,Th)O₂ to beryllia dissolved varies as a function of maximum particle size (Table 6). The results in this table imply that there is a change in the relative surface areas of the two components as grinding proceeds. With the material used, grinding to a maximum particle size of 500μ gave the highest yield of (U,Th)O₂ for the smallest loss of beryllia to the leachant.

In Run 7 (Figure 6), the fines (less than 53μ in size) were removed physically before leaching. The results were less favourable compared with Runs 8 and 9, since there was a smaller amount of (U,Th)O₂ dissolved for beryllia lost to the leachant. This confirms the effect of differing behaviour of the (U,Th)O₂ and BeO in the comminution process.

The physical nature of both fuel particles and matrix is very important; any changes will affect the comminution process, and in turn this may have a major effect on the leaching process. A more detailed study of the effect that changes in the physical properties of the fuelled beryllia and the comminution process variables have on leaching is required. The present study is limited to the two types of material used and the manner in which it was prepared for leaching.

### 3.2 Beryllia Residue Dissolution

Beryllia is readily soluble in boiling sulphuric acid. Using massive beryllia specimens, Ekstrom et al. (1962) and Warren et al. (1962) showed that the dissolution rate is of the order 1 mg cm⁻¹ min⁻¹. With comminuted high density beryllia in the size range from 295μ to 211μ dissolution rates of 40 mg min⁻¹ g⁻¹ were obtained in preliminary experiments with 10M H₂SO₄ at 140°C. This concentration was found to give the highest rate of dissolution and above 10M the dissolution rate decreased significantly. With 18M H₂SO₄ there was negligible dissolution. The reaction rate was temperature-dependent with an apparent activation energy of 29 kcal/mole.

In the leach residue there are small quantities of unleached UO₂ and ThO₂. It is important to know how these oxides behave in the residue dissolution step. Selecting 10M H₂SO₄ as the residue dissolver, batches of comminuted fuelled beryllia of varying average particle size were digested for a given period, and the results (Table 7) show that the beryllia is selectively dissolved. Note that these particular batches were not leached with nitric acid before being digested with
sulphuric acid. There is direct evidence in this table that uranium was leached from the \((U, Th)\)O\(_2\) fuel particles, so any \((U, Th)\)O\(_2\) remaining in the UO\(_2\) residue will be selectively removed, for example with the \(-52 + 72\) BSS fraction 81 per cent of the BeO dissolved but only 0.4 per cent of the ThO\(_2\) and 4.5 per cent of the UO\(_2\).

These results (Table 7) and actual residue dissolutions (Table 8) illustrate that sulphuric acid preferentially dissolves the beryllia, thus behaving in the reverse manner to nitric acid/fluoride solution. A more selective head-end process may be possible, combining the differential but reciprocal effects of both the nitric acid fluoride and the sulphuric acid in a two-step leaching process.

One other interesting feature of the residue dissolution experiment was the solubility of the beryllia. Generally beryllium concentration rose from zero to about 8.0M during the batch dissolution, the sulphuric acid concentration decreasing. Normally an 80 per cent dissolution of the beryllia could be expected in this (Table 8). Biermann (1963) found that beryllia will dissolve in aqueous solutions of its own salts and the effect noticed in the residue dissolution experiments is an example of this behaviour.

Some difficulty was experienced in handling the concentrated beryllium sulphate solutions as they began to crystallize upon cooling. Apparently in some cases the dihydrate \((Be\)SO\(_4\),2\(H_2\)O) formed as a crystalline mass. This was very difficult to dissolve in water or sulphuric acid. Immediate addition of sufficient water at the end of the reaction period prevented the formation of the dihydrate.

3.3 Multi-batch Processing

3.3.1 Chemical flow sheet for a composite leaching process

From the results of the experiments with unirradiated material it is considered unlikely that one can develop a satisfactory single batch leaching process to obtain 99 per cent. of the fissile component in solution with less than 20 per cent. of the beryllia. It seems impossible to decrease the quantity of beryllia dissolved. However, from the above information it is obvious that sulphuric acid itself is a leachant for the beryllia and should give optimum results if the bulk of the \((U, Th)\)O\(_2\) fines have been first dissolved in nitric acid solutions.

Figure 9 gives a conceptual flow sheet using both nitric acid and sulphuric acid as leachants in a two-step process, the \((U, Th)\)O\(_2\)-rich heel being recycled to the next batch. From previous studies it is known that sulphate in low concentration will inhibit the fluoride-catalysed dissolution of the thorium in nitric acid and all sulphate must be thoroughly washed from the heel (Farrell and Isaacs 1965).

Build-up of \((U, Th)\)O\(_2\) is possible as the nitric acid leach time is fixed to prevent excessive dissolution of the beryllia. This problem of heel build-up could always be overcome by inserting a heel dissolution step from time to time.

The actinide concentration likely to be encountered in the sulphate stream is important. A short leach (15 minutes, see Section 3.1.2) resulted in a very high \((U, Th)\)O\(_2\) content in the residue. After a severe sulphuric acid leach 11.5 per cent. of the original \((U, Th)\)O\(_2\) component was dissolved. Thus up to 10 per cent. of the actinides would require recovery from the sulphate stream. Fardy et al. (1967) have demonstrated in the laboratory that the Th, Pu, and U can be readily extracted from beryllium sulphate solutions by the amine, Primene – J.M.T.

Some preliminary experiments (Section 3.2) showed that the tetrahydrate \(BeSO_4\cdot4\ H_2O\) can be crystallised from the spent sulphuric acid stream at 10°C leaving only a small residual quantity of beryllium in the solution. The mother-liquor adjusted to 10M \(H_2SO_4\) can be recycled. The \(BeSO_4\cdot4\ H_2O\) crystals after washing in some \(H_2SO_4\) acid, are dissolved in water to give a low acid concentrated beryllium sulphate solution partially decontaminated from fission products and suitable for processing to recover the actinides (Fardy et al. 1967).

Beryllium sulphate decontamination by crystallisation would result in a build-up of both actinides and fission products in the sulphuric acid, which from time to time might have to be dumped, or processed for uranium if the uranium content were high enough.
3.3.2 Multi-batch processing of unirradiated oxides

Three batches of vibratory-milled fuelled beryllia were sequentially processed to test the flow sheet. The final heel was completely dissolved at the end of the third batch. The performance of each cycle is indicated by the ratio of the mass of oxide dissolved to the mass of oxide added (Table 9). Cycle 1 gave the predicted ratio expected from dissolution rate curves (Figure 5). The leaching step in Cycle 2 failed to reach this selectivity because of sulphate contamination from Cycle 1, the sulphate inhibiting the fluoride-catalysed dissolution of the thoria. In Cycle 3 greater care was taken with the sulphate wash and a significant improvement in the selectivity was obtained because of the presence of a large actinide rich heel from Cycle 2. Table 10 gives the overall results of this trial. The flexibility of the process is illustrated by the fact that the final beryllia and actinide distributions were reasonable, although the leaching step in Cycle 2 was unsatisfactory. Reasonable mass balances were obtained over the multi-batch experiment. In this trial no attempt was made to test the crystallisation step given in the flow sheet.

The beryllia residue was leached with fresh 10M sulphuric acid in five contacts per batch, the time of contact increasing progressively from 5 to 35 minutes. This procedure was adopted to avoid crystallisation in the transfer lines of the apparatus. After the completion of the sulphuric acid leaching step, the acidic beryllium sulphate solutions were combined and the acidity adjusted to 10M H₂SO₄ while hot, using predetermined density measurements for control. The solutions were then cooled to 7°C and the BeSO₄·4 H₂O allowed to crystallise. Although controlled crystallisation was not possible in the apparatus used, the results (Table 11) show that the beryllium underwent significant decontamination from uranium and thorium.

3.3.3 Multi-batch processing of irradiated oxides

A further trial of the conceptual flow sheet was attempted using irradiated (U²³⁸, Th)O₂ fuelled beryllia. This material was manually crushed and ground (Section 2.1) and then processed in a 4 inch lead walled cave (Section 2.2). However, the difficult beryllium sulphate crystallisation step was not attempted in the cave, the beryllia being dissolved in 10M H₂SO₄ (500 per cent stoichiometric excess) in one contact.

Before the multi-batch trial a single batch of the irradiated material was leached using Run 9 conditions and a forty-minute leach time. Ten per cent of the beryllia, 95 per cent of the uranium and 93 per cent of the thorium was dissolved in that time. These results indicated that the flow sheet leach conditions were suitable for this material. For the multi-batch trial leach times of 1 hour for nitric acid and 2 hours for sulphuric acid were chosen.

Table 12 gives the results for a four-batch sequential trial in terms of distribution of the elements in each stream, the distribution ratio being the mass fraction of oxide dissolved over oxide added. In the nitric acid leach a ratio of 0.1 for Be and 0.9 for U and Th could be expected for the first cycle. In later cycles the Be ratio should not change significantly and the U and Th ratio should increase. The results of the nitric acid leach give considerably lower values for the U and Th than predicted.

The distribution of the Be and the U and Th in the nitrate and sulphate streams (Table 13) is considerably less favourable than that obtained with the unirradiated material (Table 10).

The fission product release was estimated from the γ-spectra of samples taken during the nitric acid leach. The release of Ce¹⁴⁴, Ru¹⁹³, Cs¹³⁷ and Zr⁹⁵ was proportional to the mass of (U, Th)O₂ dissolved (Table 14).

In multi-batch processing the fission products were leached by the sulphuric acid. The total γ-activity of each stream was estimated. Table 15 lists the ratio of the activity to uranium concentration in each solution. The fission product activity per dissolved mass of uranium is greater in the sulphate stream by a factor of about ten.

The reason why this particular trial failed to reach the predicted separation of (U, Th)O₂ from the BeO is not evident, but the difficulties of decanting and washing the residue in the cave probably led to sulphate-poisoning of the fluoride-catalysed dissolution reaction in the nitric acid leach step.
4. CONCLUSIONS

1. Urania and thoria in solid solution can be leached readily from comminuted fuelled beryllia using nitric acid fluoride leachant.

2. Excellent mass balances were obtained in these experiments.

3. Best results with batch leaching were obtained with high mole ratio of nitric acid to oxide, and using 0.05M fluoride. Aluminium as an additive and beryllium and thorium from the reaction interfere by complexing the fluoride. A continuous leaching process should improve the separation of (U,Th)O₂ from the BeO.

4. The loss of beryllia to the nitric acid leachant in a single leach is high, reaching about 30 per cent for a total recovery of the actinides (> 99.9 per cent), and under optimum conditions 18 per cent for a 98 per cent recovery.

5. The physical properties of the fuel particles and the matrix are very important and affect the comminution process, and this may in turn seriously affect the leaching process. However, with the material used, crushing to pass a 30 BSS sieve adequately exposes the fuel particles for leaching.

6. Hot 10M sulphuric acid readily dissolves the beryllia residue yielding highly concentrated (8M) beryllium solutions, low in residual acid.

7. Sulphuric acid selectively dissolves the beryllia leaving any (U,Th)O₂ present only partially dissolved. The relative insolubility of the fuel particles in H₂SO₄ acid is due to the insolubility of the thorium in that medium.

8. Careful crystallisation of beryllium sulphate tetrahydrate from the BeSO₄-H₂SO₄-H₂O solution gives a significant decontamination from uranium and thorium.

9. It appears possible to use the differential but reciprocal dissolving power of nitric and sulphuric acids in a two-step leaching process and for this a flow sheet was developed. A crystallisation step was included to obtain low acid beryllium sulphate solution partially decontaminated from uranium, thorium, and possibly fission products.

10. This flow sheet was tested using unirradiated and irradiated material. Although the trial with irradiated material was less favourable, evidence from this trial and the previous more successful trial with unirradiated material indicates that the two-step process is feasible. It is unlikely however that losses of beryllium to the nitric acid stream could be reduced below 10 per cent for a total recovery of the actinides.

11. The fission product activity per dissolved unit mass of uranium in the sulphate stream was greater by a factor of 10 than that in the nitrate stream.

12. It is possible to fine-grind and dissolve the whole fuel((U,Th)O₂ and BeO), in either nitric or sulphuric acid if either dissolution process was favoured for a head-end in place of a selective grind-leach process.

5. RECOMMENDATIONS

1. Fuelled beryllia of the chosen composition and properties for the H.T.G.C. Reactor and irradiated to high burn-up, should be processed as indicated by the flow sheet (Figure 9) using master-slave manipulators in a hot-cell. It would be necessary to study both comminution and leaching in any one experimental trial, as the processes are inter-dependent.

2. Further research should be applied to:

(a) The development of a continuous nitric acid leaching process.

(b) The dissolution kinetics of BeO, and (U,Th)O₂ in sulphuric acid.
(c) The crystallisation of beryllium sulphate tetrahydrate in order to obtain a process for decontaminating the beryllium from the actinides and the fission products.

(d) Engineering development of the head-end equipment for leaching, solids washing, and solids-liquid separation.

(e) A separation process for the recovery of the actinides from sulphate media assuming that the simpler complete dissolution of the comminuted fuelled beryllia in sulphuric acid may be a more suitable head-end process.

6. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of Mr. S.R. Isaacs who performed the first leaching experiments (Table 1) and who developed the technique for obtaining excellent mass balances, and Mr. J.R. Coady who contributed dissolution data on BeO in H2SO4 solutions used in the residue dissolution experiments. The assistance of Mr. C. La Riviere during the leaching experiments, and of Messrs. Florence and Pakaüs who carried out the many analyses requested, was also much appreciated.

We also acknowledge the continued support and advice of Dr. R.C. Cairns, Head Fuel Cycle Development Section, who undertook with Mr. J.R. May, the initial work on the development of this process (Cairns 1964).

7. REFERENCES


### TABLE 1
SIEVE ANALYSIS FOR COMMUNICATED 1:20:2000 (U,Th)O₂ FUELLED BERYLLIA

<table>
<thead>
<tr>
<th>Sieve Size BSS</th>
<th>+52</th>
<th>-52 +72</th>
<th>-72 +100</th>
<th>-100 +150</th>
<th>-150 +200</th>
<th>-200 +300</th>
<th>-300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manually</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comminuted</td>
<td>-</td>
<td>37.3</td>
<td>17.2</td>
<td>18.4</td>
<td>8.8</td>
<td>6.5</td>
<td>11.8</td>
</tr>
<tr>
<td>Unirradiated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manually *</td>
<td>6.7</td>
<td>19.9</td>
<td>11.6</td>
<td>15.6</td>
<td>8.5</td>
<td>7.8</td>
<td>30.0</td>
</tr>
<tr>
<td>Comminuted</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vibratory-milled</td>
<td></td>
<td>35.5</td>
<td>22.0</td>
<td>13.2</td>
<td>9.7</td>
<td>4.9</td>
<td>14.7</td>
</tr>
</tbody>
</table>

* Using manipulators in a hot-cell

### TABLE 2
SINGLE BATCH LEACHING OF 1:20:450 FUEL.
MASS BALANCES AND RECOVERIES

<table>
<thead>
<tr>
<th>Maximum Particle Size (μ)</th>
<th>Comminution Losses</th>
<th>% Dissolved Based on Total Recovered</th>
<th>Mass Balances %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>UO₂</td>
<td>ThO₂</td>
</tr>
<tr>
<td>295</td>
<td>0.3</td>
<td>99.7</td>
<td>100.0</td>
</tr>
<tr>
<td>152</td>
<td>1.7</td>
<td>99.9</td>
<td>100.0</td>
</tr>
<tr>
<td>104</td>
<td>1.5</td>
<td>99.9</td>
<td>100.0</td>
</tr>
<tr>
<td>76</td>
<td>1.4</td>
<td>99.9</td>
<td>100.0</td>
</tr>
<tr>
<td>66</td>
<td>2.7</td>
<td>99.9</td>
<td>100.0</td>
</tr>
<tr>
<td>53</td>
<td>4.2</td>
<td>99.9</td>
<td>100.0</td>
</tr>
</tbody>
</table>

### DISSOLUTION CONDITIONS
- Acid : nitric 13M; 12.3 ml/g
- Temperature : 115°C
- Fluoride : 0.05M
- Leaching Time : 6 h
- Aluminium : 0.1M
- Agitation : mechanical
- Dissolver : stainless steel
### Table 3

**Single Batch Leaching of 1:20:2000 Fuel**

**Effect of Leaching Conditions on Recoveries**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Maximum Particle Size (μm)</th>
<th>% Material &lt; 53 μm</th>
<th>Nitric Acid Concentration (M)</th>
<th>Fluoride Concentration (M)</th>
<th>Aluminium Concentration (M)</th>
<th>Acid Volume ml/g Oxide</th>
<th>Leaching Time (h)</th>
<th>Per cent Oxide Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>152</td>
<td>6.4</td>
<td>13</td>
<td>0.05</td>
<td>0.10</td>
<td>3.22</td>
<td>5</td>
<td>27</td>
</tr>
<tr>
<td>2</td>
<td>152</td>
<td>14.9</td>
<td>13</td>
<td>0.05</td>
<td>0.10</td>
<td>3.22</td>
<td>6</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>13.1</td>
<td>13</td>
<td>0.05</td>
<td>0.10</td>
<td>3.22</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>152</td>
<td>12.3</td>
<td>13</td>
<td>0.05</td>
<td>0.10</td>
<td>3.22</td>
<td>1½</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>295</td>
<td>11.7</td>
<td>13</td>
<td>0.05</td>
<td>0.10</td>
<td>3.22</td>
<td>3</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>152</td>
<td>nil*</td>
<td>13</td>
<td>0.01</td>
<td>0.03</td>
<td>2.16</td>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>152</td>
<td>nil*</td>
<td>13</td>
<td>0.05</td>
<td>0.10</td>
<td>3.22</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>500</td>
<td>5.5</td>
<td>15.5</td>
<td>0.05</td>
<td>0.10</td>
<td>4.88</td>
<td>3</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>500</td>
<td>8.7</td>
<td>15.5</td>
<td>0.05</td>
<td>nil</td>
<td>4.88</td>
<td>3</td>
<td>18</td>
</tr>
</tbody>
</table>

* Fines removed physically prior to leaching

**Other Dissolution Conditions**

- **Dissolver**: stainless steel, except for Run 9 in which Pyrex glass was used
- **Temperature**: 115°C
- **Agitation**: mechanical
TABLE 4
SINGLE BATCH LEACHING OF 1:20:2000 FUEL
MASS BALANCES

<table>
<thead>
<tr>
<th>Run No.</th>
<th>% Mass Balances</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UO₂</td>
<td>ThO₂</td>
<td>BeO</td>
</tr>
<tr>
<td>1</td>
<td>102</td>
<td>101</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>101</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>99</td>
<td>98</td>
<td>102</td>
</tr>
<tr>
<td>4</td>
<td>105</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>7</td>
<td>99</td>
<td>97</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td>101</td>
<td>101</td>
<td>93</td>
</tr>
</tbody>
</table>

Dissolution Conditions as for Table 3
### TABLE 5

**EFFECT OF EXTREME LEACHING TIMES ON RECOVERIES**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Nitric Acid Leaching Time (Minutes)</th>
<th>Per Cent Oxide Dissolved* in Nitric Acid</th>
<th>Per cent Oxide Dissolved* in Sulphuric Acid</th>
<th>Mass Balance*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BeO</td>
<td>UO₂</td>
<td>ThO₂</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>10.8</td>
<td>87.8</td>
<td>87.9</td>
</tr>
<tr>
<td>11</td>
<td>360</td>
<td>31.7</td>
<td>101.2</td>
<td>101.1</td>
</tr>
</tbody>
</table>

* All figures based on oxide initially added

**DISSOLUTION CONDITIONS**

**NITRIC ACID LEACHING**

- **Acid**: 15.5 M, 4.88 ml HNO₃/g of oxide
- **Fluoride**: 0.05M
- **Dissolver**: Pyrex glass
- **Temperature**: 115°C
- **Agitation**: mechanical

**SULPHURIC ACID RESIDUE DISSOLUTION**

- **Acid**: 10.0M
- **Dissolver**: same as for nitric acid leaching
- **Temperature**: 145°C initially
- **Agitation**: mechanical
TABLE 6
EFFECT OF MAXIMUM PARTICLE SIZE ON LEACHING

<table>
<thead>
<tr>
<th>Maximum Particle Size μ</th>
<th>% Dissolved Based on Total Recovered</th>
<th>Ratio of Mass ThO₂ Dissolved to Mass of BeO Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UO₂</td>
<td>ThO₂</td>
</tr>
<tr>
<td>500</td>
<td>95</td>
<td>95.5</td>
</tr>
<tr>
<td>295</td>
<td>97.7</td>
<td>98.3</td>
</tr>
<tr>
<td>152</td>
<td>98.8</td>
<td>98.6</td>
</tr>
</tbody>
</table>

DISSOLUTION CONDITIONS

See Runs 3, 5 and 1 respectively

Table 3
### TABLE 7
SULPHURIC ACID DISSOLUTION OF 1:20:2000 FUEL
EFFECT OF AVERAGE PARTICLE SIZE ON RECOVERIES

<table>
<thead>
<tr>
<th>Sieve Size BSS</th>
<th>Average Particle Size μ</th>
<th>Masses of Oxide Initially Present (g)</th>
<th>Masses of Oxide Dissolved (g)</th>
<th>Per cent of Oxide Dissolved Based on Oxide Initially Present (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BeO</td>
<td>ThO₂</td>
<td>UO₂</td>
</tr>
<tr>
<td>-52 + 72</td>
<td>253</td>
<td>19.75</td>
<td>1.87</td>
<td>0.096</td>
</tr>
<tr>
<td>-72 + 100</td>
<td>182</td>
<td>13.0</td>
<td>1.24</td>
<td>0.064</td>
</tr>
<tr>
<td>-100 + 150</td>
<td>128</td>
<td>8.66</td>
<td>1.68</td>
<td>0.086</td>
</tr>
<tr>
<td>-150 + 300</td>
<td>79</td>
<td>8.28</td>
<td>1.01</td>
<td>0.052</td>
</tr>
<tr>
<td>-300 &lt; 53</td>
<td>&lt; 53</td>
<td>11.21</td>
<td>3.35</td>
<td>0.163</td>
</tr>
</tbody>
</table>

**DISSOLUTION CONDITIONS**

- **Acid:** sulphuric 10M, 8 ml H₂SO₄/g of BeO
- **Dissolver:** Pyrex glass
- **Temperature:** 145°C
- **Leaching Time:** 6 h
- **Agitation:** mechanical
### TABLE 8

**SULPHURIC ACID DISSOLUTION OF LEACH RESIDUES**

<table>
<thead>
<tr>
<th>Maximum * Initial Particle Size (µ)</th>
<th>Masses of Oxides Initially Present† (g)</th>
<th>Per cent of Oxides Dissolved ‡</th>
<th>Initial Volume of H₂SO₄ (ml)</th>
<th>Final Calculated Concentration H₂SO₄ (M)</th>
<th>Estimated Final Be Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>BeO 50, ThO₂ 0.049, UO₂ 0.021</td>
<td>BeO 79, ThO₂ 0.8, UO₂ 6.0</td>
<td>200</td>
<td>2.1</td>
<td>7.9</td>
</tr>
<tr>
<td>295</td>
<td>BeO 45, ThO₂ 0.110, UO₂ 0.008</td>
<td>BeO 77, ThO₂ 7.0, UO₂ 17.0</td>
<td>190</td>
<td>2.6</td>
<td>7.3</td>
</tr>
<tr>
<td>152</td>
<td>BeO 51, ThO₂ 0.820, UO₂ 0.042</td>
<td>BeO 80, ThO₂ 0.8, UO₂ 6.0</td>
<td>206</td>
<td>2.1</td>
<td>7.9</td>
</tr>
<tr>
<td>152</td>
<td>BeO 31, ThO₂ 0.095, UO₂ 0.005</td>
<td>BeO 63, ThO₂ 7.0, UO₂ 10.0</td>
<td>76</td>
<td>-0.2</td>
<td>10.1</td>
</tr>
</tbody>
</table>

* prior to nitric acid leaching

† after nitric acid leaching

‡ based on masses of oxide present after nitric acid leaching

### DISSOLUTION CONDITIONS

- **Acid**: sulphuric 10 M, volumes as shown
- **Dissolver**: Pyrex glass
- **Temperature**: 145 °C (initial)
- **Leaching Time**: 6 h
- **Agitation**: mechanical
<table>
<thead>
<tr>
<th>Charge</th>
<th>Acid</th>
<th>Nitric Acid Leach Time (min)</th>
<th>Distribution of elements in acid streams: Ratio of the mass of oxide dissolved to the mass of oxide added in each cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BeO Nitrate</td>
</tr>
<tr>
<td>Cycle 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Batch 1</td>
<td>HNO₃/HF</td>
<td>60</td>
<td>0.173</td>
</tr>
<tr>
<td>Batch 1 Residue</td>
<td>H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Batch 1 heel + Batch 2</td>
<td>HNO₃/HF</td>
<td>47</td>
<td>0.205</td>
</tr>
<tr>
<td>Batch 2 Residue</td>
<td>H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycle 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Batch 2 heel + Batch 3</td>
<td>HNO₃/HF</td>
<td>47</td>
<td>0.134</td>
</tr>
<tr>
<td>Batch 3 Residue</td>
<td>H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Batch 3 heel *</td>
<td>HNO₃/HF</td>
<td>180</td>
<td>0.001</td>
</tr>
</tbody>
</table>

* Heel Dissolve Step  

**DISSOLUTION CONDITIONS**  

**HNO₃ LEACH**  
Acid : 15.5 M HNO₃, 4.88 ml/g oxide  
Fluoride : 0.05 M  
Temperature : 115 °C

**H₂SO₄ LEACH**  
Acid : 10 M H₂SO₄, 6 x 150 ml contacts  
Temperature : 130 °C
TABLE 10
MULTI-BATCH PROCESSING OF UNIRRADIATED 1:20:2000 FUEL
MASS BALANCES AND THE DISTRIBUTION IN EACH STREAM

Total Three Batch Charge

UO₂ Mass Balance 99.5%

HNO₃ Stream
93.6%

H₂SO₄ Stream
5.9%

H₂SO₄ *
Mother Liquor
4.7%

BeSO₄ *
Solution 1.2%

ThO₂ Mass Balance 97.7%

HNO₃ Stream
88.9%

H₂SO₄ Stream
8.8%

H₂SO₄ *
Mother Liquor
5.6%

BeSO₄ *
Solution 3.2%

BeO Mass Balance 98.2%

HNO₃ Stream
17.3%

H₂SO₄ Stream
80.9%

H₂SO₄ *
Mother Liquor
6.3%

BeSO₄ *
Solution 74.6%

* Distributions after crystallisation
**TABLE II**

DECONTAMINATION OF BERYLLIUM SULPHATE FROM URANIUM AND THORIUM BY CRYSTALLISATION OF THE TETRAHYDRATE

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>Actinide</th>
<th>Actinide Concentration in Feed Solution (µg/ml)</th>
<th>Decontamination Factor (D.F.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Uranium</td>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Thorium</td>
<td>330</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>Uranium</td>
<td>8</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>Thorium</td>
<td>100</td>
<td>5</td>
</tr>
</tbody>
</table>

D.F. = \[ \frac{[\text{Actinide}]}{[\text{Beryllium}]} \text{ in feed solution} \] / \[ \frac{[\text{Actinide}]}{[\text{Beryllium}]} \text{ in product solution} \]

*A solution of BeSO$_4$ . 4 H$_2$O in water.*
### TABLE 12
MULTI-BATCH PROCESSING OF IRRADIATED 1:20:2000 FUEL
DISTRIBUTION OF ELEMENTS IN EACH CYCLE

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Charge</th>
<th>Acid</th>
<th>Distribution of elements in acid streams. Ratio of mass of oxide dissolved to the mass of oxide added in each batch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BeO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nitrates</td>
</tr>
<tr>
<td>1</td>
<td>Batch 1</td>
<td>HNO₃ + HF</td>
<td>0.114</td>
</tr>
<tr>
<td></td>
<td>Batch 1 residue</td>
<td>H₂SO₄</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Batch 1 heel + Batch 2</td>
<td>HNO₃ + HF</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>Batch 2 residue</td>
<td>H₂SO₄</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Batch 2 heel + Batch 3</td>
<td>HNO₃ + HF</td>
<td>0.175</td>
</tr>
<tr>
<td></td>
<td>Batch 3 residue</td>
<td>H₂SO₄</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Batch 3 heel + Batch 4</td>
<td>HNO₃ + HF</td>
<td>0.156</td>
</tr>
<tr>
<td></td>
<td>Batch 4 residue</td>
<td>H₂SO₄</td>
<td></td>
</tr>
</tbody>
</table>

**DISSOLUTION CONDITIONS**

**NITRIC ACID**
- Concentration HNO₃ 15.5 M; 4.88 ml/g of oxide
- Fluoride : 0.05M
- Temperature : 115 °C
- Time : 60 minutes

**SULPHURIC ACID**
- Concentration H₂SO₄ 10M
- Temperature : 145 °C
- Time : 120 minutes
TABLE 13
MULTI-BATCH PROCESSING OF IRRADIATED 1:20:2000 FUEL
MASS BALANCES AND FINAL DISTRIBUTION IN EACH STREAM
### TABLE 14

**RELATIVE RELEASE OF FISSION PRODUCTS DURING NITRIC ACID LEACHING**

<table>
<thead>
<tr>
<th>Per cent UO₂ Dissolved</th>
<th>Per cent* Fission Product Released</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce₁⁴⁴</td>
</tr>
<tr>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>35</td>
<td>37</td>
</tr>
<tr>
<td>61</td>
<td>53</td>
</tr>
<tr>
<td>81</td>
<td>80</td>
</tr>
<tr>
<td>91</td>
<td>89</td>
</tr>
</tbody>
</table>

*Percentages based on "total nitric acid leached" figures.

### TABLE 15

**DISTRIBUTION OF FISSION PRODUCTS IN NITRATE AND SULPHATE STREAMS**

| Cycle No. | Stream        | Ratio : $\gamma$ activity * \[
|-----------|---------------|----------------
| 1         | Nitrate       | 58,000         |
|           | Sulphate      | 850,000        |
| 2         | Nitrate       | 60,000         |
|           | Sulphate      | 490,000        |
| 3         | Nitrate       | 76,000         |
|           | Sulphate      | 850,000        |
| 4         | Nitrate       | 55,000         |
|           | Sulphate      | 1,000,000      |

* Gross F.P. $\gamma$ activity in counts/min/ml

† Uranium concentration in $\mu$g/ml
FIGURE 1. FUEL CYCLE FOR H.T.G.C. REACTOR USING A BERYLLIA-BASED DISPERSION TYPE FUEL
FIGURE 2. DISSOLUTION CURVES FOR (U,Th)O₂ AND BeO IN SINGLE BATCH LEACH. PENALTY OF BERYLLIA LOSS AS ACTINIDES ARE RELEASED

DISSOLUTION CONDITIONS:

- Acid: 13M HNO₃; 3.22 ml/g
- Fluoride: 0.05M
- Aluminium: 0.01M
- Temperature: 115°C
- Agitation: mechanical
- Dissolver: stainless steel
- Sieve Size: less than 152μ
FIGURE 3. DISSOLUTION CURVES FOR (U, Th)O₂ AND BeO IN SINGLE BATCH LEACH. EFFECT OF LOW NITRIC ACID AND FLUORIDE CONCENTRATIONS

DISSOLUTION CONDITIONS:

- Acid: 13M HNO₃; 2.16 ml/g
- Fluoride: 0.01M
- Aluminium: 0.03M
- Temperature: 115 °C
- Agitation: mechanical
- Dissolver: stainless steel
- Sieve Size: less than 152μ
FIGURE 4. DISSOLUTION CURVES FOR \( (U,\text{Th})_2 \) AND \( \text{BeO} \) IN SINGLE BATCH LEACH. EFFECT OF HIGH NITRIC ACID CONCENTRATION

DISSOLUTION CONDITIONS:
- Acid: 15.5M HNO\(_3\); 4.88 ml/g
- Fluoride: 0.05M
- Aluminium: 0.1M
- Temperature: 115°C
- Agitation: mechanical
- Dissolver: stainless steel
- Sieve Size: less than 500\(\mu\)
FIGURE 5. DISSOLUTION CURVES FOR (U,Th)O₂ AND BeO IN SINGLE BATCH LEACH. EFFECT OF SILICA

DISSOLUTION CONDITIONS:  
- Acid: 15.5 M HNO₃; 4.88 ml/g  
- Fluoride: 0.05M  
- Aluminium: absent  
- Temperature: 115 °C  
- Agitation: gas  
- Dissolver: glass  
- Sieve Size: less than 500 μ
FIGURE 6. DISSOLUTION CURVES FOR (U,Th)O₂ AND BeO IN SINGLE BATCH LEACH. EFFECT OF REMOVAL OF FINES (53μ)

DISSOLUTION CONDITIONS: Acid 13M HNO₃; 3.22 ml/g
Fluoride 0.05M
Aluminium 0.1M
Temperature 115°C
Agitation mechanical
Dissolver stainless steel
Sieve Size between 152 and 53μ
FIGURE 7. DISSOLUTION RATES OF THORIA AND BERYLLIA IN NITRIC ACID LEACH SOLUTIONS: EFFECT OF ACID AND FLUORIDE CONCENTRATIONS
FIGURE 8. PHOTOMICROGRAPHS OF COMMINUTED 1:20:450 COMPOSITION FUEL
(White areas indicate fuel particles)
FIGURE 9. CONCEPTUAL FLOW SHEET FOR A MULTIBATCH PROCESS USING BOTH NITRIC AND SULPHURIC ACID AS SELECTIVE LEACHANTS: THE COMPOSITE PROCESS