OPEN FILE 76/21

1/1/101 July 1967

SOUTH AUSTRALIAN GOVERNMENT DEPARTMENT OF MINES

Amdel Report

No. 545

YTTRIUM OXIDE FROM PORT PIRIE URANIUM PLANT RESIDUES

Re-issue January 1976

by

L.H. Goldney, J.D. Hayton and S. Jaworski

Investigated by: Industrial Chemistry Section
Officer in Charge: R.E. Wilmshurst

P.A. Young. Director

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES
Adelaide South Australia

CONTENTS

SUMMARY

Background

This investigation was initiated by the South Australian Government Department of Mines, following an inquiry concerning the possible production of yttrium oxide from the Port Pirie Uranium Treatment Plant Residues. Because the demand for yttrium oxide for use in phosphors was then currently in excess of world production and prices were rising, there was some urgency to develop a process which would allow early exploitation of the residues. However, it was considered desirable that the investigation should also include a study of methods for recovering scandium and rare earth oxides, which were of considerable potential value.

Objectives

The investigation was aimed at developing a process for recovering yttrium oxide from the residues at the Port Pirie Uranium Plant. A process for the recovery of scandium oxide from liquors by solvent extraction had been successfully operated at the uranium treatment plant and it was considered that a similar process probably would be effective for the extraction of yttrium and other rare earth oxides. In any case, because of the potential value of the scandium oxide in the residues, its recovery was considered to be an essential part of the process aimed at recovering yttrium.

Summary of Work Done

Calcination of the residues to convert iron sulphate to oxide, followed by water leaching of the calcined product, enabled yttrium, scandium and lanthanide elements to be extracted into a liquor containing relatively little iron. At the optimum calcination temperature of approximately 650°C, the Fe_2O_3/Y_2O_3 ratio was reduced from approximately 130 in the residue to approximately 10 in the leach liquor. By leaching at the boiling point a lower Fe_2O_3/Y_2O_3 ratio could be obtained than by leaching with cold water, but less yttrium was actually extracted. Assessment of various methods of calcining the residue showed that calcination in a fluid-bed reactor was likely to be the most effective.

Because the Fe_2O_3/Y_2O_3 ratio in leach liquors was still high, direct precipitation of the required elements as hydroxides was considered to be impractical. Direct precipitation of yttrium and lanthanides as oxalates appeared to be feasible but the scandium would not be recovered quantitatively by this procedure. Recovery of scandium and other elements by extraction with di(2-ethyl hexyl) phosphoric acid (EHPA), was therefore investigated in some detail.

A process was proposed on the basis of results obtained from treatment of material from Dam No. 6 and Dam No. 5 (West) consisting mainly of sulphates, and the capital and operating costs of a plant were estimated. However, further work showed that the bulk of the residues did not respond satisfactorily to the roasting and leaching treatment and that the overall recovery of yttrium, scandium and lanthanides was much lower than anticipated. Extraction of scandium into EHPA could be achieved from leach liquors, but high recovery of yttrium could only be obtained at concentrations of EHPA which would also enable a significant portion of the iron to be extracted.

Conclusions

Although approximately 70% of the Y_2O_3, 80% of the Yb_2O_3 and 90% of the Sc_2O_3 present in the sulphate material in Dam 6 could be recovered, much smaller proportions of these components could be recovered from the material in the other Dams which constituted the bulk of the total residues. The overall recovery of each component was not likely to exceed 10% of the amount present. In view of the limited amount of the residues for which the suggested process would be satisfactory, further investigation was not considered to be warranted.

1. INTRODUCTION

Following the visit of Mr John Dietrich, representing the Research Chemicals Division of the Nuclear Corporation of America, the South Australian Government Department of Mines requested an investigation of the extraction of yttrium oxide from the residues in the dams at the Port Pirie Uranium Treatment Plant. Production of scandium and other rare earth oxides was also considered to be desirable.

Particular interest was shown in the production of yttrium oxide since known sources of supply were inadequate to meet the increasing needs of the phosphor industry, and the market price of the material was rising.

Most of the solid residues in the dams consist of mixtures of undissolved mineral components of the original concentrate and sulphates crystallised from the uranium-depleted leach liquors. The main mineral components are rutile, hematite and partly attacked silicates.

In the dams furthest from the treatment plant the residues consist mainly of sulphates crystallised from accumulated liquor by evaporation. The material in Dam 6 consists entirely of sulphates, and Dam 5 contains a considerable quantity of sulphates in the western end. Most of the initial systematic investigation was done on the material from Dam 6.

The material for the initial experimental work was obtained from Dam 6 by Mr R. Adam of the South Australian Department of Mines on 17 August 1966. Subsequently, further samples were obtained from Dams 2 to 6 inclusive.

2. MATERIAL EXAMINED

The present investigations were carried out mainly on crystallised sulphate material collected from Dam 6 in August 1966. Material was also collected by auger sampling from Dams 2 to 5 and made into composite samples representing sections of each dam. All the samples were air-dried for a sufficient time to enable them to be ground to a conveniently small size for mixing and sampling.

Seven samples of sulphate sludge were collected from Dam 6. One of them (No. 1) represented soft clay from the bottom and was not included in the composite sample prepared for testing.

Descriptions of the samples collected are tabulated below. Analyses of the air-dried samples of a composite of the six samples from Dam 6 are shown in Table 1. The composite sample was designated Y11.

The preliminary investigations were done on the following samples:

Dept of Mines Sample No.	Amdel Sample No.	Location	
1	Y1	SE corner, soft clay,	Dam 6
2	Y2	SE corner, sulphate sludge,	Dam 6
5	Y5	S side, centre - ditto -	Dam 6
6	Y6	SW corner, "	Dam 6
7	Y7	NW corner, "	Dam 6
8	Y8	N side, centre "	Dam 6
10	Y10	NE corner, "	Dam 6
-	Y11, 17	Composite	
B4, B4A	Y12	Dam 4	
B3A	Y13	Dam 3 East	
B5A	Y14	Dam 5 East	
B3, B3A	Y15	Dam 3	
B2A	Y16	Dam 2	

For systematic work, composites containing material proportional to the weight of samples supplied were prepared from minus 25-mesh material. These samples, which were essentially similar to those used for the initial experiments, were designated as follows:

Systematic Samples, August 1966

Dept of Mines Designation	Amdel Designation	Location
-	Y11	Dam 6) Equivalent composition
-	Y17	Dam 6)
2X	Y18	Dam 2
3X	Y19	Dam 3 West
3Y	Y20	Dam 3 East
4X	Y21	Dam 4 West
4Y	Y22	Dam 4 East
5X	Y23	Dam 5 West
5Y	Y24	Dam 5 East

3. EQUIPMENT

3.1 Small Fluid-bed Reactor

The reactor consisted of a 2.5 cm (1 in.) diameter silica tube. The base of the reactor bed was formed of evenly graded corundum (Al_2O_3) particles which acted as a support for the fluidising bed and a heat exchanger to pre-heat the fluidising air. The feed material for the reactor was screened to obtain a minus 10-mesh plus 100-mesh fraction, and this material was placed in the tube to a depth of approximately 3.7 cm (1½ in.) above the corundum base. Air was blown through from the bottom to produce fluidisation.

3.2 Large Fluid-bed Reactor

3.2.1 Fluid Bed and Ancillaries

The reactor was 45.7 cm (18 in.) internal diameter, tapered in the bed area to 30.5 cm (12 in.) diameter at the distribution plate. All sections were cast refractory. A gas-fired hot wind-box was located below the distributor to provide sufficient heat for maintaining the bed contents at reaction temperature.

The distributor plate was made from 6.35 mm (¼ in.) thick heat-resisting stainless steel (Type 310).

Four bubble caps, each having eight 6.35 mm (¼ in.) discharge holes, were located on a 190.5 mm (7½ in.) pitch circle diameter. The bed overflow was located 0.813 m (32 in.) above the distributor plate, and above this point the free-board height was 2.3 m (90 in.).

A 15.3 cm (6 in.) diameter high-efficiency type cyclone was installed in the off-gas line. The cyclone off-gas was exhausted through a water-sealed 15.3 cm (6 in.) diameter 7.62 m (25 ft) long, packed scrubbing column.

Bed overflow and cyclone dust products were discharged through lock hoppers.

3.2.2 Slurry Feeding

Sulphate material from Dam 6 was used for all fluid-bed roasting tests. A Watson-Marlow variable-speed tube pump, equipped with a 1.27 cm (½ in.) diameter tube, was used for feeding the sulphate material to the reactor as a 50% slurry in water. The slurry was injected through a manifold at a point 50 cm (24 in.) above the bed-overflow port. Air and water purges were connected to the manifold to assist in clearing slurry blockages.

3.2.3 Temperature Pressure and Air Controls

Thermo-couples were located as follows: one in the wind-box, two in the bed area, two in the free-board area and one in the off-gas stream to the cyclone. All couples were connected to a multi-point recorder.

Air-purged pressure tapping points were located so as to give pressure-loss readings across the distributor bed, cyclone and scrubbing column.

All air flows were controlled through rotameters and the flow-rates were adjusted as necessary.

4. EXPERIMENTAL PROCEDURE AND RESULTS

4.1 Heat Treatment

Thermogravimetric analysis of the composite sample of Dam-6 material (Y11) showed that there was a considerable difference between the decomposition temperature of iron sulphate and of the other sulphates (Fig. 1).

Heating tests were carried out at temperatures in the range 500 to 650°C to determine the effect of temperature on the solubility of the various components.

4.1.1 Heating in a Muffle Furnace

A weighed quantity of the air-dried material in a flat silica tray was placed in a muffle furnace so that it had ready access to air. The sulphate material from Dam 6 became semi-liquid at a low temperature (approximately 100°C) and then formed a solid cake which could not be broken up in the furnace. After approximately ½ hour the tray was removed from the furnace and the contents were cooled sufficiently to allow the cake to be broken up by grinding in a porcelain mortar. The ground material was returned to the tray which was again placed in the furnace at the appropriate temperature. At ½-hourly intervals the contents of the tray were stirred by means of a small metal rake to permit access of air to as much of the material as possible. Usually the samples were allowed to remain at the chosen temperature for three to four hours. After removal from the furnace the material was cooled and weighed to determine the total amount of volatile material lost.

Preliminary samples were roasted at 500 to 800°C, systematic samples (2X-5Y) were roasted at 600 to 700°C only. Samples Y11 (Composite Dam 6) and Y23 (Composite Dam 5 West also designated 5X) evolved copious sulphuric acid fumes, formed a hard crust and gave the highest rare earth yields on leaching. For example, material from Dams 6 and 5 (West) after roasting at 700°C, yielded 80% and 40% of the total yttrium respectively, whereas material from the other dams roasted at 600°C yielded only 8 to 10% yttrium. At 700°C roasting temperature, the recovery of yttrium from the latter samples dropped to less than 1%. A typical roasting procedure was as follows:

<u>Sample Y11/9</u>. Into a 30.5 × 15.3 × 2.54 cm (12 × 6 × 1 in.) silica dish was placed 500 g of Dam 6 composite Sample Y11, ground to minus 10 mesh. The dish was placed in a furnace and heated to 720°C. After one hour the material was removed and crushed as finely as possible

then replaced in the dish and heated for a further 5½ hours. During the second heating period the material was mixed by raking at intervals of 20 minutes. Copious fumes were evolved initially but at the end of 5½ hours no more fumes were visible. The dish was removed, cooled and weighed. The material lost 60% of its weight during roasting.

The procedure with other samples was identical, except for the amounts roasted and the temperature of roasting.

4.1.2 Heating in a 2.54 cm (1 in.) Fluid-bed Reactor

Several tests were done with screened material from sulphate Sample Y11 in a 2.54 cm (1 in.) diameter fluid-bed reactor. The bed temperature was raised gradually to 600°C. Some dust was lost during the operation of the bed, so the final product was assayed to provide a basis for determining subsequent leaching efficiency.

4.1.3 Heating in a 45.7 cm (18 in.) Fluid-bed Reactor

A 90 kg (200 lb) batch of sand was added to the reactor to establish a bed and the temperature was raised to 740°C before slurry feeding commenced. During this pre-heating period, approximately 70 kg (150 lb) of sand was discharged, mainly as bed overflow. Continuous slurry feeding proceeded for a period of 3 hours 50 minutes at an average rate of 18 kg (40 lb) of slurry per hour. The slurry concentration was 48% solids by weight, giving a total dry solids feed of 33 kg (73 lb).

The bed temperature was controlled within the limits 715 to 730°C by feed-rate adjustment. The fluidising-gas temperature was maintained at approximately 1000°C.

No accurate material balance could be obtained over this limited period, but approximately 18 kg (40 lb) of cyclone-dust product and 1.5 kg (3 lb) of bed-overflow product was recovered. The bed, 16 kg (36 lb) by weight, remaining at the end of the operation was a mixture containing sand but no separation was attempted.

The cold air flow was maintained at 3800 litres per minute which gave a space velocity at operating temperatures of 2.9 m (9.5 ft) per second at the distributor and 1.3 m (4.2 ft) per second in the 45.7 cm (18-in.) diameter section.

The pressure loss through the bed was 12.7 mm (0.5 in.) Hg when slurry feeding commenced. This fell to 0.79 mm (0.32 in.) Hg at the end of operations.

The other pressure readings averaged:

Distributor	132.08 mm (5.2 in.) Hg
Cyclone	13.97 mm (0.55 in.) Hg
Scrubber	6.35 mm (0.25 in.) Hg

At the end of the run, the bed-overflow product still consisted mainly of sand and therefore was not leached. The cyclone product consisted of a fine red material and was considered to be representative of the original sulphate. The cyclone product contained:

Y_2O_3	0.28%
Sc_2O_3	0.030%

Results of leaching the cyclone product with hot water are shown in Table 2 (Y26).

4.2 Leaching

With the exception of Samples Y11/4, Y11/5 and Y26 which were heated in a fluid-bed reactor and therefore suffered some loss through dusting, all the heated samples were evaluated in terms of original air-dried material. The total Y_2O_3, Yb_2O_3, Sc_2O_3 and Fe_2O_3 in the fluid-bed samples were determined by actual analysis, but for all other samples the amounts of these components were calculated from the amounts in the original dried material.

To save time and to avoid possible erroneous results due to effects of washing, the solids were leached with measured volumes of liquor and the volume of the pulp was carefully marked on the glass vessel so that adjustments could be made if necessary before filtration. After leaching, the pulps were filtered as rapidly as possible under suction and the liquor volume was recorded as that of the original liquor. The leaching tests were done at room temperature and also at near the boiling point (nominally 90 to 100°C).

4.2.1 Leaching at Room Temperature

A weighed amount of solid and a measured volume of water were placed in an Erlenmeyer flask which was then stoppered and shaken for two hours on a wrist-action shaker.

Initially, tests were done at various solid:liquid ratios to determine the effect on the solubility of the components.

After leaching, the pulp was filtered and the liquor was assayed for the required components.

4.2.2 Leaching at Elevated Temperature

The solid and liquor were placed in an Erlenmeyer flask which was then covered with a small watch-glass to prevent undue loss of water by evaporation. The flask was placed on a hot-plate. The contents were maintained at just below the boiling point of water for one hour, then cooled, adjusted to the original volume, mixed and filtered.

A typical leaching procedure was as follows:

> A 15-g portion of roasted material (Y11/7), equivalent to 30.0 g of the original composite of Dam 6 (Y11), was placed in a 250 mℓ conical flask with 40 mℓ of water. The contents were boiled gently for one hour. A second test was carried out under similar conditions except that the flask was shaken on a wrist-action shaker for two hours at ambient temperature. The volumes were then carefully adjusted to the original level and the contents of each flask were filtered on a Buchner funnel. The pH values of the resulting liquors were recorded and the liquors were assayed for the required components.

The results of roasting and leaching are shown in Tables 2 and 3. The results in Table 2 apply only to sulphate from Dam 6 and also show the effect of leaching at various solid/liquid ratios.

The proportion of iron dissolved from samples of sulphate material heated in a fluidised bed showed small but significant decreases, probably because of more efficient oxidation of the ferrous sulphate under such conditions. The proportions of the yttrium, ytterbium and scandium dissolved were relatively constant, although there was a significant lowering in the amounts of yttrium and ytterbium dissolved at boiling point in the higher density slurries. Generally, the recoveries of yttrium, ytterbium and scandium, expressed as percentages of the total of each in the solid, were encouraging. The recoveries of ytterbium and scandium were consistently in excess of 90% and amounts dissolved are, in fact, considered to represent virtually complete recovery of the three elements when allowances are made for variations in experimental procedure and in analytical accuracy.

The material from Dam 5 and Dams 2, 3 and 4 combined behaved in a similar manner to the sulphate material from Dam 6, but recoveries by leaching were generally lower. Iron was removed almost completely by leaching the heated material at boiling point, but the recoveries of yttrium, ytterbium and scandium were also considerably lower.

The higher losses of iron and the other components from these samples when leached at boiling point are almost certainly the result of lower acidity levels in the liquors.

The aqueous liquors obtained by leaching the heated material are much more suitable for extraction of scandium and lanthanide elements by phosphate type solvents than liquors obtained by direct solution of the sulphates, because of the much smaller relative amounts of iron present. On the other hand, the relative amounts of iron and other elements such as aluminium and magnesium would still be much too high to permit any reasonable grade of product to be obtained by direct precipitation as, say, hydroxides. Probably yttrium and lanthanides could be precipitated from the liquors as oxalates in a fairly pure form but the subsequent recovery of scandium from the liquor would be difficult. It therefore seemed more desirable to operate a solvent extraction system which would also enable scandium to be recovered, because subquent separation of scandium from the other components is relatively simple.

4.3 Extraction with EHPA

A leach liquor was prepared by first roasting 500 g of Dam 6 composite at 720°C for a total of 6½ hours (Y11/9), and then leaching the roasted material with 1000 ml of boiling water.

Aliquots of the liquor were contacted with EHPA-kerosene solutions containing 5% nonanol, at an aqueous to organic ratio of 10. The EHPA concentration ranged from 0.1N to 1.0N as determined by titration against standardised alcoholic potassium hydroxide solution.

The liquors were shaken in separating funnels for two minutes, then the phases were allowed to separate and the aqueous layers were analysed.

The concentrations of the elements in the organic layer were calculated by difference. Extraction data for Y, Sc and Fe are given in Table 4. The results showed (as expected) that scandium would extract completely at EHPA concentrations as low as 0.1N, but that the yttrium extraction was less favourable. At 0.4N EHPA, 77% of the yttrium and 21% of the iron were extracted. At higher concentrations of EHPA the extraction of iron increased rapidly; e.g., at 0.6N, 98% of the yttrium and 50% of the iron were extracted.

4.4 Separation of Composite Samples by Sedimentation

This was done by settling water suspensions of samples for fixed time intervals thus producing 'light' and 'heavy' fractions and an aqueous solution. It was hoped that rare earths would collect preferentially in one of the fractions. This did happen to a slight degree in the light fraction, but the rare earths were no more readily recoverable from this material than from the original material.

A typical separation by sedimentation was conducted as follows:

(1) A 50-g sample of Y3 (composite of Dam 3 East) was added to 400 ml of water in a 600-ml beaker over a period of 30 seconds. Mechanical stirring was maintained throughout.

(2) Stirring was continued for 10 minutes.

(3) The mixture was left standing for 20 seconds.

(4) Supernatant liquor containing the 'light' fraction was poured off in 10 seconds into another 600-ml beaker.

(5) The remaining 'heavy' residue was washed with 200 ml water by stirring manually for 30 seconds and standing for 20 seconds.

(6) The supernatant liquor was poured off and discarded. The heavy residue was collected on a Buchner funnel.

(7) The supernatant liquor from Step (4) was again stirred manually for 30 seconds, left standing for another 20 seconds and another heavy fraction was collected. This was combined with the previous one yielding a total 'heavy' fraction. The 'light' fraction was obtained by filtering the supernatant liquor mentioned above. The 'heavy' and 'light' fractions were further washed with water, dried at 130°C, and weighed.

The 'heavy' fraction comprised 33% and the 'light' fraction 56% of the total, leaving 11% dissolved in the aqueous fraction.

Respective fractions were analysed for yttrium, scandium and iron. No significant rare earth concentration was noted in any particular fraction. The results are given in Table 5.

5. DISCUSSION

5.1 Preliminary Experimental Work

Results of preliminary tests on air-dried sulphate material from Dam 6 showed that much of the iron could be rendered insoluble in water by heating the sulphates to a temperature in the vicinity of 600°C, without affecting the solubility of yttrium, scandium, and ytterbium sulphates. By applying this form of preliminary treatment, the subsequent recovery of yttrium and scandium could be greatly simplified.

More detailed studies have been made on fresh samples of material from Dam 6 (collected in August 1966) and also on samples from Dams 2 to 5 inclusive.

Practically all of the yttrium, scandium and ytterbium was dissolved from the Dam 6 material by water leaching at ambient temperature after heating at approximately 650°C. By leaching at boiling point the amount of iron dissolved was reduced to less than half the amount leached at room temperature. Much lower proportions of the yttrium, scandium and ytterbium were dissolved by similar treatment of the material from Dams 2 to 5 inclusive.

Despite the elimination of much of the iron (the Fe_2O_3/Y_2O_3 ratio decreased from approximately 130 in the original solid to approximately 10 in liquors derived from hot leaching of heated material), the amounts of impurities in the liquors were still comparatively high in relation to the required components. The liquors would contain aluminium and magnesium sulphates as well as iron sulphate, so direct precipitation of the yttrium, scandium, etc. as hydroxides would be impractical. The 'rare earth' constituents (i.e., yttrium, ytterbium, etc.) probably could be precipitated as insoluble oxalates from the low-iron liquors, but the scandium would not be precipitated quantitatively and its subsequent recovery from the liquors containing oxalate would be difficult. To ensure the recovery of scandium, treatment of the liquor by solvent extraction would be preferable.

The essential details of solvent extraction by di(2-ethyl hexyl) phosphoric acid (EHPA) are already available from previous investigations (Canning, 1971) so design of a suitable plant to treat known quantities of liquor would not be difficult.

Variation of the temperature at which the sulphate material was heated had little effect on the solubilities of the components investigated — namely Fe, Y, Yb and Sc. Thus, composite material from Dam 6 heated at 500, 600 and 650°C showed little difference due to the different heating temperatures.

Surprisingly, the amount of iron dissolved by either cold or hot leaching remained reasonably constant although some fall had been expected in the amount dissolved from the samples heated at the higher temperatures.

At this stage, a tentative process was proposed as a basis for estimating the probable capital and operating costs for a Treatment Plant incorporating as much as possible of the existing equipment at the Uranium Treatment Plant.

The proposed process can be divided into the following stages:

1. Roasting. Conversion of as much as possible of the iron sulphate in the solid material to insoluble iron oxide. Optimum conditions for temperature and time of heating to be determined. The type of equipment to be used also remains to be decided on, but a fluidised-bed heater to operate on slurry is preferred.

2. Leaching. Leaching with water at or near the boiling point. Existing equipment should be adequate and conditions are fairly well established.

3. Solid-Liquid Separation. Either counter-current decantation using the existing thickeners, or direct filtration could be considered. Direct filtration probably would necessitate installation of additional equipment.

4. Solvent Extraction. Much information is available already on extraction of scandium and the lanthanides by EHPA. The liquor derived by leaching the heated solids would be less complex than the original uranium-free liquor and would contain relatively larger proportions of scandium, yttrium and ytterbium with respect to other extractable components (e.g., Fe), so extraction conditions should be favourable.

5. Product Recovery. A considerable amount of work would be needed to determine suitable conditions. At this stage of the project an initial oxalic-acid sulphuric-acid strip system was contemplated, to remove components such as iron, titanium, and vanadium in soluble form and precipitate yttrium and lanthanides as insoluble oxalates. Scandium would be recovered by subsequent stripping with sodium hydroxide as in the

previous small-scale plant. Further treatment of the various products would depend on the grade of material required.

The largest single item of equipment required in addition to that already available would be the unit for heating the material before leaching. Other essential equipment of a substantial value which would also be required includes a larger solvent extraction plant and ancillary items such as a furnace for igniting products, additional filters, etc. As a very approximate estimate, a capital outlay of $250,000 (1967) might be needed for equipment to treat between 100 and 200 tonnes of solids per day, for an expected return of approximately 100 kg (200 lb) Y_2O_3 and 10 kg (20 lb) Sc_2O_3.

5.2 Laboratory Roasting Tests

The composites Y11 (Dam 6) and Y23 (Dam 5, West = 5X) when roasted at 700°C gave the highest yields of rare earths (e.g., 70% and 45% yttrium oxide) whereas the materials from the remaining dams after roasting at 600°C yielded only about 10%. At 700°C the recovery fell almost to zero. The rare earths are apparently present in a more soluble form in Dams 6 and 5 West than in the remaining dams.

An unroasted sample (Dam 3 East) was leached with hot and cold water and yielded 6% of its total yttrium content. After roasting at 600°C this sample still yielded only 6% yttrium when leached, while at 700°C the amount leached was below the limits of detection. This result is typical of those obtained for most of the residues containing solid mineral material and the conclusion is reached that roasting reduces the solubility of the iron, but has no other advantageous effect.

From Tables 2 and 3, it appears that the optimum temperature range for roasting Dam 6 material is 700 to 750°C. Below this range iron will go into solution significantly, whereas above it rare earths become insoluble.

5.3 Fluid-bed Roasting

Although previous operations were not successful because of solids fusion, sintering and caking in the bed area, no difficulty was experienced with the final run. The bed remaining at the end of operations was free of sintered material.

The start-up operation when slurry feeding is commenced appears to be the critical period. From the experience gained in these limited operations, it appears essential to establish a relatively large bed of coarser base material before feeding commences. Slurry feeding should not be attempted before the base-bed temperature is raised to at least the nominal operating temperature. A high space velocity should be maintained.

Over extended operations, an addition of a small percentage of coarse sand material to the slurry feed may be required to maintain a stable bed. During the test run, the bed quantity was reduced over the operating period (as shown by pressure-loss measurement) but operation was still stable at the lower level.

Operation of a larger fluid-bed reactor appears quite feasible. By visual observation of the physical characteristics of this material during heating from ambient to calcination temperature, it seems unlikely that successful operation of other types of calcination would be possible.

5.4 Leaching

The superiority of hot leaching is shown by the results in Tables 2 and 3. For roasted material from Dam 6, the iron content of liquor derived by hot leaching was only one third to one tenth as high as in liquor derived by cold leaching. This is, however, achieved at the expense of precipitating about one fifth of the rare earths.

5.5 Extraction with EHPA

The following observations are made from the results shown in Table 4:

Extraction of Scandium. As expected, scandium is fully extracted at concentrations of EHPA as low as 0.1N at an organic/aqueous ratio 1:10.

Extraction of Yttrium. The yttrium extraction is less favourable than that of scandium. With 0.5N EHPA, 90% yttrium is extracted but approximately 50% of the iron is also extracted.
The use of 0.4N EHPA seems to offer a possibility of recovering most of the yttrium while limiting the proportion of iron extracted.

5.6 Separation of 'Heavy' and 'Light' Fractions by Sedimentation

No significant concentration of Y_2O_3 or Sc_2O_3 was found in either the heavy or light solid fractions obtained by sedimentation in water. Although the heavy fraction consisted mainly of rutile and iron oxides, the rare elements were still present in approximately the same proportion as in the light fractions. Only small proportions of the rare elements were soluble in water, either by direct treatment or after roasting to approximately 650°C. The results are similar to those obtained by Vodic (1967), on larger composite samples. There appears to be no advantage gained by elutriation, since no concentration of rare elements can be achieved nor can a salable rutile product be obtained.

6. CONCLUSIONS AND RECOMMENDATIONS

Results of analysis of composite samples from all the solid tailings confirmed the previous figures for yttrium oxide and scandium oxide at approximately 0.13 and 0.018% respectively. However, with the exception of sulphate material from Dam 6 and part of Dam 5, the yttrium and scandium are not readily obtained in a water-soluble form. Roasting before leaching serves only to reduce solubility of iron by conversion of iron sulphate to iron oxide, but this step could not be avoided if any leaching treatment were contemplated.

Roasting in a fluid-bed reactor would be feasible and superior to any other method.

From the results obtained, the conclusion is reached that only the limited amount of sulphate material contained in Dam 6 and part of Dam 5 could be treated to recover yttrium and scandium oxides. The quantity of each oxide available for recovery in this material is approximately:

Y_2O_3	26 tons
Sc_2O_3	4 tons

Unless a definite market were available for scandium oxide at an acceptable price, consideration of further treatment of the residues would seem to be unwarranted.

7. REFERENCES

CANNING, R.G. (1961). The recovery and separation of scandium, yttrium, thorium and lanthanides by solvent extraction. *Proc. Australas. Inst. Min. Metall.* No. 198, 113-51.

VODIC, P. (1967). Laboratory concentration tests on Port Pirie Uranium plant Residue. *Amdel Report 539*.

8. ACKNOWLEDGEMENT

The assistance of Mr B.H.J. Waters in preparation of this Report is gratefully acknowledged.

APPENDIX A

ESTIMATED QUANTITIES OF YTTERBIUM, YTTRIUM AND SCANDIUM IN PORT PIRIE TAILINGS DAMS

From the estimated approximate tonnages of solids tailings and sulphate sludge at Port Pirie, and the analyses (Table 3) of the two series of samples detailed under 'Material Examined', the following figures have been calculated:

Dam		Component		Preliminary Investigation Samples			Systematic Series August 1966	
No.	Residue Wt ton			Yb_2O_3	Y_2O_3	Sc_2O_3	Y_2O_3	Sc_2O_3
2	30 000	Assay,	%	0.02	0.125	0.015	0.15	0.018
		Wt,	ton	6	37.5	4.5	45	5.4
3	80 000	Assay,	%	0.016	0.116	0.013	0.14*	0.018*
		Wt,	ton	12.8	92.8	10.4	112	14.4
4	55 000	Assay,	%	0.027	0.155	0.019	0.145*	0.021*
		Wt,	ton	14.8	85.2	10.4	79.7	11.5
5	25 000†	Assay,	%	0.018	0.122	0.018	0.125	0.029
		Wt	ton	4.5	30.5	4.5	31.2	7.2
	8 000Φ	Assay,	%	0.023	0.165	0.029	0.165	0.029
		Wt,	ton	1.8	13.2	2.3	13.2	2.3
6	10 000Φ	Assay,	%	0.029	0.127*	0.015*	0.127*	0.015*
		Wt,	ton	2.9	12.7	1.5	12.7	1.5
Total	208 000	Av.assay,	%	0.02	0.13	0.016	0.14	0.02
		Wt,	ton	42.8	272	33.6	294	42.3

* Average figures.

† Tail.

Φ Sludge.

Of the above totals, approximately 26 tons Y_2O_3 and 4 tons Sc_2O_3 were present (1966) as soluble sulphates in sludges from Dams 5 and 6.

To dissolve the values contained in the solids tailing material, a strong acid attack, similar to the original leaching operation during uranium extraction (approximately 25% H_2SO_4 at 100°C), appears to be required.

TABLES 1 to 5

FIG.1

TABLE 1: PARTIAL ANALYSES OF AIR-DRIED TAILING MATERIAL — %

Component	Sample Identification							
	Y1	Y2	Y5	Y6	Y7	Y8	Y10	Y11
Fe_2O_3	10.7	11.9	12.7	11.7	14.0	11.3	13.2	13.2
Y_2O_3	0.035	0.13	0.125	0.125	0.12	0.12	0.12	0.125
Yb_2O_3	0.015	0.035	0.033	0.036	0.032	0.034	0.29	0.03
Sc_2O_3	0.008	0.013	0.012	0.019	0.017	0.020	0.014	0.016

TABLE 2: TREATMENT OF SULPHATE MATERIAL
Dam 6 Composite Sample Y11

Conditions																					
Heating																					
Temperature,	°C	500	500	500	500	500	500	600	600	600	600	600	600	650	650	650	650	650	650	600(a)	600(a)
Time,	h	4	4	4	4	4	4	4	4	4	4	4	4	6	6	6	6	6	6	6	6
Weight loss, %		40	40	40	40	40	40	42	42	42	42	42	42	43	43	43	43	43	43	nd(b)	nd
Leaching																					
Pulp solids	%(c)	33	20	10	33	20	10	33	20	10	33	20	10	33	20	10	33	20	10	15	15
Temperature	°C(d)	A	A	A	B	B	B	A	A	A	B	B	B	A	A	S	B	B	B	A	B
Times	h	2	2	2	1	1	1	2	2	2	1	1	1	2	2	2	1	1	1	2	1
Leaching Efficiency, %																					
Y_2O_3		82	88	88	78	85	85	85	76	80	77	88	88	90	95	88	70	100	100	100	100
Yb_2O_3		100	100	100	80	95	100	95	100	100	75	95	100	95	90	100	75	95	100	90	85
Sc_2O_3		95	95	95	90	90	100	95	95	95	95	95	95	95	95	95	95	95	95	95	90
Fe_2O_3		25	28	30	11	10	9	27	29	29	13	12	10	26	25	24	13	10	10	20	9
$\frac{Fe_2O_3}{Y_2O_3}$ in liquor		30	33	36	18	12	12	34	40	38	20	15	12	28	27	29	22	10	10	16	9

(a) Samples heated in 25.4 mm (1 in.) diameter fluid-bed reactor.

(b) nd = not determined.

(c) $\% \text{ solids} = \frac{\text{Wt solids}}{\text{Wt solids + Wt water}} \times 100$

(d) A = ambient, approx. 20°C.
B = 90 to 100°C.

TABLE 3: RECOVERY OF RARE ELEMENTS AND IRON FROM DAMS 2-6 BY ROASTING AND SUBSEQUENT LEACHING

Origin*	Sample No.	Roasting Temp. °C	Leaching Temp. °C	Proportion of Components Leached				Components in Original Material,%			
				Y_2O_3,%	Yb_2O_3,%	Fe_2O_3,%	Sc_2O_3,%	Y_2O_3	Yb_2O_3	Fe_2O_3	Sc_2O_3
Dam 6 (Clay layer)	Y1	–	–	–	–	–	–	0.035	0.015	10.7	0.008
	Y1	650	RT	91	77	3	100	–	–	–	–
	Y1	650	100	71	76	0.[illegible]	30	–	–	–	–
Dam 6	Y5	–	–	–	–	–	–	0.115	0.027	14.8	0.015
	Y5	750	RT	64	65	0.03	7.9	–	–	–	–
	Y5	750	100	48	60	0.04	2.4	–	–	–	–
Dam 6†	Y11	–	–	–	–	–	–	0.125	0.030	13.2	0.016
	Y11	500	RT	87	97	27.5	100	–	–	–	–
	Y11	500	100	84	93	10.4	94	–	–	–	–
	Y11	600	RT	77	87	27.6	94	–	–	–	–
	Y11	600	100	82	93	11.8	90	–	–	–	–
	Y11	650	RT	95	83	24.8	94	–	–	–	–
	Y11	650	100	82	90	10.8	89	–	–	–	–
	Y11	720	RT	80	87	6.1	88	–	–	–	–
	Y11	720	100	58	77	0.7	75	–	–	–	–
Dam 6†	Y17	–	–	–	–	–	–	0.130	0.029	12.4	0.015
	Y17	700	100	67	–	0.63	70	–	–	–	–
	Y17	750	RT	77	–	1.6	84	–	–	–	–
	Y17	750	100	66	–	0.6	84	–	–	–	–
	Y17	800	RT	56	–	0.1	Φ	–	–	–	–
	Y17	800	100	13	–	0.1	Φ	–	–	–	–
Dam 6δ	Y26	720	100	62	–	3.0	80	–	–	–	–
Dam 5 East (B5A)	Y14	–	–	–	–	–	–	0.122	0.018	24.1	0.018
	Y14	720	RT	2.7	5.6	0.02	Φ	–	–	–	–
	Y14	720	100	0.8	0.5	0.02	Φ	–	–	–	–
	Y14	720	RT	Φ	Φ	<0.01	Φ	–	–	–	–
	Y14	750	100	Φ	Φ	<0.01	Φ	–	–	–	–
Dam 5 West (5X)	Y23	–	–	–	–	–	–	0.165	0.023	21.5	0.029
	Y23	600	RT	42.5	–	33	55	–	–	–	–
	Y23	600	100	48.5	–	6.6	62	–	–	–	–
	Y23	700	RT	37.5	–	4.9	62	–	–	–	–
	Y23	700	100	35	–	2.4	48	–	–	–	–
Dam 5 East	Y24	–	–	–	–	–	–	0.125	0.023	21.5	0.029
	Y24	600	RT	8	–	[illegible]	58.5	–	–	–	–
	Y24	600	100	8	–	[illegible]	58.5	–	–	–	–
	Y24	700	RT	4	–	–	Φ	–	–	–	–
	Y24	700	100	4	–	–	Φ	–	–	–	–
Dam 4 (B4 + B4A)	Y12	–	–	–	–	–	–	0.155	0.027	27.8	0.019
	Y12	720	RT	5.8	10	<0.01	10.5	–	–	–	–
	Y12	720	100	4.9	8.9	<0.02	0.05	–	–	–	–
	Y12	750	RT	Φ	Φ	<0.01	Φ	–	–	–	–
	Y12	750	100	Φ	Φ	<0.01	Φ	–	–	–	–

(Continued)

TABLE 3: CONTINUED

Origin*	Sample	Roasting Temp. °C	Leaching Temp. °C	Proportion of Components Leached				Components in Original Material, %			
				Y_2O_3,%	Yb_2O_3,%	Fe_2O_3,%	Sc_2O_3,%	Y_2O_3	Yb_2O_3	Fe_2O_3	Sc_2O_3
Dam 4 West	Y21	–	–	–	–	–	–	0.110	0.017	16.0	0.016
	Y21	600	RT	20	–	–	44	–	–	–	–
	Y21	600	100	18	–	–	44	–	–	–	–
	Y21	700	RT	11	–		Φ	–	–	–	–
	Y21	700	100	9	–		Φ	–	–	–	–
Dam 4 East (4Y)	Y22	–	–	–	–	–	–	0.180	0.026	22.3	0.026
	Y22	600	RT§	6.7	–	–	Φ	–	–	–	–
	Y22	600	100	6.7	–	–	Φ	–	–	–	–
	Y22	700	RT	0.1	–	–	Φ	–	–	–	–
	Y22	700	100	Φ	–	–	Φ	–	–	–	–
Dam 3 East (B3A)	Y13	–	–	–	–	–	–	0.142	0.022	17.1	0.018
	Y13	720	RT	8.0	5.5	0.01	Φ	–	–	–	–
	Y13	720	100	4.0	5.2	0.01	Φ	–	–	–	–
Dam 3 (B3 + B3A)	Y15	–	–	–	–	–	–	0.116	0.016	22.0	0.013
	Y15	750	RT	Φ	Φ	0.04	Φ	–	–	–	–
	Y15	750	100	Φ	Φ	0.06	Φ	–	–	–	–
Dam 3 West (3X)	Y19	–	–	–	–	–	–	0.120	0.018	21.7	0.018
	Y19	600	RT	10	–	1.9	17.8	–	–	–	–
	Y19	600	100	8.3	–	0.34	5.5	–	–	–	–
	Y19	700	RT	Φ	–	–	Φ	–	–	–	–
	Y19	700	100	Φ	–	–	Φ	–	–	–	–
Dam 3 East (3Y)	Y20	–	–	–	–	–	–	0.160	0.019	24.7	0.018
	Y20	600	RT	6.3	–	–	20.3	–	–	–	–
	Y20	600	100	6.3	–	–	6.7	–	–	–	–
	Y20	700	RT	Φ	–	–	Φ	–	–	–	–
	Y20	700	100	Φ	–	–	Φ	–	–	–	–
Dam 2 (B2A)	Y16	–	–	–	–	–	–	0.125	0.018	22.0	0.0146
	Y16	750	RT	Φ			Φ	–	–	–	–
	Y16	750	100	Φ	–	–	Φ	–	–	–	–
Dam 2 (2X)	Y18	–	–	–	–	–	–	0.150	0.020	25.6	0.018
	Y18	600	RT	8	–	0.04	5.5	–	–	–	–
	Y18	600	100	6.5	–	0.04	2.7	–	–	–	–
	Y18	700	RT	0.13	–	–	1.0	–	–	–	–
	Y18	700	100	0.13	–	–	1.0	–	–	–	–

---

* Department of Mines designation in parentheses.

† Y11 and Y17 are composites of Dam 6 material having almost identical compositions.

Φ Less than 0.001%.

δ Fluidised-bed roasting, cyclone product.

§ RT = Room temperature (approx. 20°C).

TABLE 4: EXTRACTION OF RARE ELEMENTS WITH EHPA
EHPA-Kerosene solutions: 0.1-0.9N
Aqueous liuqor Y/11/9/3
Dam 6, Roast at 720°C, Hot water leach

Organic/Aqueous Volume Ratios	EHPA Normality	Concentration, Aqueous Phase after Extraction			% Extracted		
		Y_2O_3 g/l	Fe_2O_3 g/l	Sc_2O_3 g/l	Y_2O_3	Fe_2O_3	Sc_2O_3
Original aqueous phase: 1:10	-	0.36	0.45	0.059	-	-	-
1:10	0.1	0.29	0.36	*	27	20	100
1:10	0.3	0.18	0.40	*	55	11	100
1:10	0.4	0.09	0.34	*	77	21	100
1:10	0.5	0.04	0.30	*	89	33	100
1:10	0.6	0.01	0.23	*	98	49	100
1:10	0.8	*	-	*	100	-	100
1:10	0.9	*	0.16	*	100	64	100

* Below detection (less than 0.001 g/l).

TABLE 5: DISTRIBUTION OF HEAVY, LIGHT AND SOLUBLE FRACTIONS OF ELUTRIATED SAMPLE ex DAM 3 EAST (3Y)

Fraction	Weight Distribution	Milligramme per Gramme			Milligrammes Present		
	g	Y_2O_3	Fe_2O_3	Sc_2O_3	Y_2O_3	Fe_2O_3	Sc_2O_3
Original (3Y)	100	1.60	247	0.18	160	-	18.0
Heavy (3YH)	33	1.10	-	0.25	36.3	-	8.2
Light (3YL)	56	2.04	-	0.16	113.7*	-	8.8*
Soluble (3YA)	-	-	-	-	10	28	1.0
Y/25/1†	-	<0.025	0.12	Φ	<0.5	0.25	<0.05

* Calculated by difference.

† Y/25/1 is leach liquor from 3YL. 20 g of 3YL were roasted at 650°C yielding 18 g of roasted material which was leached with 50 mℓ of hot water for 1 hour.

Φ Below detection.

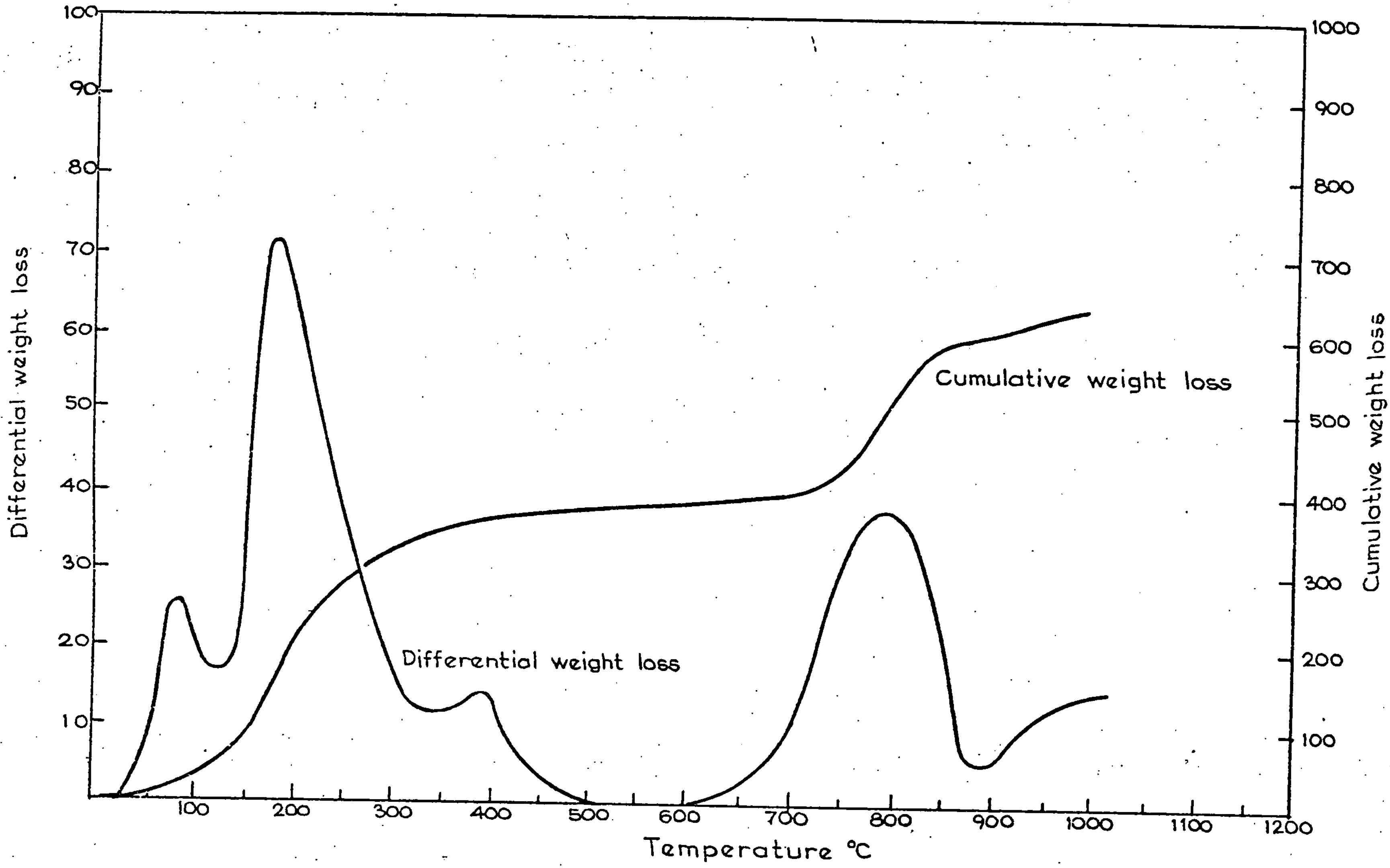

FIG. 1: THERMOGRAVIMETRIC ANALYSIS OF COMPOSITE SAMPLE FROM DAM 6