IAEA-TECDOC-420

ADVANCES IN URANIUM REFINING AND CONVERSION

PROCEEDINGS OF A TECHNICAL COMMITTEE MEETING
ON ADVANCES IN URANIUM REFINING AND CONVERSION
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN VIENNA, 7-10 APRIL 1986

A TECHNICAL DOCUMENT ISSUED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1987

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Printed by the IAEA in Austria
May 1987

FOREWORD

One of the most important steps in the Nuclear Fuel Cycle is the Uranium Refining and conversion which goes from the yellow-cake to three different products: uranium dioxide (UO_2), natural metallic uranium (U) and uranium hexafluoride (UF_6). Although its added value is small, may be 2-4% of the total cost of front-end, it is decisive for producing fuel for both types of reactors: natural uranium (Magnox and Candu) and enriched uranium (LWR). In this step of the cycle the uranium hexafluoride is produced which is very important for the enrichment of uranium.

The total volume of this industry, at the present time, is nearly of 40,000t U per year and at the end of the present century it would have reached the 60.000t U/a level.

The Agency held an Advisory Group meeting on the production of yellowcake and uranium fluorides in Paris, June 1979 and its proceedings were published in 1980. During these seven years, significant improvements have been made in technology and in equipment for the uranium refining and conversion, particularly from the environmental, safety and economic viewpoints. The refining and conversion of reprocessed uranium that can be extracted by treating irradiated fuel become equally important for recycling recovered fuel.

In response to the growing interest in these topics, the IAEA convened a Technical Committee Meeting on "Advances in Uranium Refining and Conversion" at its Headquarters from April 7 to 10, 1986 with the attendance of 37 experts from 21 countries. This Technical Document contains the 20 papers presented during the meeting.

The Agency wishes to thank all the scientists, engineers and institutions who contributed to this Meeting with their papers and their participation. Special thanks are due to the Chairmen, Messrs. H. Page (U.K.), A.W. Ashbrook (Canada), R. Faron (France), E. Leyser (Federal Republic of Germany), A.G.M. Jackson (South Africa), I.S. Chang (Republic of Korea) and J.A. Vercellone (Argentina). The officers of the IAEA, responsible for the organization of the meeting, was Mr. M. Ugajin and for editing the document was Mr. J.L. Rojas of the Nuclear Materials and Fuel Cycle Technology Section.

EDITORIAL NOTE

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PART I

RECENT ADVANCES IN THE REFINING OF FRESH URANIUM MATERIALS

THE REFINING AND CONVERSION OF URANIUM YELLOWCAKE TO URANIUM DIOXIDE AND URANIUM HEXAFLUORIDE FUELS IN CANADA: CURRENT PROCESSES

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Abstract

In Canada, uranium yellowcake is now refined at Blind River and the uranium trioxide produced is shipped 500 km south to Port Hope where it is converted to uranium dioxide and hexafluoride fuels.

There have been some significant changes in the processes used in these new plants. Perhaps the most significant is the production of uranium tetrafluoride from uranium trioxide using a "wet" process. In this paper the current processing methods are reviewed, with special emphasis on changes from the previous methods.

INTRODUCTION

Eldorado Resources Ltd. has operated uranium refining facilities at Port Hope, Ontario, since 1942. It was not, however, until 1955 that solvent extraction was used to produce nuclear grade uranium trioxide. In 1958 the production of uranium dioxide was commenced to provide fuel for domestic CANDU reactors. Conversion facilities were added in 1970 to produce uranium hexafluoride for export.

In 1975 a decision was made to build a new refining and conversion facility in the Port Hope area. The outcome was, however, that a new refinery was built at Blind River in northern Ontario (some 500 km north of Port Hope) and a new uranium hexafluoride plant built at the existing Port Hope facility. The Blind River refinery came on-stream in 1983 and the Port Hope conversion facility in 1984.

Today, in Canada, uranium yellowcake is refined at Blind River and the uranium trioxide produced is shipped 500 km south to Port Hope where it is converted to uranium dioxide and hexafluoride fuels.

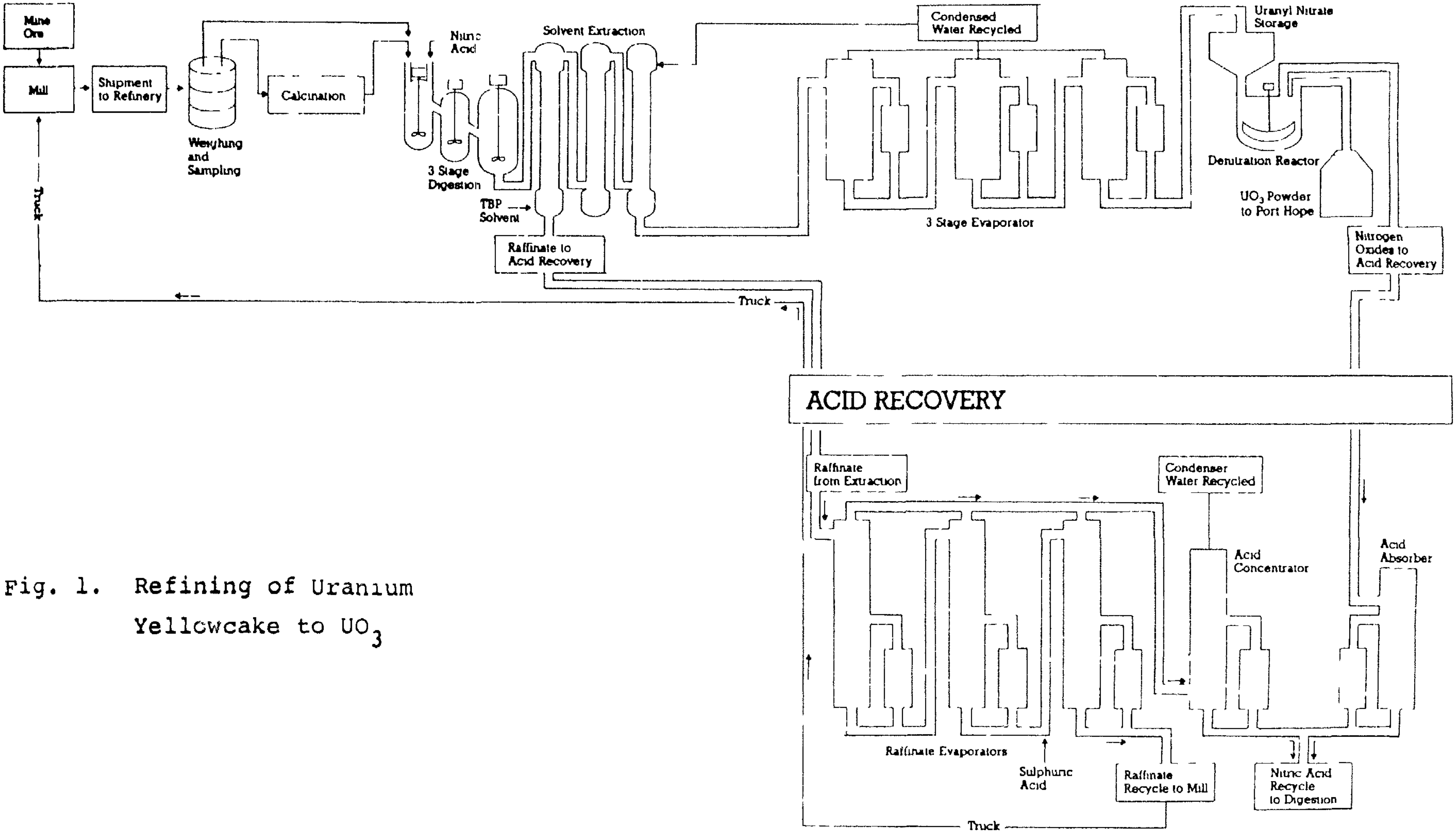

Fig. 1. Refining of Uranium Yellowcake to UO_3

There have been some significant changes in the processes used in these new plants. Perhaps the most significant is the production of uranium tetrafluoride from uranium trioxide using a ''wet'' process. In this paper the current processing methods are reviewed, with special emphasis on changes from the previous methods.

THE REFINING PROCESS

The refining of uranium yellowcakes (concentrates) to nuclear grade uranium trioxide (UO_3) at the Blind River facility of ERL is shown schematically in Figure 1. It varies little from the process used previously at Port Hope. The component steps in this process are:

- weighing, sampling, analysing and blending of the concentrates
- digestion of the concentrates in nitric acid
- purification of the digested concentrates by solvent extraction
- evaporation of the pure uranyl nitrate solution resulting from solvent extraction to uranyl nitrate hexahydrate (UNH)
- denitration of the UNH to produce UO_3
- recovery of nitric acid from the SX raffinate by evaporation with sulphuric acid
- recycle of the concentrated raffinate to uranium mills
- shipping UO_3 to Port Hope

Each of the above component parts of the process is briefly described below.

Weighing and sampling, etc.

This is generally the normal approach taken in the industry. An auger sampling technique was adopted for the BRR, although both auger and falling stream methods had been employed at Port Hope.

Digestion

Concentrates are dumped from the drums and fed to digestion tanks in a continuous two-tank cascade system. Dissolution is with concentrated (13M) nitric acid to produce a slurry containing about 400 kg m^{-3} U at a free acid concentration of less than 2M. Solids concentration in the slurry is normally less than 1 per cent, and is comprised largely of silica. Phosphoric acid may be added at this stage to reduce thorium extraction in the solvent extraction circuit.

The two-tank system operates continuously and feeds four hold (feed) tanks, which then feed the solvent extraction circuit.

Off-gases from digestion - largely nitrogen oxides - are fed through a venturi scrubber, and the resultant liquor returns to the digestion tanks. Non-condensibles go to the nitric acid recovery circuit (see below).

Solvent Extraction

This circuit differs from that employed previously at the Port Hope facility in that it uses Mixco (Oldshue-Rushton) - rather than pulse - columns, which are arranged in two parallel trains. Each train contains 3 columns, one each for extraction, scrubbing and stripping.

Dimensions of the extraction columns are 11.3 m in height and 1.1 m in diameter. The scrub and strip columns are smaller, being 9.0 m in height and 1.1 m in diameter. To reduce entrainment carryover between columns, solvent settling tanks are employed. These also provide for some surge capacity in the circuit.

The digestion feed is contacted with a solvent comprising 22 vol per cent tributylphosphate (TBP) in a saturated hydrocarbon diluent - ISOPAR M. The O/A ratio used in extraction is about 4, and at a temperature of approximately 60°C.

Scrubbing of impurities from the loaded solvent occurs in the second column, and is achieved using water at an O/A ratio of 15. Scrub liquor is recycled.

Finally, the uranium is stripped from the solvent phase, again with water but at an O/A ratio of 1.2, to produce a pure uranyl nitrate solution normally referred to as OK liquor.

As in all solvent extraction processes used in the refining of uranium, there is a need to maintain solvent purity. A bleed (~10%) of stripped solvent is treated with a sodium carbonate solution prior to recycle to extraction. After contacting with the carbonate solution the aqueous and solvent phases are separated by centrifuges. The solvent phase is returned to the extraction circuit, while the aqueous phase containing the impurities is acidified and the resultant organic (non-soluble) product is filtered on a pre-coat pressure tube filter.

Evaporation of the OK Liquor

The OK liquor resulting from stripping the purified uranium from the solvent normally contains about 100 kg m^{-3} of uranium. This is evaporated and concentrated to some 1200 kg m^{-3} uranium (uranyl nitrate hexahydrate, UNH) in a three-stage evaporator. Evaporation is achieved in the first stage by steam heating. In the second and third stages, overhead steam from the preceding stage is used as the energy source. After the third stage the steam is condensed, and used as the strip water in the solvent extraction circuit.

Product from the third evaporator stage, molten UNH, is contained in a heated tank which feeds the denitration pots.

Denitration

Denitration of the UNH to UO_3 is carried out in heavy-walled, semi-spherical vessels stirred by an agitator. This is the same technology employed previously at the Port Hope facility.

The UNH is fed continuously to the denitration pots (currently 12 in all) where it is thermally decomposed at about 280°C to UO_3. The reaction products, nitrogen oxides, acid, and water, are scrubbed to condense water and acid. The scrubbed vapors then go to absorbers to produce nitric acid.

Raffinate Treatment and Recycle

Raffinate from the solvent extraction circuit accounts for almost all of the wastes generated at the BRR. It is recycled, after treatment, to uranium mills at Elliot Lake, some 50 km north of the Refinery. Because of the importance of raffinate recycle, a special circuit was installed in the BRR.

Raffinate from the solvent extraction circuit contains nitrate salts and impurities from the uranium concentrates. It is necessary to remove nitric acid, and this is achieved by evaporation of the raffinate with the addition of sulphuric acid to decompose nitrate salts and produce sulphates and nitric acid.

From the extraction column in the solvent extraction circuit the raffinate is pumped to hold tanks where it is settled, and then pumped to a raffinate evaporation circuit comprising three evaporation stages. Partial evaporation in the first stage is effected in a shell and tube heat exchanger employing the excess heat in the overheads from the third stage of the OK liquor boildown evaporator. Vapors from this stage (dilute nitric acid) go to the first nitric acid concentrator.

In the second stage of raffinate evaporation, sulphuric acid is added resulting in the conversion of nitrates into nitric acid which is sent to the second concentrator for recovery. In the final stage of evaporation, the concentrated raffinate is drawn off into tanks at a density of between 1.6 and 1.7 kg m^{-3}. Generally the sulphuric acid concentration is about 450 g/L, nitrate content less than 1 per cent, and contains uranium at 1-3 kg m^{-3}.

The concentrated raffinate is transferred to tank trucks and transported to the uranium mills at Elliot Lake to be introduced into the milling circuits. Here, the sulphuric acid in the raffinate contributes to the dissolution of ore, and the uranium in the raffinate is recovered in the mill. Impurities in the raffinate go with the mill tailings to the tailings pond.

Nitric Acid Recovery

Recovery of nitric acid in the BRR is achieved in two acid absorbers and two acid concentrators, each set operating in parallel.

Off-gases from the concentrate digestor and denitration fume scrubbers pass through the acid absorbers where, in contact with water, nitric acid is produced. Uncondensed nitrogen oxide from the absorbers enter a catalytic converter which converts the NO_x to nitrogen and water before exhaust to atmosphere. The aqueous (dilute nitric acid) phase from each

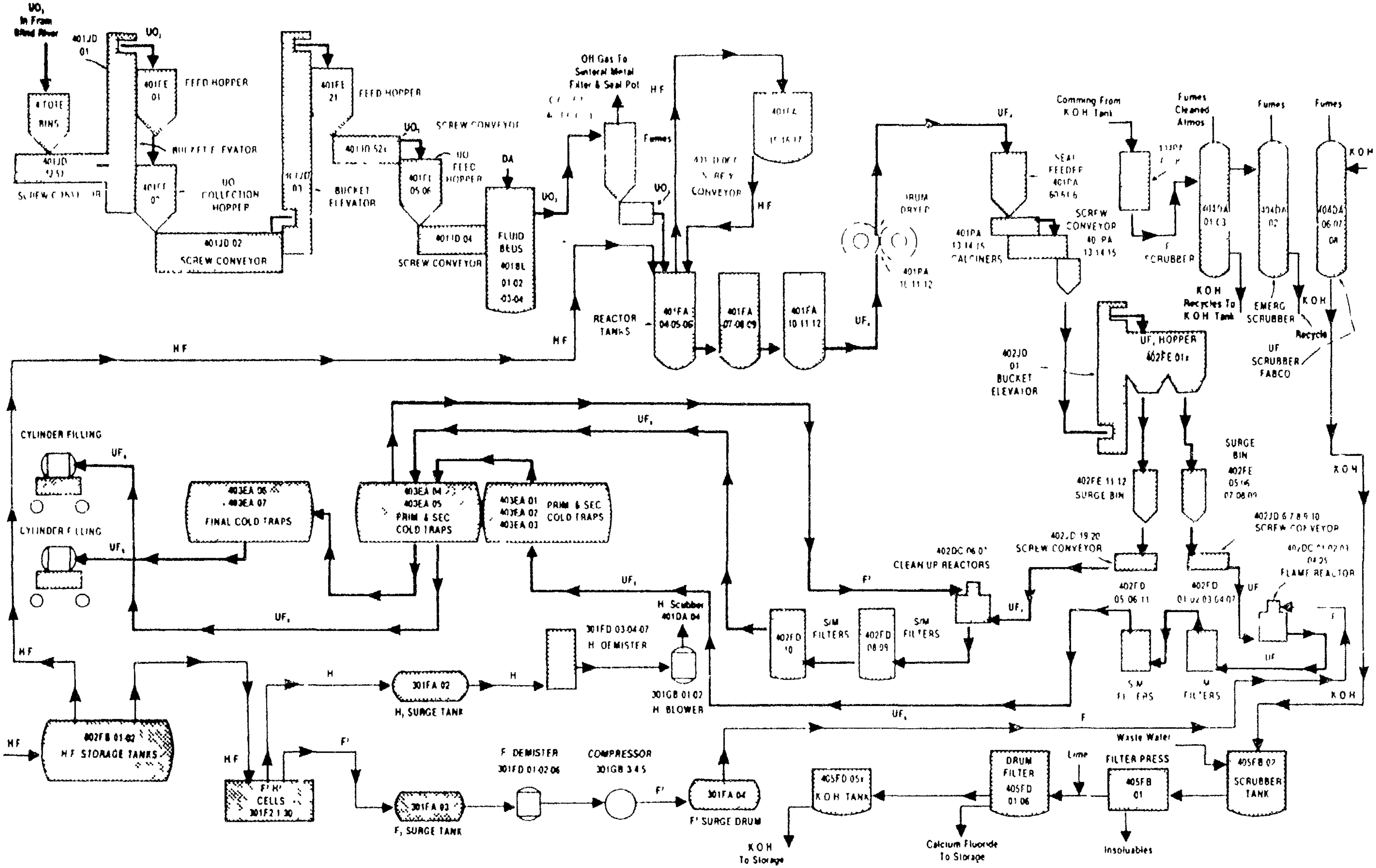

Fig. 2. Conversion of UO_3 to UF_6

acid absorber, together with vapors from the second and third stage raffinate evaporators, is sent to the acid concentrators. Here, the nitric acid is concentrated to about 13M, which is then returned to the digestion stage.

Uranium Trioxide Transportation

The UO_3 product from the refinery is shipped to Port Hope in 10t tote bins. Each bin is filled from two denitration pots (concurrently), and is sampled continuously. Bins stand on load cells during filling, and are accurately weighed prior to shipping.

After analysis of the sample for each tote bin, they are shipped to Port Hope on a specially designed flat-bed truck, which hauls three bins, or about 30t (net) of UO_3 (39 gross weight).

THE CONVERSION PROCESSES

The processes used for the conversion of UO_3 to both UF_6 and UO_2 are shown schematically in Figures 2 and 3. The major difference in conversion carried out in the new conversion facility at Port Hope (UF_6W) is the use of a "wet-way" process for the production of UF_4. Developed by Eldorado, the process provides several advantages over the dry process employed in the east UF_6 plant, which was brought on-stream in 1970.

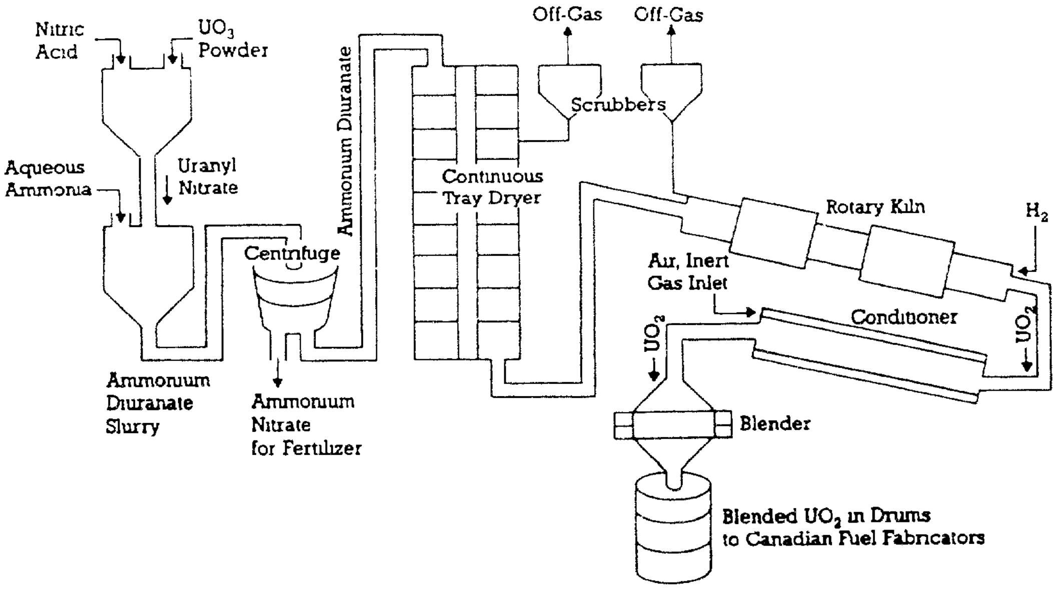

Fig. 3. Conversion of UO_3 to UO_2 Fuel Powder

COMPONENT STEPS IN THE CONVERSION OF UO_3 TO UF_6

A schematic of the UF_6 process is shown in Figure 2. The component steps in this process comprise:

- UO_3 receiving
- conversion of UO_3 to UO_2
- conversion of UO_2 to UF_4
- conversion of UF_4 to UF_6
- hydrogen fluoride recovery
- effluent treatment

Each unit process is described briefly below.

UO_3 Receiving/Feeding

UO_3 is shipped from Blind River to Port Hope in 10t tote bins. When received at Port Hope, the cover caps are replaced by valves. The tote bin is then inverted over the receiving screw conveyer and emptied by gravity. The screw conveyers feed a bucket elevator, which conveys the UO_3 to a primary feed surge hopper, through a tramp screen to remove lumps. Material passing the screen is fed, via a surge hopper, to a pulveriser and thence via a bucket elevator to the final UO_3 feed hopper.

UO_3 to UO_2

Pulverised UO_3 from the final feed hopper is screw fed to fluid beds in which the reduction to UO_2 occurs. Hydrogen is used as the reducing gas. The UO_2 product is then conveyed through a cooling screw to a feed hopper.

UO_2 to UF_4

UO_2 is fed via screw conveyers into a series of three reaction tanks. Here the UO_2 is slurried with hydrofluoric acid to convert it to UF_4. The conversion is carried out continuously in a series of three tanks in a cascade process at about 90°C. Product slurry from the last tank is fed to a drum drier where the UF_4 is dried, and the aqueous HF driven off and the vapors scrubbed to recover dilute HF solution. This is returned to the UF_4 reaction tanks. From the drum drier the UF_4 is calcined to remove the remaining water.

UF_4 to UF_6

UF_4 is transported to the fluorination process via screw conveyers and discharged into a bucket elevator. The elevator carries the UF_4 to the eighth floor, where it is discharged to a tramp screen to remove 7 1/8" material. After screening the UF_4 falls to a surge bin. From here, it is fed via screw conveyers to both the flame reactor and the clean-up reactor surge bins.

Flame reactors are fed from screw feeders, which also maintain a seal against the flame reactor pressure. UF_4 and fluorine (pre-heated to 450°C) are reacted at the UF_4 powder dispersers at the top of the reactor. Most of the reaction of UF_4 with F_2 occurs in the top 2m of the reactor, at 455-549°C, under a positive pressure of some 2kPa.

Unreacted products and ash fall to the bottom of the reactors and are collected in heated ash cans. These are changed as required. After cooling for several months the material is recycled to the flame reactors.

Product UF_6, containing small amounts of UF_4, HF and non-condensible gases and particulates leaves the reactor through primary sintered metal filters to secondary filters. Particulate matter from the filters is collected in ash cans.

Filtered UF_6 is then fed to cold traps where it is separated from HF and F_2 which is routed to the clean-up reactors.

In the clean-up reactors excess UF_4 is reacted with the gases from the UF_6 cold traps in a manner similar to that of the flame reactors, and operate at about 400°C. Products from the clean-up reactors (UF_6 gas, unreacted UF_4 and ash) are discharged by a screw conveyer to seal hoppers, where UF_6, HF and non-condensibles is drawn through clean-up reactor primary and secondary filters, the gases going to the cold traps. Unreacted UF_4 is then fed to the flame reactors.

UF_6 collected in the primary and secondary cold traps is heated and fed to the final cold traps, from where it goes to cylinder filling.

Fluorine Production

Fluorine is produced by the electrolysis of anhydrous HF in KHF_2 in 12,000 amp cells with individual rectifiers, in the usual way.

Fluorine is collected in a surge drum, and is then compressed through sintered monel demisters to the feed drum, and thence to the flame reactors. Hydrogen produced in the electrolysis goes to a surge drum, through demisters and compressors, and is scrubbed of HF in a water scrubber. The scrubbed hydrogen then passes through a potassium hydroxide seal pot to atmosphere.

Hydrogen Fluoride Recovery

One of the major reasons for adopting the "wet-way" UF_4 process was its ability to recover and reuse HF. This not only reduced operating costs but also the amount of waste being generated. The main HF recovery system employs water scrubbing of HF-containing gaseous streams. The general scheme is shown in Figure 4.

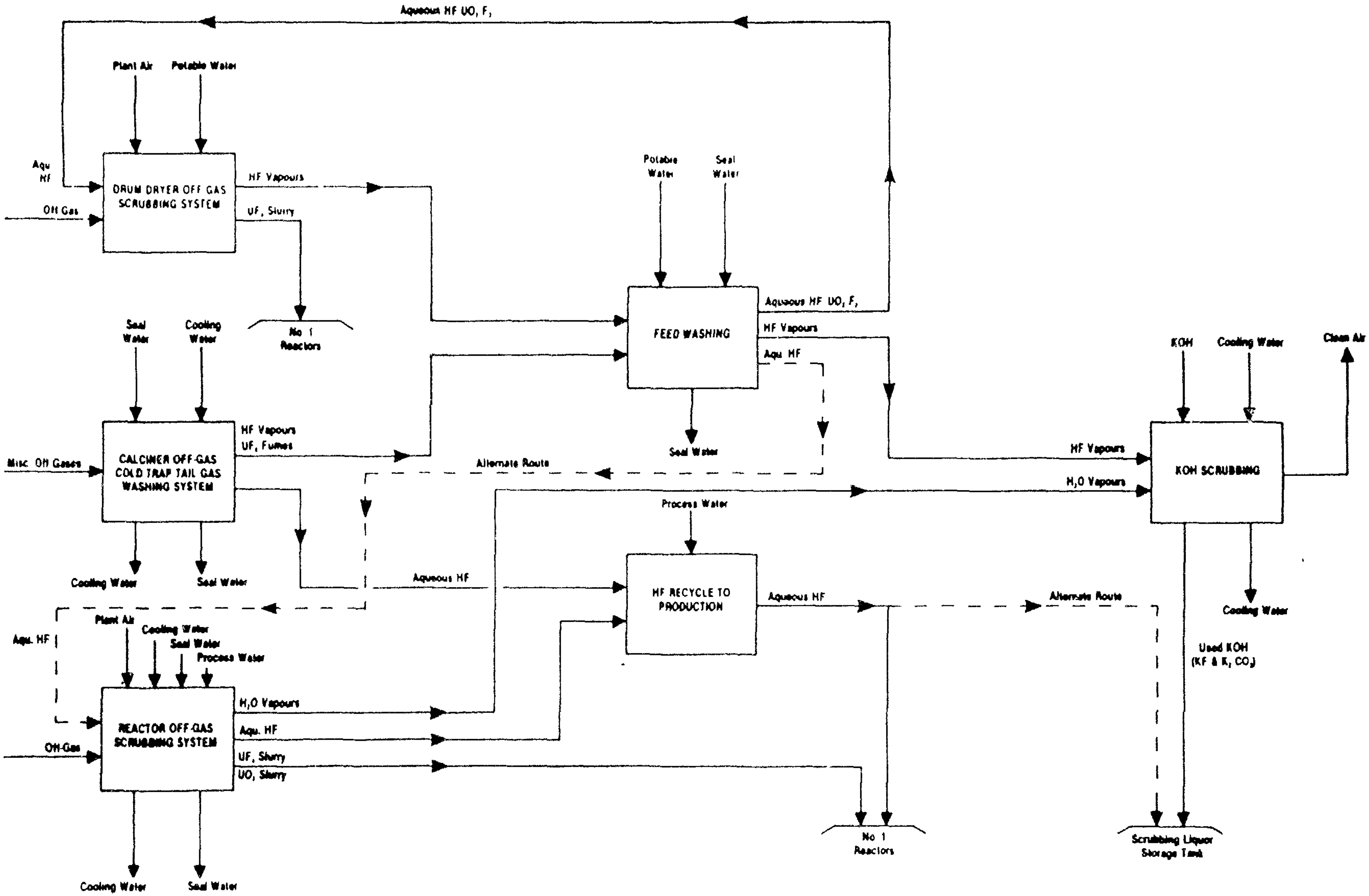

Fig. 4. HF Recovery System

Effluent Treatment

The overall effluent treatment process is divided into four functional areas -

- uranium recovery and equipment cleaning
- fluoride and carbonate removal
- potassium hydroxide regeneration and storage
- area fume removal and scrubbing

These areas are shown schematically in Figure 5.

Conversion of UO_3 to UO_2

Uranium trioxide from the Blind River refinery is dissolved in nitric acid to produce a uranyl nitrate solution of about 200 g/L U (Figure 3). This solution is precipitated with anhydrous ammonia to produce an ammonium diuranate (ADU) slurry. The ADU is separated by centrifugation, and the wet solid is dried using a Weismont drier.

After drying, the ADU is fed to rotary kilns where it is reduced to UO_2 by hydrogen (cracked ammonia). The product UO_2 is packaged for shipment to fuel fabricators for fuel pellet production and encapsulation into fuel bundles for CANDU reactors.

The ammonium diuranate produced in the ADU step is evaporated to 550-600 g/L ammonium nitrate and sold locally as a fertiliser.

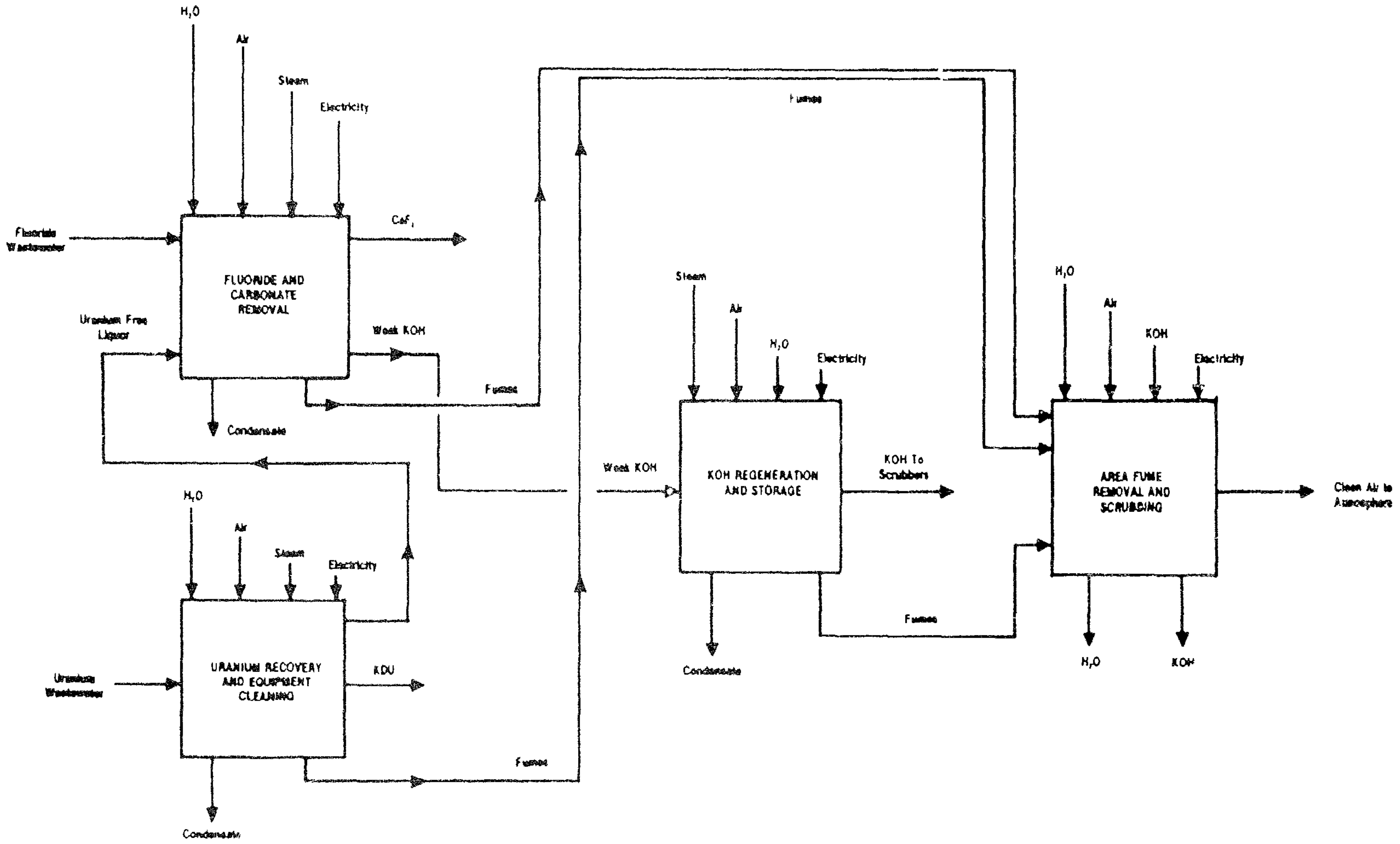

Fig. 5. Effluent Treatment

RECENT ADVANCES AND PRESENT STATUS OF URANIUM REFINING IN INDIA

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Abstract

The present requirement of reactor grade natural uranium-di-oxide and metal for power and research reactors are met by indigenous production. The purity of the final product is achieved by solvent extraction process using Tri butyl-phosphate. This involves handling of large quantities of slurry and pulping, filtration and evaporation operations. The calcination and reduction are carried out in rotary furnaces which are more amenable for smaller scale of operations.

An extraction unit has been developed for uranium extraction directly from slurries, thus eliminating a number of process steps that are normally involved with the conventional perforated plate pulsed columns. Developmental efforts were also directed towards the studies on recovery of Uranium by Ammonium-Uranyl-Carbonate (AUC) route & calcination of AUC & reduction of UO_3 (obtained by ADU route) in the fluidized bed reaction systems.

This paper brings out the process developments, which have taken place in India in the recent past, that would make the refining operations much more simpler and adoptable for larger scale of operations.

INTRODUCTION

India, like other countries in the world, has followed the conventional route for refining of Uranium to get the reactor grade Uranium-di-Oxide and metal. The refining process essentially involves purification by selective extraction of uranium using tri-butyl-phosphate (TBP), precipitation as ammonium-di-uranate and subsequent calcination and reduction to UO_2 followed by stabilization under controlled conditions to enable it to be handled in open atmosphere. The UO_2 powder thus obtained, is finally pulverized and blended to get a homogeneous product, free from agglomerates and suitable for pelletizing. A flowsheet of the process, starting from yellow cake, is given in fig.1. For making the metal, the UO_2 is hydrofluorinated and the UF_4 is reduced with magnesium.

For extraction of uranium from crude uranyl nitrate solution, perforated plate, pulsed columns are used which are operable with clear filtered solution. However, magnesia used at earlier stage of precipitation of yellow cake, has been leading to fine silica particulates being carried over to the filtered solution. This gives rise to some operating problems in the extraction columns. The silicious material accumulates at the interphase, resulting in entrainment in the extract phase. The pipe lines, sieve - plates, valves and even the column heads get deposited with silica resulting in frequent cleaning and washing operations. Further, the cake obtained after filtration of crude uranyl nitrate solution contains appreciable amount of soluble uranium. The cake has, therefore, to be pulped and filtered three to four times to recover uranium and for decontamination

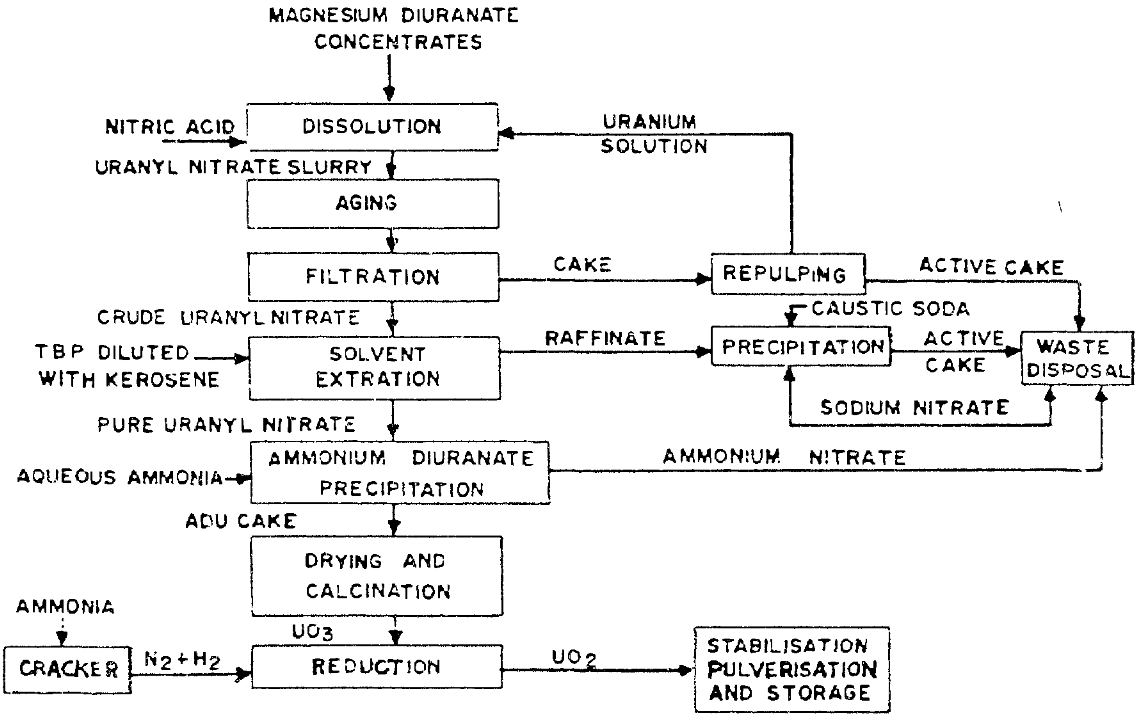

Fig.1. Production of nuclear grade uranium oxide.

of the cake to satisfactory levels. The leach liquor, thus obtained, is concentrated by evaporation and then taken for extraction along with the main stream.

In view of the above problems, there was a long felt need to evolve a system where the slurry can directly be processed. A new extraction unit has been developed by the Process Development Group of Nuclear Fuel Complex (NFC) for extraction of uranium directly from such slurry [1] which will be discussed in detail in the text.

Presently the pure uranyl nitrate solution is precipitated with ammonia as ammonium di-uranate. The precipitate thus obtained is amorphous in nature and leads to formation of agglomerates during its further processing. It was realised that if uranium is precipitated as ammonium uranyl carbonate the precipitate would be crystalline in nature with better flow charecteristics and amenable for adopting fluidized bed operations for the subsequent stages of processing. Development work carried out in this regard at Nuclear Fuel Complex is also described in this paper.

As mentioned earlier, the calcination and reduction operations for the ammonium-diuranate are presently carried out in rotary furnaces. Efforts were also directed towards the development of fluidized bed reactor system in view of its obvious advantages for reduction of UO_3 to UO_2. The work carried out in this aspect at the Chemical Engineering Division of Bhabha Atomic Research Centre is also covered.

A CONTRACTOR FOR EXTRACTING URANIUM DIRECTLY FROM SLURRIES

The development of this contractor for extraction,directly from a slurry, was carried out in three steps. Experiments were carried out on a single stage unit first, then a pilot scale solvent extraction unit with seven stages was designed and operated for about one year (1). The salient features of the unit are :

i) It has neither any moving part nor any control valve in the slurry line,

ii) air lift pump is used for inter stage aqueous transfer and also for mixing the aqueous and organic phases for mass transfer,

iii) organic flow takes place by naturally available hydraulic gradient,

iv) high organic/aqueous ratio is maintained to ensure aqueous phase dispersal and minimum entrainment loss of solvent in the raffinate.

Experiments with slurry containing as high as 15% solids were conducted on the pilot scale unit with no operating problems, though the solid content in the crude slurry obtained after dissolution of the yellow cake is of much lower order.

Based on these experiments, a plant scale unit capable of handling about 350 lph of aquous slurry and 700 lph of solvent was designed, fabricated and commissioned. The unit is in operation for more than one and a half years (2).

Description and operation

The schematic diagram of the newly developed slurry extractor unit and the flow arrangement are given in fig.2. The plant scale unit also consists of seven stages. Each stage has a mixer, disengagement section and settling tank. The disengagement sections have been provided with mist eliminators with their exhaust connected to a common exhaust header. The slurry feed is metered and fed at the extract end while the raffinate is pumped out in metered quantity at the other end. The aqueous stream is transferred from stage to stage by air lift pump from extract end to raffinate end, while the organic flows from raffinate end to extract end counter currently by gravity. The overall level difference in the 7 stage settling tanks is about 300 mm.

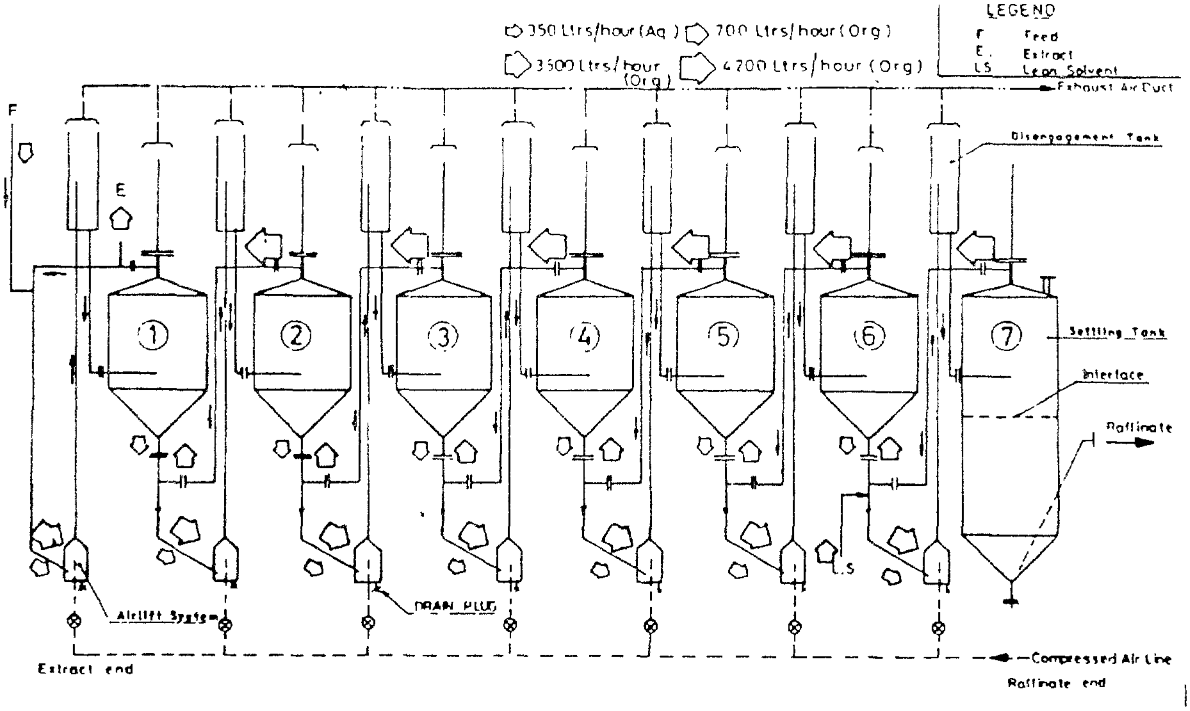

Fig.2. Schematic diagram of slurry extraction system (U.O.P).

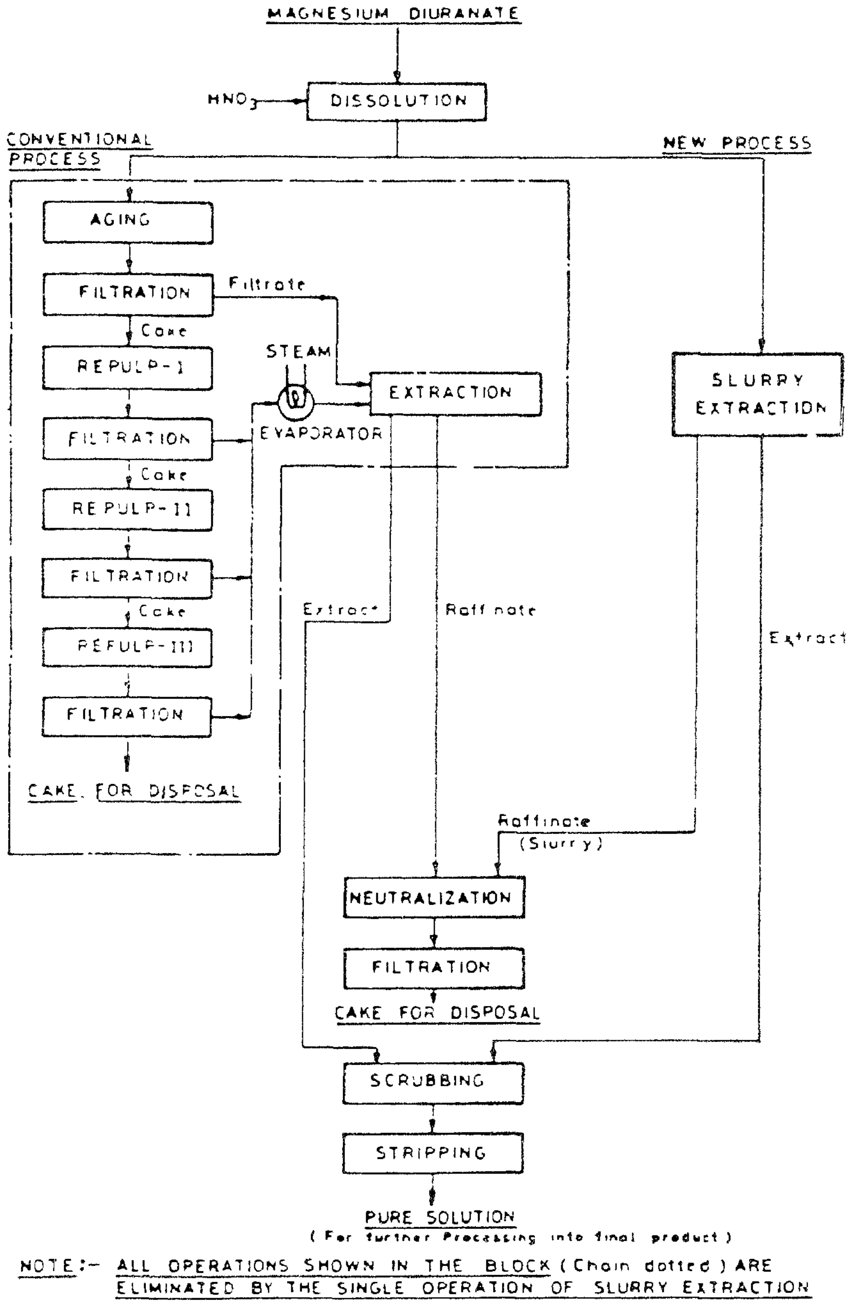

Fig.3. Solvent extraction of uranium.

Lean solvent is admitted at the seventh stage at the desired flow rate through a rotameter to get about 85 to 90% saturation of the solvent with respect to uranium. Slurry feed is checked for uranium concentration, free acidity and percentage of solid before it is admitted to the slurry extractor. Stage efficiency of the order of 85 to 90% has been achieved, though the contact time is of the order of a few seconds.

350 lph of feed is admitted at the extract end which gets mixed with about 3500 lph of recirculated solvent from the first stage. The mixed phase is pumped into the disengagement section by the first stage air lift pump. The air from the disengagement section is vented out through the mist eliminator. The mixed phase, then, flows into the settling tank through a tangential entry. Organic gets separated from the mixed phase, rises to the top and flows out of the settler.

From this, 700 lph overflows as an extract while the rest (about 3500 lph) gets recycled and comes in contact with the fresh slurry.

Similarly about 4200 lph of clear organic flows out from the top of the second stage settling tank by the suction of the second stage air lift pump. Out of this 700 lph flows upward into the first stage settling tank through the down corner due to gravity. The down corner has been sized such that the upward velocity of the organic is low enough to permit the aqueous flow downwards. About 3500 lhp of organic along with 350 lph of aqueous from second stage settling tank is pumped to the third stage disengagement section and then to the settling tank and thus the flow continues. A clear cut interphase is allowed only in the last stage settling tank where the raffinate is withdrawn from the bottom by an airlift arrangement. The recycle rate of organic at each stage is very important for efficient operation of the systems. The organic recirculation flow is controlled such that O/A ratio is always more than 10:1 in mixing stages. Operating conditions remain stable once the flow pattern is set in each stage. Fig.3 gives the operations involved in the conventional process that are eliminated by the newly developed slurry extraction unit.

Advantages

i) The slurry can directly be extracted without any filtration, repeated pulping and evaporation of wash liquor; thus a huge saving on labour, handling operations and energy.

ii) Uranium in the raffinate is controlled to the permissible level and no further treatment is necessary.

iii) The system can be operated over a wide range of plant capacity.

iv) No moving parts are involved and so practically no maintenance and operation is more reliable.

v) The unit can be stopped and restarted at will without disturbing the equillibrium.

vi) As the number of operations are grossly reduced the plant is compact and neat.

vii) Huge energy saving and also saving in space and civil work.

viii) Air borne activity at the mist eliminator exhaust duct is well within the permissible limit.

AMMONIUM URANYL CARBONATE (AUC) PROCESS FOR RECOVERY OF URANIUM FROM PURE URANYL NITRATE SOLUTION

In view of the excellent flowability of powder by carbonate route, its amenability to fluidized bed operations and single stage pelletization, an experimental set up was installed and operated to study the process parameters.

The schematic diagram of the process steps involved is shown in fig.4 for precipitation of AUC from pure uranyl-nitrate.Ammonia, carbon di-oxide and air were passed through the uranyl nitrate solution, which was also added continuously in the mix tank. The solution was stirred and also continuously recirculated through a circulation pump. The mix-tank was provided with internal steam heating coils and temperature of about 60°C to 70°C was maintained in the tank. The pH was controlled between 8 and 8.5. Uranyl nitrate solution with uranium concentration of 100 gm/l and 200 gm/l were used. The AUC slurry was continuously withdrawn from the recirculation stream filtered in pan filters and dried in tray driers.

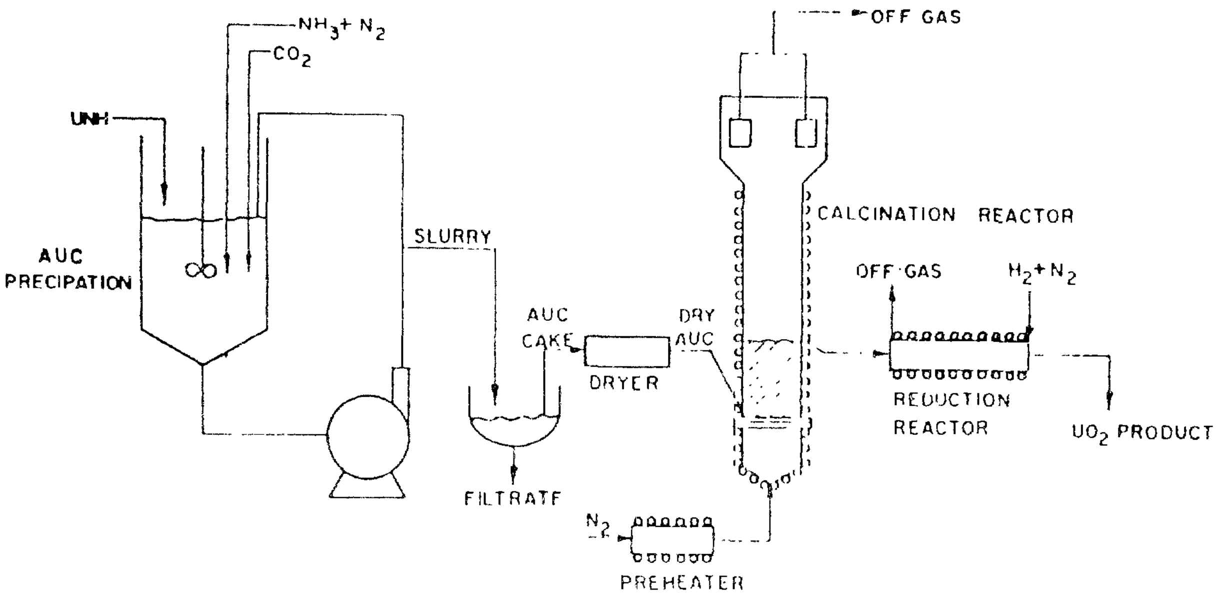

Fig.4. AUC route for preparation of UO_2.

The dried AUC powder was calcined in 75 mm dia fluidized bed reactor. Temperature in the range of 600 to 650°C was maintained in the bed and N_2 gas velocity of 3 to 5 cm/sec. was used. The studies were conducted with powder feed rate from 5 to 16 kg/hr. The UO_3 powder was subsequently reduced in rotary furnace. The UO_2, thus obtained, was observed to have better tap density and required only single stage pelletization. The pellets were also of better finish and their acceptability was better.

However, the process variables need further studies for large scale operations and to obtain the UO_2 powder of acceptable and consistent metallurgical characteristics suitable for sintering.

FLUIDIZED BED REDUCTION OF URANIUM TRI-OXIDE TO URANIUM DI-OXIDE

Rotary furnace is presently being used for reduction of uranium trioxide to uranium oxide and for hydrofluorination of the dioxide. As the fluidized bed reactor offers a more efficient and compact system, studies were conducted to evaluate various operating parameters and to assess the feasibility of its replacing the presently employed rotary furnace for reduction operation (and subsequently for hydrofluorination as well).

The Uranium tri-oxide powder (UO_3) used was composed of extremely fine particles, the average particle size being about 19 μ. The loose packing density was 2.2 gm/cc and the tap density was 2.6 gm/cc approximately. The composition of the powder varied somewhat with different feed stocks used for different experimental runs (may be because of variations in ADU - calcination conditions). A powder composition with O/U ratio of about 2.75 could be taken as the average.

A 75 mm diameter glass column was used for determining the fluidization characteristics of the UO_3 powder. The data thus obtained, formed the basis for the selection of operating gas velocity range and bed height for reduction reactor. A sintered porous metal disc (20 μ meanpore size) was used as the gas distributor for these studies and subsequent reduction trials.

Description and Operations (3)

The reduction reaction with hydrogen is exothermic and the rate of reaction becomes significant only at temperatures about 350°C and, therefore, the final runs were conducted in the operating temperature range of 450°C to 600°C where the reaction rate is quite high and mass transfer becomes the controlling factor.

Fig.5 shows the schematic diagram of the experimental set up employed for the fluidized bed reduction trials. The reactor was a 75 mm N.B. pipe with a 150 mm disengagement section at the top. The UO_3 powder was admitted in the bed above the distributor while the product discharge was by bed overflow. The reactor was provided with suitable heating and temperature control arrangement. The UO_2 product receiver was a cylindrical vessel equipped with porous metal filters. The feed gas, a mixture of H_2 and N_2 in the ratio 3 : 1 was preheated to about 300 to 350°C before it was admitted to the reactor.

Once the steady state operation had been achieved a few powder samples were withdrawn from the product overflow line for determination of O/U ratio such that they are not exposed to the atmospheric air. In certain trial runs no on-line samples were drawn and the UO_2 powder produced was directly hydrofluorinated in rotary furnace reactor. The amount of UO_2F_2 formed in the UF_4 product was taken as a measure of the conversion efficiency in the fluidized bed reduction reactor.

Table 1 shows a summary of a few of the trial runs conducted. Samples for the first three runs were analysed by online sampling(O/U determination) while the product for the last two runs was directly hydrofluorinated and analysed for UO_2F_2 content.

The results obtained from these preliminary trial runs look to be encouraging. However, more studies are required before the process can be adopted for production operation.

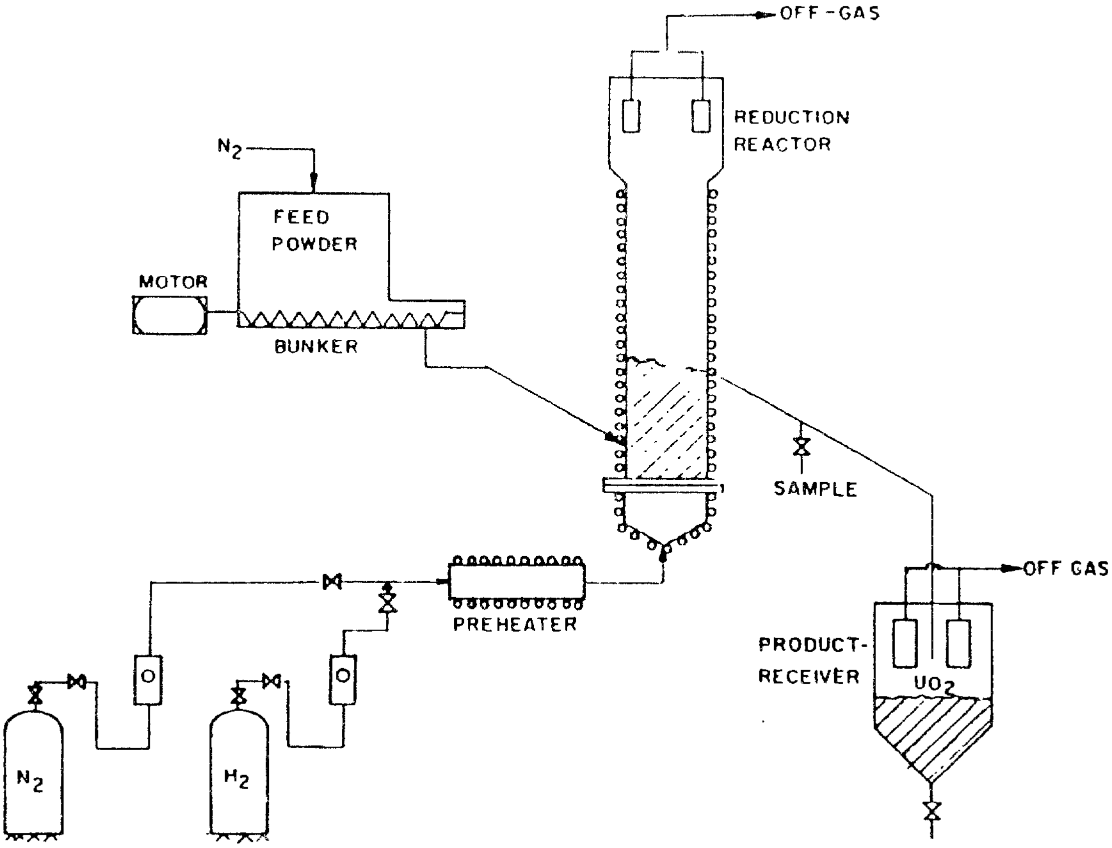

Fig.5. Fluidized bed reduction set-up.

Table - 1

Run No.	Average UO_3 feed rate (kg/hr.)	Total gas Feed rate (l/m)	Feed gas H_2/N_2 molar ratio	Feed gas velocity (cm/sec)	Bed-Temp. (°C)	Product composition (Wt UO_2)	Hydrogen excess %
1	8	28	3:1	5.6	430-460	86.8	71.4
2	10	35	3:1	7.0	450-600	84	73.1
3	10	32.5	3:1	6.3	550-600	99.5	61.5
4	6	25.5	3:1	5.1	550-600	99.5	106
5	8	28	3:1	5.6	500-600	99.5	71.4

Acknowledgement

The authors convey their sincere thanks to Shri R.K. Garg, Director, Chemical Engineering Group, BARC and Shri K. Balaramamoorthy, Chief Executive, NFC for their keen interest and constant encouragement for these studies.

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OPERATING EXPERIENCE OF A PILOT PLANT FOR THE PRODUCTION OF URANIUM DIOXIDE FROM URANIUM ORE CONCENTRATE

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Abstract

Pakistan's heavy-water moderated power reactor (CANDU TYPE) is fuelled with natural uranium dioxide. Chemically pure, compactable and sinterable uranium dioxide powder is required to suit the production of reactor grade fuel pellets.

A pilot plant for the production of natural uranium dioxide from the indigenous uranium ore concentrate to meet the CANDU fuel specifications has been established. This paper concerns with the operating experiences of the pilot plant.

1. INTRODUCTION

Uranium dioxide (UO_2) powder for the production of fuel pellets with density close to the theoretical, is produced from the ammonium diuranate or ammonium uranyl carbonate. In the early studies refining of yellow cake by solvent extraction and the production of small quantities of UO_2 for laboratory studies from ammonium diuranate was reported [1]. Since then the studies were further extended to produce natural uranium dioxide, suitable for the fuel fabrication for Karachi Nuclear Power Plant (KANUPP).

Various studies have been reported on the influence of precipitation, calcination and reduction conditions on the sinterability of UO_2 powder [2,3]. These unit operations influence the physical properties of UO_2 powder (i.e. surface area, bulk density, tap density and particle size). These physical properties affect the sintered density of UO_2 fuel pellets.

The physical properties of UO_2 powder have been controlled by optimisation of the process and operations parameters at each stage. Equally important is the chemical purity of UO_2 powder for neutron economy.

In the present studies the parameters for the extraction of uranium by using TBP-Kerosene mixture, subsequent precipitation, calcination and reduction processes have been optimised. UO_2 powder so produced has been used for the reactor grade pellet production.

2. MATERIAL SPECIFICATIONS

Specifications of the uranium dioxide powder include requirement of chemical purity and sinterability. The chemical purity of UO_2 required for the KANUPP fuel is given in Table-I. Impurities like boron, cadmium and gadolinium are highly deleterious due to their higher neutron absorption cross section areas i.e. 755; 2,550 and 46,000 barns respectively. Equivalent boron content (EBC) of UO_2 powder impurities is determined and the total EBC shall not be >1.2.

Anionic impurities e.g. carbon and fluorine are also undesirable and have marked effect in the fabrication of fuel pellets and their subsequent irradiation.

TABLE-I The Permissible Impurities Level in UO_2 Powder for KANUPP Fuel Fabrication.

Impurity	Max. Level in ppm, U basis
Al	25
B	0.3
C	200
Ca	50
Cd	0.2
Cr	15
Cu	10
Dy	0.15
F	30
Fe	50
Cd	0.10
Mg	10
Mn	5
Mo	2
Ni	20
Si	30
Th	200

Though the physical properties of powders are now well founded and their maximum and minimum limits have been laid down but their requirement varies with the fuel manufacturer. Nevertheless the acceptability of powder is entirely based on the "Sintering Performance Test". The powder characterization and the "performance test" are given in Table-II.

A. Characterization

TABLE-II. Natural UO_2 Powder Characterization and Performance Test.

Parameter	Required range
1. Surface area m^2/g	5.0 - 7.5
2. Moisture (Wt.%)	0.4 max.
3. O/U ratio-corrected for moisture	2.07 - 2.14
4. Bulk density (g/cm^3)	0.75 - 1.25
5. Tap density (g/cm^3)	1.75 - 2.15
6. Fisher Particle size(μm)	0.8 - 1.2
7. Green density (g/cm^3)	
a) inside die at 276 MN/m^3	5.6 - 6.0
b) out of die at 276 MN/m^3	5.1 - 5.4
8. Compressibility factor at 276 MN/m^3	1.8 - 2.2
9. Biggest particle size CD-80	0.015" max.

B. Performance Test

A total of 10 test pellets shall be cold pressed at 276 MN/m^2 (40,000 Psi) with a dwell time of 30 seconds maximum at pressure without addition of any binder or lubricant to a density of 5.1 - 5.4 g/cm^3 with a variation of not more than ± 0.05 g/cm^3 from the average.

The pellets shall be fired in an atmosphere of H_2 of dissociated NH_3 for two hrs. at 1650 ± 25°C. The temperature profile shall have a gradient of 200°-300°C. The pellets shall give a sinter density of more than 10.53 g/m^3 (96% TDS). Average sintered density variation shall not be more than ± 0.05 g/cm^3.

3. PROCESS DESCRIPTION

3.1 Dissolution

Stainless steel dissolvers fitted with paddle type agitators are used to dissolve yellow cake (Y.C.) and uranium dioxide pellets. The pellets before dissolution are preheated at a temperature of 350-400°C for about 12 hours. Heating and cooling jackets have been provided for steam heating and cold water circulation. The dissolved uranium in the form of uranyl nitrate solution is filtered through a plate and frame filter press. The feed solution i.e. crude uranyl nitrate prepared for the extraction step contains 300 ± 10 g/l of uranium and 3±0.1 N free acidity.

3.2 Solvent Extraction

A battery of columns have been used for extraction, scrubbing and stripping. For pulsation of the column, pulsating pumps of variable stroke length and frequency have been used. The solutions to the column are fed through proportionating feed dosing pumps.

The operational parameters are as follows:

a) Extraction Parameters

- Solvent composition	30% TBP + 70% Kerosene oil
- Flow rate of solvent to crude uranyl nitrate	3 : 1
- Pulse amplitude	14 - cm
- Pulse frequency	12 c/min

b) Scrubbing Parameters

- Flow rate of uranium organic to 4 N HNO_3 solution.	12:1 approx
- Pulse amplitude	11 cm
- Pulse frequency	12 c/min.

c) Re-extraction(Stripping) Parameters

- Flow rate of U-organic complex to DMW	1 : 1
- Pulse amplitude	13-14 cm.
- Pulse frequency	12 c/min.

Refined uranyl nitrate (UNH) solution so obtained is fed to the precipitation vessels for the production of ammonium diuranate (ADU).

3.3 Precipitation

Physical properties of UO_2 Powder are dependent upon the precipitation conditions. The influence of precipitation parameters is discussed in section 4.

Process/operating parameters have been studied and optimsed; the values are given as below:-

- Precipitation temperature	50°C
- Percent uranium precipitation (pH 3.5) 1st stage	50±5
- Percent uranium precipitation (pH 7.2) 2nd stage	50±5

The ADU slurry is fed to the thickner and subsequently filtered using rotary drum vaccum filters(RDVF). ADU is then transferred to the repulper, slurry so obtained is again filtered by DRVF. ADU cake is dried at 120°C and ground to (-) 10 mesh.

3.4 Conversion of ADU to UO_3

ADU is fed to three zone furnace. Each zone is controlled by independent heating circuit. The temperature of first zone is kept at 260°C, second zone at 270°C and third zone at 280°C. The residence time of powder is kept one hour.

3.5 Calcination of UO_3 to U_3O_8

Orange oxide (UO_3) is conveted to U_3O_8. The calcination temperature is 530 - 550°C. This temperature gives U_3O_8 which flows smoothly when fed to the reduction furnace.

3.6 Reduction of U_3O_8 to UO_2

U_3O_8 is fed to a rotary type furnace with a provision to supply dissociated ammonia ($N_2 + 3H_2$) mixture) stream. The powder is reduced at a temperature of 625 - 650°C.

The powder (UO_2) so obtained is hihgly pyrophoric and has to be stabilised. Stabilization is done by the addition of dry ice into UO_2 Powder [4]. Partial pressure of oxygen in an inert atmosphere of solid/gaseous carbon dioxide leads to the formation of U_3O_8 monolayer on the UO_2 Powder. The powder once stabilised is very stable towards oxidation. The reduction temperature has a direct bearing on the physical properties of the UO_2 Powder. This aspect is discussed in section 4.

4. DISCUSSION

4.1 Extraction of Uranium

In the solvent extraction section the free acidity of crude uranyl nitrate solution has marked influence on the extraction efficiency. The extraction efficiency decreases with the decrease of free acidity. The results of studies under pilot plant conditions have been given in Fig. 1. It has been observed that the free acidity > 3 N results in the uptake of deleterious impurities into the organic complex e.g. boron, cadmium, gadolinium etc. [5].

The uranium concentration of feed solution also affects the extraction efficiency. The optimum uranium content in the feed solution is found to be 300 g/l. Further increase of uranium in feed solution leads to increase uranium in raffinate.

The throughput has also a bearing on the extraction efficiency. Throughput will have to be increased, keeping the capacity of the column in view. Such that the extraction efficinecy is maintained and the ratio of organic to acqueous flows is such that the uranium is in stoichiometric balance. The organic to aqueous ratio found optimum for the operation is 3 : 1.

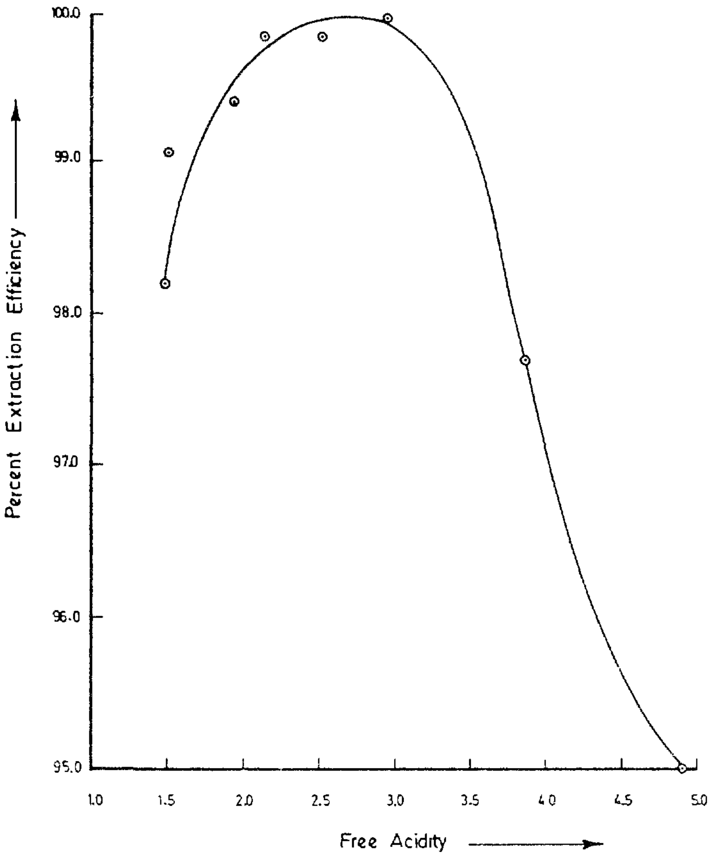

FIGURE 1: Percent Extraction Efficiency Versus Free Acidity.

Scrubbing of the uranium organic complex is essential for the removal of left over impurities. The strength of nitric acid had to be kept more than 3 N to prevent transfer of uranium into aqueous phase. Nevertheless the practice of scrubbing with UNH solution is preferred [6]. This is advantageous in further increasing the uranium concentration in the loaded organic. Increasing the uranium saturation of the solvent results in reducing co-extration of impurities [7].The main disadvantage is the loss of refined UNH solution and in handling of aqueous obtained from the scrubbing column. For scrubbing 4N nitric acid solution is being used.

Re-extraction(stripping) of uranium has been effectively accomplished in the columns by keeping the U-organic complex and DMW. It has been observed that the increase in temperature to 60°C enhances the efficiency of stripping [8].

4.2 Precipitation of ADU from UNH

Precipitation step for the production of ADU has a bearing on the physical properties of uranium dioxide produced for the nuclear fuels.

The size of ADU crystallites , and agglomerates decreases with increasing pH. Precipitation at pH >7 gives ADU of very fine particle size, which poses difficulty in settling and filteration. The settling rate in second stage at pH 7.1±0.1 is given in Fig.2. The settling rates are an index to sintered density. Lower the settling rate of ADU slurry higher the sintered density of UO_2 prepared from it. This ADU on reduction of UO_2 gives powder which is difficult to process but sinter to high sinter densities.

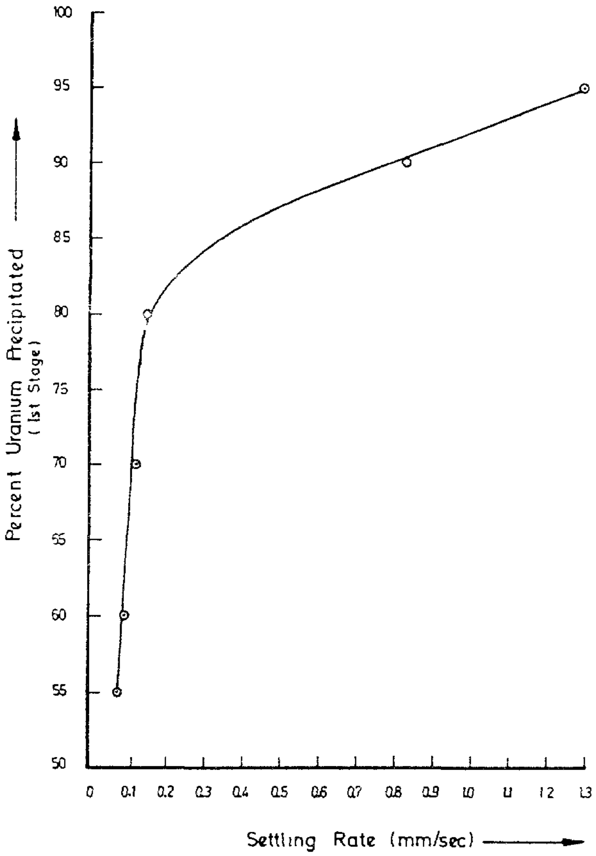

FIGURE 2 : Settling Rate of ADU in 2nd Stage at pH 7.1 ±01(50°C

On the other hand ADU precipitated at low pH i.e. 3.5 gives course particles and agglomerates. The UO_2 powder produced from this ADU is less pyrophoric and easily compactable but gives low sintered densities(Table-III). Such a powder is not suited for fuel pellet fabrication as such. This type of powder has to be ball milled/micronised to get good results.

TABLE-III. Effect of PERCENT Precipitation at 1st Stage on the Physical Characteristics of UO_2 Powders and Sintered Densities.

Uranium Percent Precipitation*	Physical Characteristics of UO_2** Powders			Sintered Density g/cm³
	Bulk Density g/cm³	Tap Density g/cm³	Surface Area m²/g	
50	1.15 - 1.25	1.85-2.10	4.5 - 7.0	10.5-10.6
60	1.25 - 1.30	2.00-2.15	3.5 - 5.0	10.3-10.4
70	1.30 - 1.40	2.10-2.30	3.0 - 4.0	10.2-10.3

* Precipitation Temperature 50°C

** Reduction Temperature 625°-650°C

To achieve a balance, two stage precipitation is preferred [2]. This gives a blend of coarse and fine crystallites that filter easily. The second stage precipitation of pH 7.1 ± 0.1 also ensures that all the uranium is recovered from the solution. UO_2 powder obtained from the ADU gives intermediate surface area and other physical properties. UO_2 so produced is not highly pyropharic but needs stabilisation and sinters to very high sintered densities e.g. greater than 96% of theoretical.

4.3 Conversion of ADU to UO_2

This step has been carried out in three stages :-

a) Conversion of ADU to UO_3

b) Calcination of UO_3 to U_3O_8

c) Reduction of U_3O_8 to UO_2

It is ensured that each material in step a & b is completely converted. The process parameters are adjusted to get smooth flowing material in the electrical resistance furnaces.

Care is taken to avoid micro and macro-sintering in steps(a) and (b). Such pre-sintering would tend to reduce the surface area of the final product i.e. UO_2. The temperature of calciner is also very important factor in determining the physical properties of the UO_2 Powder.

The most important step is the reduction of U_3O_8 to UO_2. This step is carried out in the reducing environment of either hydrogen or dissociated ammonia. The surface area of UO_2 powder independent of the parent ADU is governed by the reduction temperature. Higher reduction temperature results in lowering of surface area, whereas, lower reduction temperature increases it as shown in Table-IV. On

TABLE-IV. Effect of Reduction Temperature on Surface Area of UO_2 Powder

Reduction Temperature (C°)	Surface Area (m^2/g)
625	6.0 - 7.0
630	5.0 - 6.0
640	3.5 - 4.5
650	3.0 - 4.0

the other hand, high temperature of calcination and reduction will increase bulk and tap densities, whereas, low temperature will decrease their values. High reduction temperatures result in presintering of the crystallites present in UO_2 agglomerates. It has been observed that powder reduced at high temperature i.e. > 650°C manifests marked decrease in surface area, this supports the view point of gross pre-sintering of the fines taking place in the powder.

4.4 Influence of Physical Parameters on the Sintering Characteristics of UO_2 Powders

The powders are characterised generally for the following:

a) Surface area

b) Bulk density

c) Tap density

d) Particle size

e) Compactability factor

The range of these physical parameters is given in Table-II. The acceptability of powder is not only based on the physical characteristics but on its performance on sintering (performance test) as mentioned in Table-II.

In general powders with high surface area, low bulk and tap densities and small particle size sinter to high densities. But there are process and economic constraints e.g. powders with high surface area are difficult to compact and handle. Powders with high bulk and tap densities sinter to low sintered densities but are fairly good in compaction. Powders with particle size >1.2μm tend to yield pellets of low sinter-density, such powders would need ball milling/

micronising for use in pellet fabrication. Thus the cost for the entire pellet fabrication is obviously a polydimensional function. It is therefore necessary not to optimise the process parameters at each step of UO_2 processing but to corelate the monotonous function of the cost as well [9]. The specifications are thus based on a compromise in process contraints, product requirement as well as economic considerations.

5. CONCLUSION

By using indigenous yellow cake and recycled material,uranium dioxide to meet the KANUPP requirements has been successfully produced. The observations during the operations conformed with the information already available in litrature [1 - 9].

6. ACKNOWLEDGEMENT

The author is thankful to N.K.Qazi, M.T. Qureshi and N.A.Chughtai for the experimental and technical work and M.Salim for the valuable suggestions and discussions for the preparation of the manuscript.

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PURIFICATION AND CONVERSION OF URANIUM FROM IRON AND THORIUM CONTAINING DEPOSITS

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Abstract

Acid leaching of uranium deposits is not a selective process. Sulfuric acid solubilizes half or more of the thorium depending on the mineralogy of this element. In uranium recovery by solvent extraction process, uranium is separated from thorium by an organic phase consisting of 10 vol% tributylphosphate(TBP) in kerosin diluent. Provided that the aqueous phase is saturated with ammonium nitrate and pH of the solution is lowered to 0.5 with sulfuric acid. In other words the separation of uranium and thorium depends on the way that the relative distributions of the two materials between aqueous solutions and TBP vary with sulfuric acid concentration. Under these conditions the extraction of iron(III) into TBP drastically diminishes to a tolerable level. Uranium can be stripped from the organic phase by distilled water,denitrated and delivered for electrolytic reduction. Uranium can be precipitated as uranium tetrafluoride by the reaction between uranous and hydrofluoric acid. Thorium is later recovered from the waste leach liqour after removal of sulfate ions.

INTRODUCTION

In uranium purification with tributylphosphate from nitric acid solutions, ferric ion and thorium can accompany uranium (VI) to the organic phase in significant amounts and may appear as major impurities[1]. The high iron contamination in uranium concentrate is undesirable, because it interferes with enrichment of uranium.[2] The allowable amount of thorium in uranium concentrate according with the specifications established by different conversion plants is shown in table (I).

Table (I)

The product quality of the salable yellow cake according with the specifications established by the conversion plants (1).

	British nuclear fuel (UK)	Comurhex (FRANCE)	Eldorado (CANADA)	Allied chemicals (USA)	Kerr Mc Gee (USA)
U	40	60	50	75	60
Th	n.a	n.a	2.0		2.0
Fe				0.15	

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(1) limits with penalties for exceeding values.

An enormous amount of work has gone into the development of extractive methods for uranium to meet the problems which have arizen in the extraction of uranium from ores, the purification of uranium and the recovery of uranium from reprocessing stage.[3] Solvent extraction by TBP has long been applied as a means of separating numerous elements from uranium in nitrate solutions. In this method uranium is effectively separated from thorium and iron employing TBP in a proper extraction conditions.

EXPERIMENTAL

The raw material is the sulfuric acid leach solution from thorium and iron containing deposits. The deposits lack the presence of considerable amounts of many spesific elements such as molybdenum, titanium, vanadium and boron. Leach solution is saturated with ammonium nitrate and the PH of the solution is lowered to 0.5 by the addition of sulfuric acid. Uranium is fractionated away from thorium and iron by 10 vol% TBP in kerosin diluent. Thorium can be recovered from the waste leach liquor, ofter removal of sulfate ions by barium nitrate and using 30 vol% TBP/diluent. Uranium is stripped from the organic phase by distilled water and delivered for electrolytic reduction.

The solution of uranyl nitrate is denitrated by means of sulfuric acid, crystals of uranyl sulfate, $UO_2(SO_4)_2$,$3H_2O$ is obtained. A solution of 100 gU/l and 35% hydrofuoric[4] acid is reduced electrolytically in a single compartment cell heated in a bath over

90°C. The masking effect of fluoride ion decreases reoxidation rate of U (IV) on the anode. Graphite is used as anode and monel-400 as cathode. current density is about 0.5 Am/cm^2 and potential 6-7 volts. The solution is stirred vigorously. The current efficiency is about 20% and the recovery of uranium is more than 95%.

DISCUSSION

The fractionation of uranium (VI) depends on the concentration of uncomplexed TBP in the organic phase. Thus one of the most important variables is the degree of solvent saturation with uranium which is more strongly complexed by TBP than iron and thorium. Thorium is successfully masked by the addition of sulfuric acid.

Using no membrane and complex cell causes decrease in current efficiency[5]. The anode is renewed after each electrolysis in order to prevent crumbling of graphite. Stirring is continued for one hour after the current is stoped. Very filtrable and washable particles of UF_4, $0.75H_2O$ precipitated and studied by X-ray diffraction spectra.

Hydrated uranium tetrafluoride grains grow to 70-100 micro meters and kept suspended in the electrolytic cell. The hydrated uranium tetrafluoride produced contains no significant impurities of Al, B, Ca, Fe, Th, Mo, V and Ti because the traces of these elements are further removed at uranium tetrafluoride precipitation stage.

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DEVELOPMENT OF A TECHNOLOGY TO MAKE UO_2 STARTING FROM "YELLOWCAKE" REFINED WITH AMINES IN A SULPHURIC ENVIRONMENT

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Abstract

The development carried out at a pilot scale certifies the advantage of purifying "yellow cake" by tertiary amines and to obtain AUTC nuclear purity through direct precipitating elution.

Furthermore, this product being adequately conditioned in its mother liquor as well as straightly reduced in a batch furnace by dissociated ammonia produces an UO_2 free flowing meeting the standard specifications required for nuclear fuel used at Atucha I.

The second stage of this technology is in way of being optimized, although sintered densities of 10,40 and 10,60 g/cm3 are obtained we are still having problems with the grain growing in the pellets which we are at the present time trying to improve it by adjusting the sintering heat treatment.

We want to make acquainted that starting from sulphuric solutions of ore treatment it is possible, with the same technology and without intermediate precipitation, get an AUTC nuclear purity of same characteristics as the one obtained through the former methodology.

FABRICABILITY OF AUTC (Ammonium Uranyl Tricarbonate) AND NUCLEAR PURITY STARTING FROM ADU TREATMENT IN A SULPHURIC ENVIRONMENT TERTIARY AMINES AND STRAIGHT PRECIPITATING ELUTION.

Operative Technique

a) Sulphuric Disolution

The ADU produced at the Concentration Plants with a standard analysis is hereunder shown:

U_3O_8 according to dry sample	85,74 %		
$SO_4^=$	1,76	V_2O_5	< 0,05
P_2O_5	0,8	CO_3	0,37
Fe	1,18	Zr	< 0,1
SiO_2	1,28		
Mo	< 0,03		

The same is delayed in water and then attacked with concentrated sulphuric solution (SO_4H_2), so as to obtain a final solution of about 150 g/l of Uranium having a pH of 1,2 to 1,3 and a P.D.R. Powder Oxyreducer higher than 400 mV. From this mother liquor which is previously filtered through a vacuum filter, an aliquot part is taken and diluted in water and raffinate coming from the Solvent Plant. This concentration is here adjusted to 20 g/l of uranium and its pH reaches the value of 1,3. Being the same arranged and filtered through a line filter it meets the requirements to enter in the Process of Extraction through Solvents.

b) Extraction through Solvents Process

A five stages battery of mixers-settlers of the compact type contacts now the impure Uranyl Sulphate solution with a tertiary amines solution (Alamine 336 or Adogen 364) 0,1 M with the aggregate of Isodecanol 3% in Volume and so doing the passage of uranium from the aqueous phase to the organic phase is accomplished.

Amines solution is in this way enriched in U with a concentration of about 7 g/l, the raffinate which comes out from the Plant after passing through a safety decanter has an uranium concentration < 10 ppm (lower than ten parts per million); the 50-60 % of same is recycled in order to condition the liquids in stage a). What is left runs to the Effluents area to be then neutralized, concentrated and recuperated as crystalized ammonium sulphate $SO_4(NH_4)_2$.

The solution of amines charged with uranium is also washed in mixers-settlers performed in two stages of reverse current of SO_4UO_2 PN pH = 1,5 solution which is then being sent to decantation. Once this has been completed its joining to the following stage is produced.

$$[2\ R_3\ N]_{org} + [H_2\ SO_4]_{aq} \rightleftharpoons [(R_3NH)_2SO_4]_{org}$$

$$[2(R_3NH)_2\ SO_4]_{org.} + [UO_2(SO_4)_3]_{aq} \rightleftharpoons [(R_3NH)_4\ UO_2(SO_4)_3]_{org.} + 2SO_{4\ aq}$$

$$[(R_3NH)_4\ UO_2(SO_4)_3] + [5\ (NH_4)_2\ CO_3] \rightleftharpoons [(NH_4)_4\ UO_2\ (CO_3)_3]_{aq} + \text{etc.}$$

c) Precipitating Elution

The present operation is performed in batch as follows:

A measured quantity of Uranium amine saturated solution is first added and that is maintained to a temperature of 45°C, then a measured quantity of ammonium carbonate solution and

AUTC analysis produced at CFC

Elements	
Ag	0,05-0,5
Al	≤ 25
B	< 0,2
C	< 100
Ca	25
Cd	< 0,1
Co	< 1
Cr	10 - 25
Cu	1 - 3
Dy	< 0,03
Eu	< 0,03
Fe	< 10 - 50
Gd	0,03
In	< 1
Mg	3 - 10
Mn	< 2
Mo	< 4
Ni	< 4 - 20
Pb	< 5
Si	< 30
Ti	7 - 15
V	< 10
Zn	< 20
S	30 - 50
B	< 0,2

ammonium sulphate saturated in Uranium are added having these determined concentrations and being as well heated to 45°C. The pH has to be here controlled to the value of 9. All these are stirred for a time of 30 minutes letting it then drawn off for 30 minutes to favor good crystallization.

d) Crystals arrangements

With the 70% of the mother liquor previously separated from the organic solution in a special decanter disposition of crystals is achieved. A stirring of this precipitation during a time of 120 minutes obtaining, in so doing, worn out edges preparing the structure of the future UO_2 with free flowing characteristics.

e) Filtering and washing of AUTC

Filtering is put through a centrifuge machine and the washing is in two stages performed. In the first stage the material is washed with 20% ammonium bicarbonate solution saturated first in uranium and then with methanol that in addition to moving out any organic solution traces that might be left kept back favors crystal deshydration, this allows the AUTC to have a moisture not higher than 0,5 %.

SPECTROGRAPHIC ANALYSIS OF AN UO_2 SAMPLE.

CFC POWDER - UO_2 PLANT NATIONAL TECHNOLOGY

It was accomplished by the Chemistry Department -

Management of Chemistry Processes and CFC Laboratory

Elements	Specif RBU	Lot 1 M 326	Lot 2 M 333	Lot 3 M 337	Lot 4 M 343
Si µg/gU	100	≈ 50	30-40	< 30 D	≈ 30
Cd "	1	< 0,1 ND	< 0,1 ND	<0,1 ND	< 0,1 ND
B "	0,2	< 0,1 D	< 0,1 D	<0,1 D	< 0,1 D
Ca "	100	10-25	< 10 D	<10 D	< 10 D
Ag "	2	< 0,05 D	< 0,05 D	<0,05 D	< 0,05 D
Fe "	100	25-50	15-25	15-25	≈ 25
Mn "	50	2 D	< 2 D	< 2 D	< 2 D
Cr "	200	< 10 D	< 10 D	<10 D	< 10 D
Ni "	50	< 4 D	< 4 D	< 4 D	< 4 D
Al "	50	5-15	< 5 D	< 5 D	< 5 D
Mg "	50	< 1 D	< 1 D	< 1 D	< 1 D
Cu "	25	< 1 D	< 1 D	< 1 D	< 1 D
Mo "	50	< 4 D	< 4 D	< 4 D	< 1 D
Co "	6	< 1 ND	< 1 ND	< 1 D	< 4 D

D; Detected

ND: No Detected

f) Conversion to UO_2

The conversion to UO_2 stage has here always been carried out in a tray furnace. The characteristics of the operations has in general terms been performed as follows:

Racks of four trays are loaded with an AUTC height of 1,5 cm each; they are then introduced in the vestibule without heating staying in nitrogen atmosphere for some minutes. Then they are carried to the heating area at a temperatura of 700°C being them submitted to an alternative treatment for a period of 20 minutes in dissociated ammonia (NH_3); then 40 minutes in Nitrogen (N_2) and again for 20 minutes in dissociated ammonia. Racks are transferred to a cooling area at a temperatura of 120°C and the same said treatment in equal times as at the heating area is then given. From here they are taken to a cooling area with a temperature of 70-80°C and passing finally to a passive area where the oxygen-uranium rate is adjusted with a nitrogen treatment being they then put into hermetic containers (drums).

Physical characteristics of UO_2 powder

Test	Apparent density g/cc	Flowing sec.	Specific surphase m^2/g	Rate 0/U	Moisture
LG 3	1,80	1,00	5,59	2,12	0,23
LG19	1,88	1,10	5,42	2,09	0,18
LG24-1	1,86	1,10	5,62	2,10	0,20
LG36-1	1,80	1,10	6,76	2,15	0,26

The following are the latest results obtained with the pellets sintered at 1700°C in dry hydrogen atmosphere with 2 m^3/h volume and a pressure of 30 milibars in an experimental furnace.

RESULTS OBTAINED IN AN EXPERIMENTAL FURNACE

AT COMPLEJO FABRIL CORDOBA (ARGENTINA)

Test N°	Pressure t/cm^2	Density in green g/cm^3	Sintered density g/cm^2
LG 3	3,4	5,37	10,32
"	3,34	5,47	10,43
"	3,63	5,58	10,50
"	4,08	5,67	10,56
"	4,30	5,73	10,58
"	4,60	5,79	10,60
LG 19	3,04	5,33	10,17
"	3,71	5,54	10,40
"	4,23	5,69	10,50
"	4,97	5,80	10,58
"	5,92	5,97	10,62
LG 24-1	3,11	5,34	10,35
"	3,78	5,56	10,49
"	4,23	5,70	10,55
"	4,52	5,79	10,58
"	5,04	5,90	10,62
LG 36-1	3,56	5,42	10,43
"	4,23	5,61	10,55
"	4,37	5,65	10,57
"	4,52	5,67	10,58

. External characteristics of pellets:	good
. Internal porosity of pellets:	good
. Size :	Specified

. Grain size in crossed section of pellets:

- external area : 8 µ
- central area : 70 µ

RESULTS OBTAINED IN A PRODUCTION FURNACE AT CENTRO ATOMICO EZEIZA

Green pellets have been obtained through the pressing process at Complejo Fabril Córdoba. From two different lots a number of ten green pellets each at its corresponding working pressure have been separated. Half of this material from each group has been sintered at Complejo Fabril Córdoba attaining the results shown in the preceding table, while the other half has been sintered in the Production Furnace at Centro Atómico Ezeiza with the following results:

Test N°	Pressure t/cm^2	Density in green c/cm^3	Sintered density g/cm^2
LG 24-1	3,11	5,34	10,46
"	3,78	5,56	10,50
"	4,23	5,70	10,52
"	4,52	5,79	10,53
"	5,04	5,90	10,50
LG 36	3,56	5,42	10,49
"	4,23	5,61	10,54
"	4,37	5,65	10,54
"	4,52	5,67	10,56

- External characteristics of pellets: good
- Internal porosity of pellets: good
- Size : Specified
- Grain size in crossed section of pellets:
  - external area : 11,9 μ
  - central area : 12,5 μ

At this time [illegible] is being intended to change sintering conditions in order to obtain sintering densities at a lower compacting pressure and procure a better grain growing of the sintered pellets.

g) Recovery of Reagents and Effluents

As it is said in b) the 50-60 % of raffinates sulfuric solution that comes out from the Extraction through Solvents Plant is recovered to uranyl sulfate (SO_4 UO_2); the remainder of this liqueur is used to neutralize the mothers liqueur from AUTC crystallization that have to be put away from the circuit due to its high sulfate content. Furthermore, all acid vapors or ammoniacal vapors coming out of the process and which are absorbed in different absorption towers are added to these solutions, being uranium drawn out through Precipitation as ADU and solutions where uranium has already been removed are being concentrated getting ammonium sulfate as final product fertilizing quality ($SO_4(NH_4)_2$ (it meets IRAM Argentine Specifications N° 22410 - CDU 631.841.1).

IRAM Specification N° 22410

REQUIREMENTS	Unit	Min	Max
Ammoniacal Nitrogen		20,5	
Sulphur		23,4	
Free acidity expressed as sulphuric acid (H_2SO_4)	g/100 G	--	0,1
Moisture		--	1
Caught in siever IRAM 850/ µ		15	--
Sieved IRAM 450 µ		--	30

Standard analysis of ammonium sulfate carried out at C.F.C.

REQUIREMENTS	Unit	Obtained Results
Ammoniacal Nitrogen		21,03
Sulphur		24,03
Free acidity expressed as sulphuric acid (H_2SO_4)	g/100 G	0,08
Moisture		0,6
Caught in Siever IPAM 850/ μ		17
Sieved IRAM 450 μ		28

We have arrived to this alternative since Safety Specifications applied in the Argentine Republic do not allow liqueurs with sulfates higher than 400 mg/l to be vacated, and because from an analysis estimate cost performed in advance offer significant savings in the operation cost that if calcium oxides were used to neutralize the same liqueurs.

h) A future outlook of this Methodology

According to tests which have been carried out and opportunitely informed, the present methodology intends to obtain, starting from impure solutions, AUTC which meet Nuclear Purity Specifications. This means that the possibilities offered by the sulfuric leaching treatment of ores appropiately clarified, filtered and conditioned are very promissory and there exists the certain possibility that an AUTC nuclear purity may directly be obtained, it means without the previous step through ADU precipitation.

Representative analysis for liquors to be treated

U_3O_8 -------- 1,80 g/l
Fe -------- 11,90 "
Cu -------- 5,25 "
pH -------- 1,40 "
P.O.R. -------- 500 mv

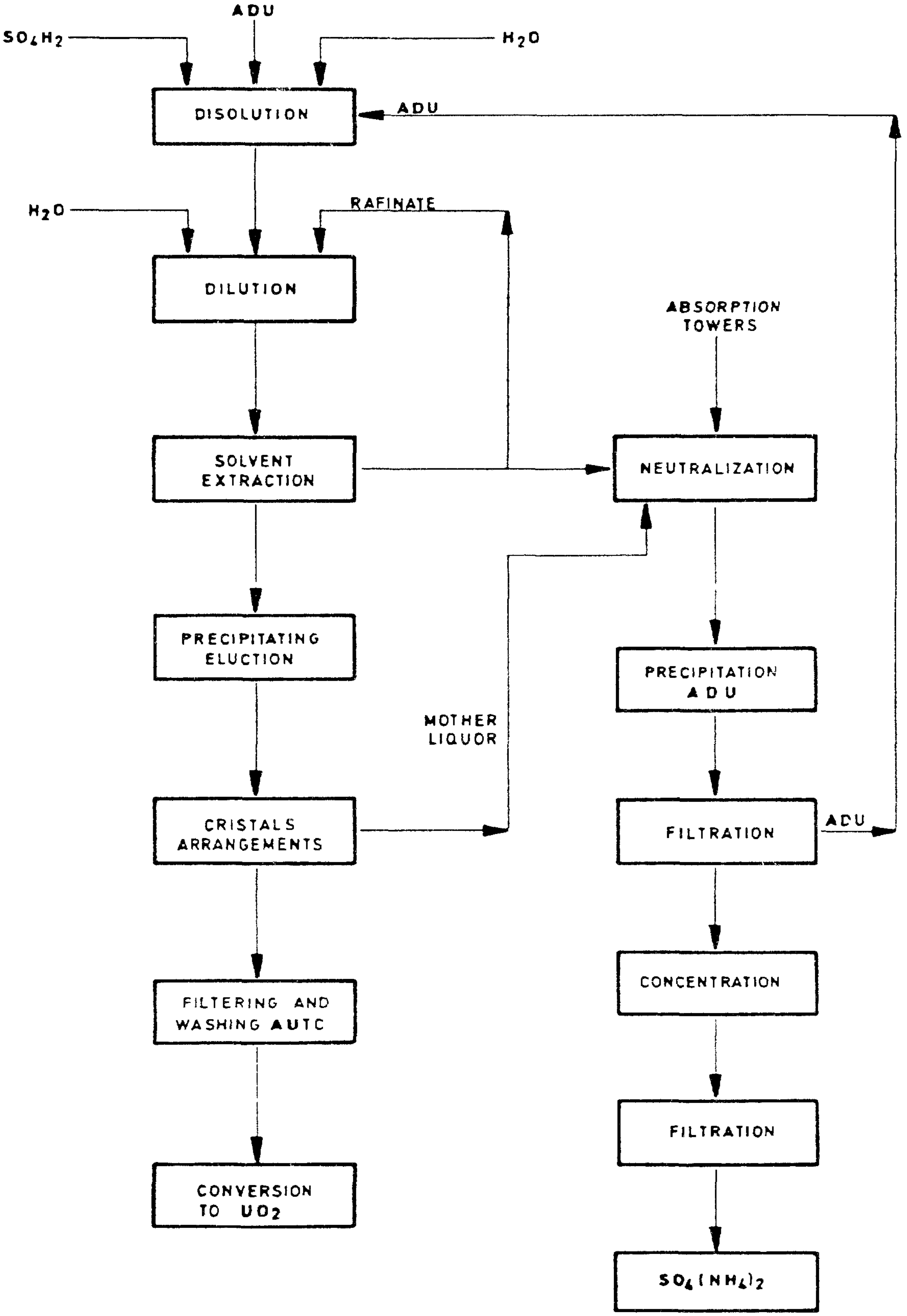
From these liquors purified by amines was AUTC obtained which representative analysis in three main impurities: Silex, Iron and Copper gave the following results being the remaining impurities in according to Nuclear Purity Specifications:

Si ---------- 30 ppm
Fe ---------- 80 ppm
Cu ---------- 20 ppm

Quality Control, Radioprotection and Safety Specifications taking into account during operation at a Pilot Plant

Quality Control

The Section responsible for the Quality COntrol at Complejo Fabril Córdoba, with activities based on verifying the fulfilment of Proceeding Manuals, Chemistry and Physics Laboratory Manual, Inspection and Testing Plan, Operating Manual, Commissions and Functions Manual, as well as others, is at the present time preparing the "Quality Control Manual" that will govern the Quality Control Program and to which Plants will have to obey.



Flow-sheet of the process.

STATUS OF URANIUM REFINING AND CONVERSION PROCESS TECHNOLOGY IN KOREA

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Abstract

The nuclear grade uranyl nitrate solution is prepared from yellow cake in the purification pilot plant, at Korea Advanced Energy Institute(KAERI), Korea. This pilot plant has several 15 cm diameter pulsed columns which perform a series of extraction, scrubbing and stripping processes in the air pulsation mode. In the pulsed extraction column, the crude uranyl nitrate solution of 2N free-acidity get in contact counter-currently with the dispersed phase of 40% TBP/dodecane mixture. The uranyl nitrate is then extracted into the organic phase and subsequently reextracted into the aqueous phase to yield a purified uranyl nitrate solution in the stripping column. The final uranyl nitrate solution thus produced is well within a nuclear grade purity and the small uranium content in the raffinate aqueous phase and the stripped organic phase, less than 10 ppm and 100 ppm respectively, shows that all the processes in the plant are satisfactory. Moreover, Mo content of 1500 ppm in the yellow cake is reduced down to less than 1 ppm in the purified uranyl nitrate solution.

For the production of sinterable UO_2 powder, ammonium uranyl carbonate (AUC) is precipitated in the saturated ammonium carbonate solution using nulcear grade uranyl nitrate solution together with ammonia and carbon dioxide gases.

The free-flowing and granular type AUC powder is then converted into sinterable UO_2 powder by reaction with hydrogen gas in a fluidized bed reactor.

All parameters, which can control O/U ratio, flowability, tap density, specific surface area, pore size and its distribution, have been studied.

1. INTRODUCTION

The construction of nuclear power plant in Korea started with Kori NO. 1 nuclear reactor 1971 and increased rapidly through the oil crisis in 1970's. As of 1986, 5 nuclear power reactors are in operation and 4 more reactors are under construction.

Along with increased nuclear power generation, Korean government undertook the project for the localization of nuclear fuel manufacturing technology. The policy of Korean government for the nuclear fuel is that nuclear fuel for pressurized water reactor(PWR) will be manufactured using transfered technology from foreign fuel vendors, and fuels for Wolsung reactor(CANDU) will be produced by KAERI using domestically developed conversion and fabrication technology. KAERI has established a conversion and fabrication research laboratories in 1979 and 1978, respectively, to develop the fuel manufacturing technology and to train man-power in the field of nuclear fuel. Utilizing this facilities and accumulated experience in fuel manufacturing, the development of Wolsung nuclear reactor fuel was started in 1981.

In September 1984, 24 fuel bundles made by KAERI using RBU-UO_2 powder(West Germany) were loaded in Wolsung reactor and were discharged after successful performance.

In November 1985, another 24 fuel bundles using KAERI-UO_2 powder are loaded again in Wolsung reactor and are under burn-up.

Therefore, we believe that the technology development for the CANDU type nuclear fuel manufacturing was successfully fulfilled and we plan to expand the capacities of conversion and fabrication facilities in order to supply all the the fuels needed for Wolsung reactor by ourselves.

2. DESCRIPTION OF PROCESSES

The processes of the pilot plant at KAERI are consisted of two parts; first, a 20 kg-U/hr (100 ton-U/yr) capacity of dissolution, filtration and purification. second, a 25 ton-U/yr capacity of UO_2 powder production. The block diagram of uranium refining and conversion processes is shown in Fig.1.

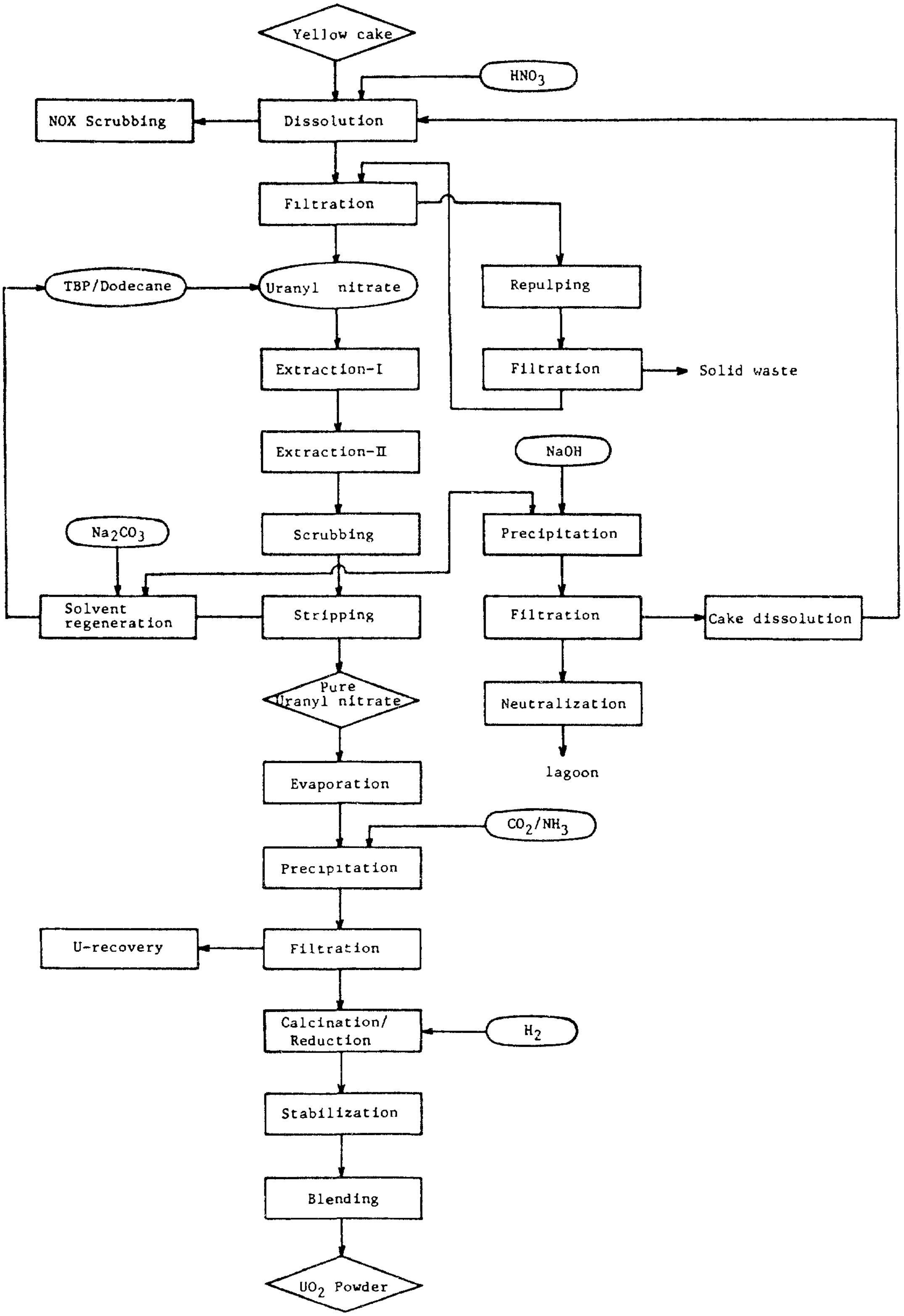

Fig.1. Block diagram of uranium refining and conversion processes.

3. DISSOLUTION AND FILTRATION

It takes about 2.0-2.5 hours for each operation in dissolution. First, about a 250 l of 10 N HNO_3 is introduced into the dissolver and preheated up to 50-60°C and then slowly added U_3O_8. The temperature of the dissolver should be kept at 70-80°C while paying attention to the temperature rising due to the exothermic reaction. The final free acidity is controlled to 1.5-2.0 N and the final uranium concentration becomes about 900 g-U/l. During the dissolution the emitted NOX gas is scrubbed with about 10 % NaOH in a packed column, and end point is chosen at about pH 10 in NaOH solution, and then uranium recovery or waste treatment process is used according to the degree of the uranium content. The dissolved uranyl nitrate solution is aged for 2 hours at 95°C for silica aging and proceeded to the filtering system to remove the insoluble materials.

Two set of rotary filters are used for filtration. The first filter is for the removal of the slurry in the aged solution and second filter for the recovery of the uranium contained in the first filter cake and treated as a repulped slurry. The uranyl nitrate solution from the first filter becomes almost clarified. At this stage, the uranium concentration is about 350 g-U/l and free acidity about 1.5-2.0 N (1). The cake from the second filter, after estimating the uranium content, is used for the uranium recovery or treated as waste through the neutralization step. The neutralization is carried out with lime.

4. PURIFICATION

Purification process is consisted of extraction, scrubbing, stripping and solvent regeneration sections. In extraction, there are two extraction columns, one for strong liquor (uranyl nitrate solution from dissolution) and the other for weak liquor (uranyl nitrate solution from the bottom of the strong liquor extraction column).

Main equipments are perforated pulse column for purification, mixer and packed column for solvent regeneration. The level of interface at each column can be controlled with the pressure difference checked from the air purge system using two dip tubes which are attached to the column disengaging section. Pulse energy generated by the air pulsation mode is introduced in the column through the pulse leg (2). The aqueous solution as the continuous phase and the organic solvent, 40 % TBP in dodecane by vomule % , as the dispersed phase, are used in this process (3). All pumps are diaphragm type metering pumps having

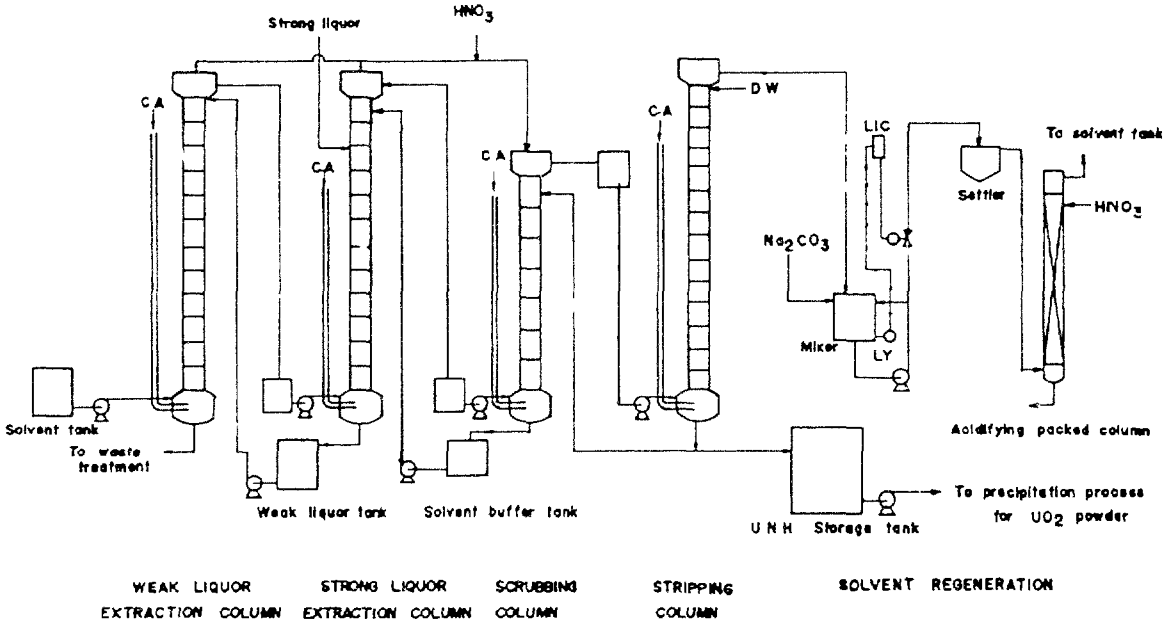

Fig 2. Purification system

a good accuracy and explosion- and acid-proof. Each column diameter is 15 cm, effective height for both extraction columns 6 m each, scrubbing column 4 m, and stripping column 7 m. The overall diagram is shown in Fig.2.

4-1. Extraction

The aqueous "strong liquor" solution produced through dissolution and filtration processes which contained 350 g-U/l and 1.5-2.0 N of free acidity, is fed to the top of the strong liquor extraction column. This aqueous solution flows contercurrently with the organic solvent. The slightly loaded solvent from the top of the weak liquor extraction column is fed to the bottom of the strong liquor extraction column through the pulsation leg. The aqueous solution from the bottom of the strong liquor extraction column is fed to the top of the weak liquor extraction column, and fresh organic solvent which is pre-equilibrated with nitric acid is entered into bottom of this column. Two flows are also contacted counter-currently each other. The dispersed phase hold-up appears a parabolic distribution along the column axis and shows a maximum at 1/3 position from the bottom of the column and the overall mean hold-up is about 10%. The uranium concentration of the loaded TBP from strong liquor extraction column is about 145 g-U/l corresponding to about 90 % of its capacity, and the uranium content of the raffinate(liquid waste) from weak liquor column is dropped down below 20 ppm.

The control element in the extraction process is molybdenum content, which is contained about 1500 ppm in yellow cake as shown in Table 1. The amount of Mo content in the pure uranyl nitrate solution which is bottom product of the stripping column is checked every 4 hours. The uranium concentration of the loaded TBP from the top of the two extraction columns is continuously determined by recording the data with densimeter installed at the top of the column and converting into concentration with the known value of the solution density. Samples are taken from the sampling points along the column axis and local hold-up and the uranium concentration between two phases are determined from these samples. The uranium content in the raffinate is also checked every 4 hours interval.

Table 1 Comparision of impurities in purified UN solution and nuclear grade UO_2 powder.

	Yellow cake	Purified UN solution	Nuclear grade UO_2 powder
U		135g-U/ℓ	*87
Mo	*0.15	0.73	2
Fe	*0.35	10	20
Si	*0.40	10	10
Ca	10		2
Mg	4	1	2
Cu		1	20
Ni		5	5
Cr		5	11
Mn		1	1
B		0.1	0.2
Pb		0.3	1

* Unit : percent, others : ppm based on U

4-2. Scrubbing

The loaded TBP from the extraction step is scrubbed using a part of the stripped uranyl nitrate solution. Because of 1500 ppm of Mo content, the acidity of scrubbing solution is adjusted up to 4 N by adding 15 N HNO_3 solution through the top of the column. The flow rate of the scrubbing solution is about 10 % of that of the loaded TBP and aqueous solution from the bottom of this column is recycled to the strong liquor extraction column. In each phase, uranium concentration coming out of column top and bottom is kept nearly the same as the inlet concentration and the overall mean hold-up in the column is controlled up to 10 %.

4-3. Stripping

The demineralized water is used as the stripping solution and the flow rate is adjusted to maintain the uranium concentration of 130-135 g-U/l in the pure uranyl nitrate solution. In order to keep the operation temperature about 50-55°C, the demineralized water and loaded TBP are preheated to 65°C and 55°C, respectively, and is fed into the column top and bottom. The uranium concentration in the uranyl nitrate solution from the column is constantly determined by the measurement of the density and the Mo content is analyzed every 4 hours. Particularly, when the uranium concentration of the product is over 140 g-U/l, uranium content in the stripped TBP is increased by gram-order. In addition, the stripped TBP solution coming out of the top of the column passes the coalescencer filled with the teflon wool in order to remove the very fine particles of aqueous phase entrained with organic phase. The purity of uranyl nitrate solution is well agreed with the nuclear grade of the UO_2 powder and Table 1 shows the comparison of the feed materials and purified uranyl nitrate solution with the nuclear grade UO_2 powder.

4-4. Solvent regeneration

In the solvent regeneration process, about 8 % (wt) sodium carbonate solution is contacted with the stripped TBP solvent in order to remove all impurities. The flow rate of the sodium carbonate solution is about 10 % of that of solvent and two phases are mixed by recirculation using centrifugal pump and then sent to the settler through the teflon wool (4). The solvent is contacted conter-currently with 2 N nitric acid solution in the packed column in order to acidify. The aqueous solution from the packed column is used as weak liquor, and acidified organic solvent is recycled to the weak liquor extraction column. The sodium carbonate solution used for regeneration is treated with the sodium hydroxide solution to recover the uranium.

5. EVAPORATION/CONCENTRATION OF URANYL NITRATE SOLUTION

In this process, the concentration of the uranyl nitrate solution from the solvent extraction increases from 130 g-U/1 to 420 g-U/1. The evaporator is a cylindrical form with 40 cm in diameter and has a teflon lining in order to prevent the intake of impurities possibly generated from the cylinder wall and has an internal electric heater as the heating source.

The solution temperature is controlled at $103^{\circ}C$ and the solution is kept evaporated at higher concentration without boiling, and one batch operation is terminated by the density measurement of the uranium nitrate solution.

The advantages obtained from concentration/evaporation as follows;

- Possible control of particle characteristics such as size distribution of the final UO_2 powder.
- Smaller scale equipments, that is, smaller capacities of AUC precipitator, filtration receiver or storage tank because of the decreased volume of the uranium solution to handle. For instance, when a 420 g-U/l solution is used instead of a 130 g-U/l uranium nitrate solution, then the AUC precipitator's volume becomes 60 l instead of 140 l.
- Reduction of gas and power consumption. It is better to keep constant ammonium carbonate concentration in the mother liquor to obtain the constant precipitation conditions. As a result, the amount of ammonia and carbon dioxide is decreased to about 30 %.
- Reduction of liquid waste.

6. AUC PRECIPITATION

In this process AUC is prepared by the reaction of CO_2 and NH_3 with the uranium nitrate solution according to the total reaction equation;

$$UO_2(NO_3)_2 + 6NH_3 + 3CO_2 + 3H_2O \longrightarrow (NH_4)_4UO_2(CO_3)_3 + 2NH_4NO_3$$

The precipitator made from stainless steel, is a cylindrical form with 40 cm in diameter and the slurry is circulated from the bottom part of the precipitator to the central part by using the pump.

Carbon dioxide and ammonia gases are introduced into solution through circulation lines. The precipitation is carried out batchwisely and preceeded as following three steps;

- Preheating; In order to obtain ammonium carbonate solution and to raise the temperature up to 58°C, gases are fed into the precipitator. Solution is heated with both heat of reaction and external hot water circulation.
- Uranyl nitrate solution feeding; AUC particles are produced at 58°C while feeding uranyl nitrate solution together with ammonia and carbon dioxide gases. Crystals deposit at the gas nozzle and often plug the gas feeding line. In this case the distilled water is automatically injected through nozzle and wash them out according to the pressure built in the gas lines.
- Cooling; For easy handling of AUC slurry and for the reduction of uranium content in the mother liquor, the reaction solution is cooled down to below 20°C and furthermore ammonia and carbon dioxide gases are introduced.

One AUC particle is calcined and reduced to one UO_2 particle (5) in the AUC conversion process, the particle size distribution and shape of UO_2 particles depend completely on AUC particles. Consequently, granular shape of AUC particles, that is, granulation is essential for this AUC conversion process. Hence, it is very important to control the size and shape of AUC particles in the precipitation.

- Morphology; One of the advantages of the AUC conversion process is the excellent flowability of UO_2 powder, which has granular shape. The excellent granulation is mainly due to attrition of AUC particle edges by external circulation. During the precipitation, the long AUC crystals (shown in Fig.3), having the ratio of length to diameter over 1:10, are generated depending on pH but these are not desirable products. It is necessary to control the ratio 1:1 to 1:3 , possibly with wide range of pH values between 7.8 and 10.

-Size distribution; As it is known(6), the size distribution depends on the desupersaturation rate from the showering point in the earlier stage of precipitation. The operation parameters for the rate control are temperature, gas feed rate, operation time, and uranium concentration in the uranyl nitrate solution, but the easiest way to control the rate is uranium concentration itself. As a result, 420 g-U/l of solution is used in this process.

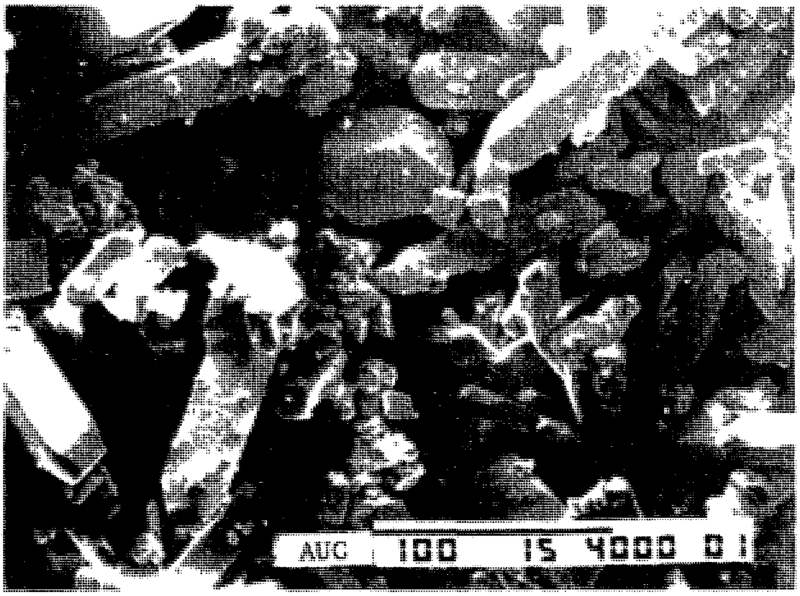

Fig.3.Scanning electron micrograph of AUC crystal
(X 3,000)

7. FILTRATION

AUC particles produced from the precipitation process are separated from the mother liquor and dried. The average AUC particle size is about 40 µm, which is relatively large, so simple vacuum filter can be used. In order to increase drying rate, methyl alcohol is used as washing solution.

8. CALCINATION AND REDUCTION

The AUC particles are converted into the UO_2 particles by reaction with hydrogen gas in a fluidized bed reactor according to the following equation;

$$(NH_4)_4UO_2(CO_3)_3 + H_2 \longrightarrow UO_2 + 4NH_3 + 3CO_2 + 3H_2O$$

This fluidized bed reactor is 17 cm in diameter and 220 cm in height. The AUC powder are fed from the hopper using the vibrating feeder at the top of the bed. In order to prevent the loss of the UO_2 powder, a catridge filter was used and back-flushed every 20 minutes. The calcination and reduction is consisted of the following three steps;

-AUC feeding; The reaction occurs at 520°C with 13 % of hydrogen and 87 % of steam atmosphere and the temperature can be adjusted by feeding rate of AUC powder. In this step, either hydrogen concentration or temperature changes within 10 % doesn't significantly influence the powder characteristics.

-Pyrohydrolysis; The UO_2 powders are only treated in the atmosphere of steam in this step. This treatment influences significantly on the UO_2 powder characteristics and it is the step to control the tap density, specific surface area, pore size and its distribution together with time and temperature. The tap density changes virsus time at 650°C are shown in Fig.4.

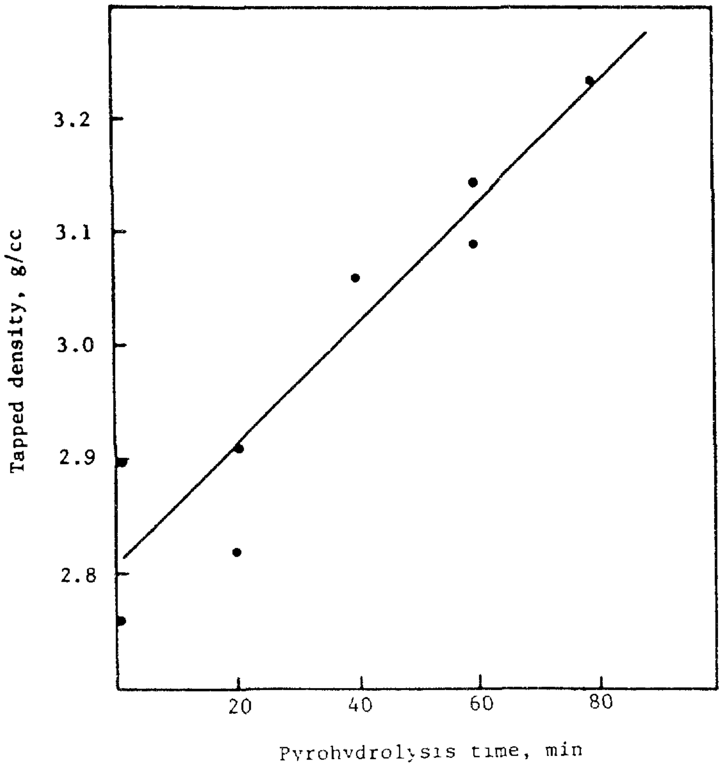

Fig. 4. Tapped density change of UO_2 powders vs pyrohydrolysis time.

-Reduction; This step is for the lowering O/U ratio to 2.0 from 2.2 resulted from the pyrohydrolysis step.

The UO_2 particle characteristics affect mainly on the sinterability. For instance,specific surface area gives great deal of effect on the sintered density as shown in Fig.5. Accordingly, it is very important to control and adjust the characteristics of the UO_2 powder, possibly in this step. However, these characteristics are interrelated each other and it is impossible to adjust independently,

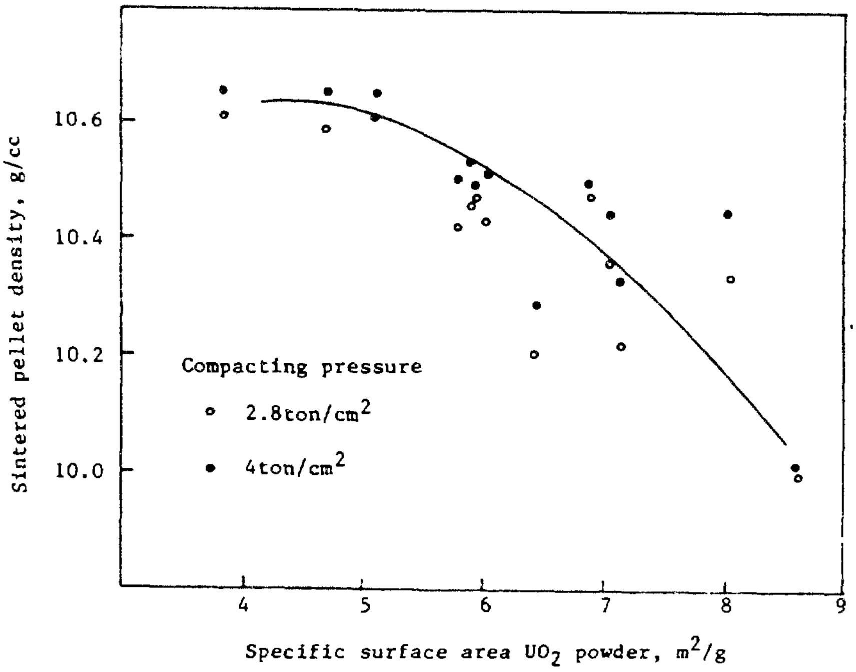

Fig. 5. Relationship between surface area of UO_2 powder and sintered density of pellets.

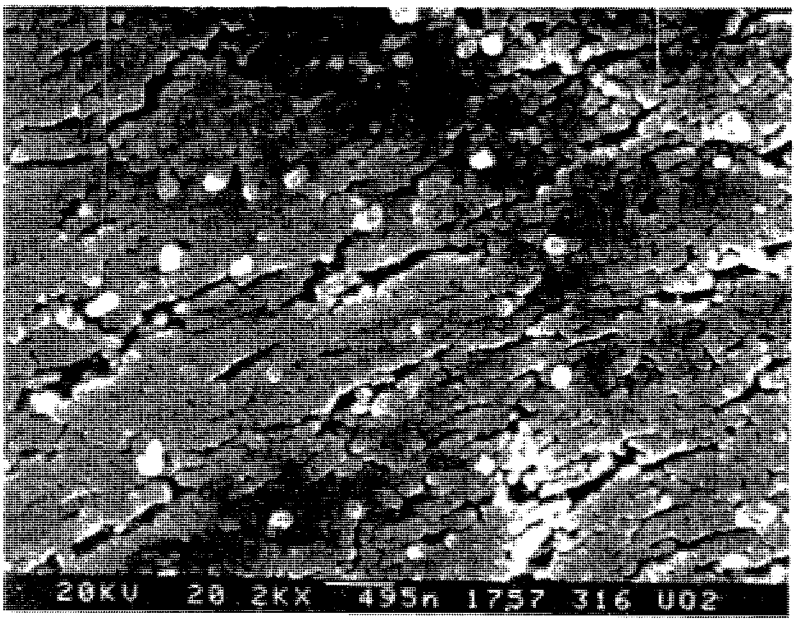

Fig.6. Scanning electron micrograph of UO_2 powder (X 20,000)

that is, a smaller tap density means a large pore in UO_2 particles and also leads to increase in specific surface area. This interrelationship can be explained by the change of a monocrystalline to a polycrystalline UO_2 particle. As shown in Fig.6, UO_2 particle has a great number of small crystallites. The larger the size of the crystallite, the bigger the tap density, and the smaller the specific surface area. Consequently, the crystallite size must be controlled for the sinterable UO_2 powders.

9. STABILIZATION

This step is the partial oxidation process of UO_2 to have a stable oxidized film on the UO_2 particle surface (7) and increase of the ratio of O/U in the controlled oxygen atmosphere. Since the O/U ratio of UO_2 powders is varied with O_2 concentration, temperature and time, O/U ratio can not be controlled only by the operation parameters. That is, specific surface area should first be controlled.

10. URANIUM RECOVERY

The filtrate contains 600-800 ppm of uranium, because $CO_3^{=}$ ions tend easily to form complex ions with UO_2^{++} ions in the mother liquor (8). Hence, it is essential to eliminate $CO_3^{=}$ ions in order to recover uranium from the filtrate. The filtrate is heated up to 98°C ,with stirring, to remove $CO_3^{=}$. The final solution pH turns to about 9 with precipitation of ammonium diuranate(ADU). The uranium content of final liquid waste becomes below 2 ppm.

11. CONCLUSION

The project to localize uranium refining and conversion technologies, as a part of HWR fuel manufacturing, has been successfully completed throughout the in-file test, out-of-file test and even through the actual irradiation in a commercial power reactor. This accumulated technologies and experiences will help us to expand our capacity in order to supply all the fuels for the Wolsung reactor in the near future.

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RESEARCH AND DEVELOPMENT OF UF_6 CONVERSION IN JAPAN NOW AND SUBJECTS IN FUTURE

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Abstract

PNC is engaging the following R&D'S of UF_6 conversion.

① Rifining and Conversion Pilot Plant (200TU/Y) which produces UF_6 from uranium concentrates by the PNC process
② UF_6 conversion of reprocessed uranium (4TU/Y) by dry process

PNC has accoumulated many important experiments and been making many improvements.

We have to solve the following subjects to commercialize the UF_6 conversion in future.

① The high cost's problem owing to small domestic UF_6 market
② Adaption of the most appropriate process for Japan's demand

These subjects will be solved by combining reprocessing, conversion and enrichment facilities at the same site to reduce total fuel cycle cost.

We are willing to contribute the world's UF_6 conversion industry by developing the latest technology.

1. Introduction

Originally PNC process was developed for the metal fuel production in Japan, which produces UF_4 directly from ore without the yellow cake production.

With the development of the Light Water Reactor which uses slightly enriched uranium, the feed material UF_6 became needed to produce after UF_4 production process.

So that PNC started to develop the succeeding process in 1976 and then succeed to produce UF_6.

Based on these success, PNC started to construct the UF_6 conversion pilot plant of 200T/year in 1979 to promote further industrialization and supply UF_6 to the enrichment pilot plant on the same site.

This plant was improved to produce UF_6 not only from ore but from the yellow cake which is the current material in the world

From the operation, we found the merits of the PNC process from yellow cake and with enrichment plant.

On the other hand, with the start up of Tokai Reprocessing plant, it became needed to develop the recycling technology of reprocessed uranium to LWR through UF_6 conversion and enrichment.

So that the conversion test facility (CTF－Ⅱ) of reprocessed uranium was constructed in the same plant.

From the tests of CTF－Ⅱ, we found the merit in co-conversion with reprocessed and natural uranium.

The reseach and development of UF_6 conversion by PNC process before the pilot plant construction has already been reported at the previous IAEA AdUisory Group Meeting held in Paris in 1980 〔1〕, therefore we will report here the experiences at the pilot plant of PNC process and CTF－Ⅱ of reprocessed uranium and the future subjects.

2. UF_6 conversion in Japan now.

The following development has been carried out in Japan

(1) The pilot plant test of refining and conversion

① Feeds : Yellow cake in the world and domestic ore.

② Process : PNC process (see Fig-1)

③ Capacity : 200tu/year

④ Start up : March 1982

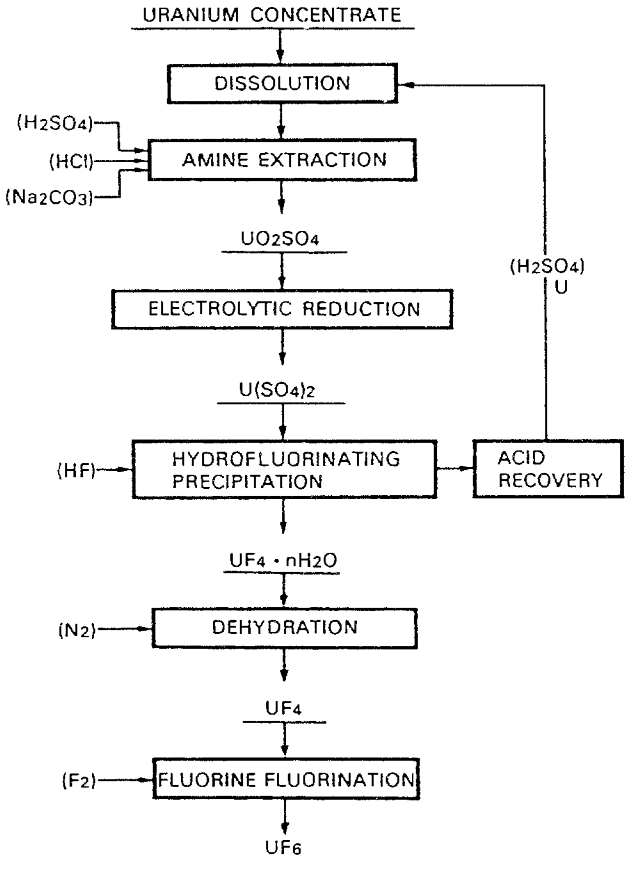

Fig.1 REFINING AND CONVERSION PILOT PLANT

(2) The UF_6 conversion test for reprocessed uranium. (CTF-Ⅱ)

① Feeds : reprocessed uranium, UO_3 (U235 below 1.6%)

② Process : conventional dry process (See Fig-2)

③ Capacity : 2.4 kgu/hr

④ Start up : March 1982

A theme (2) will be reported in another session.

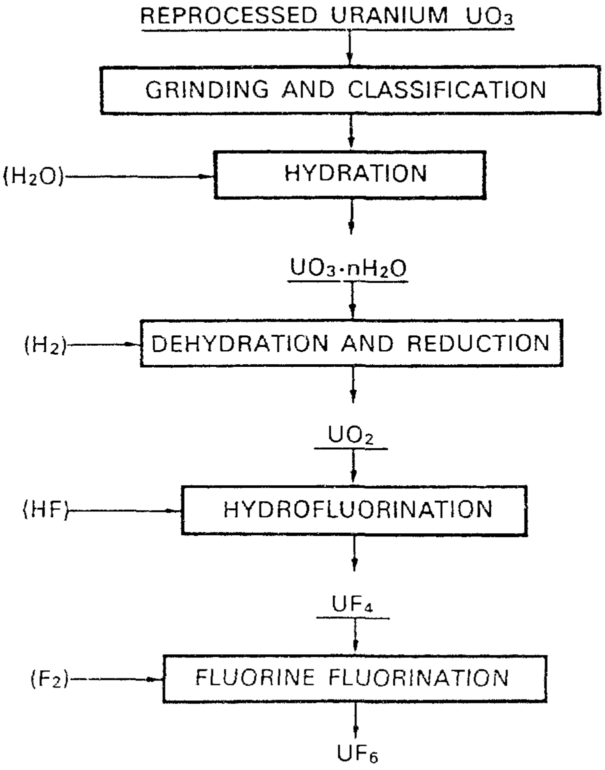

Fig-2 CONVERSION OF REPROCESSED URANIUM

3. The experiences and improvements of the Rifining and Conversion pilot plant.

(1) Process flow (See Fig-3)

The PNC process consists of the following steps.

① Dissolusion with sulfuric acid (See Fig-3)

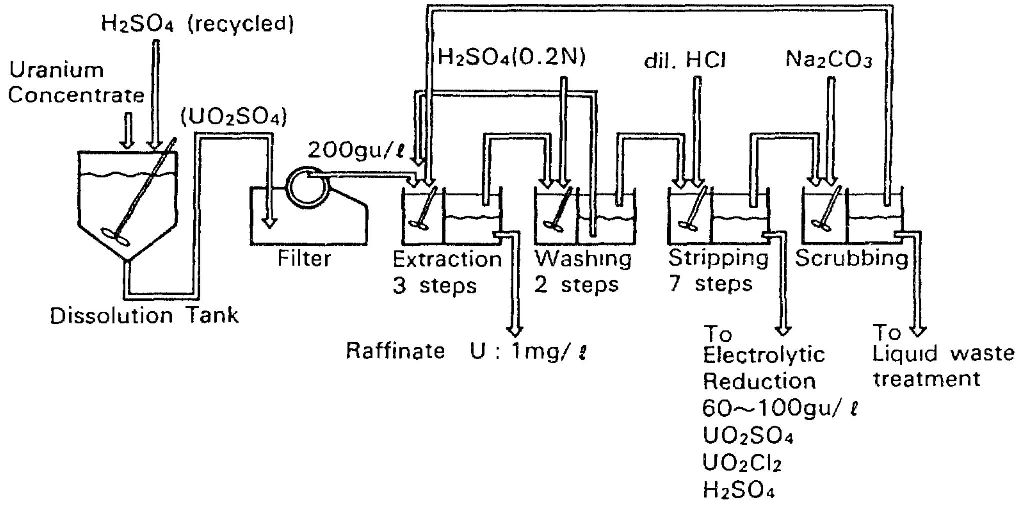

Fig-3 URANIUM CONCENTRATE DISSOLUTION AND AMINE EXTRACTION

Yellow cake is dissolved with sulfuric acid, then the residue is filtrated out.

② Amine extraction (See Fig-3)

Dissolued uranium is extracted into tri-n-octyl amine solvent, selected from impuriries, by forming negative complex ion $[UO_2 (SO_4)_3]^{-4}$.

The equipment consists of 4 stage extracting, 2 stage scrubbing, 7 stage stripping and 2 stage solvent scrubbing mixer settlers.

③ Electrolytic Reduction (See Fig-4)

Uranyl (UO_2^{2+}) solution is reduced into uranous (U^{4+}) solution by the electrolytic method.

Electrolytic cell is separated into an anode room and a cathode room by an anion exchange membrane.

Sulfuric acid is anolyte and uranyl sulphate is catholyte.

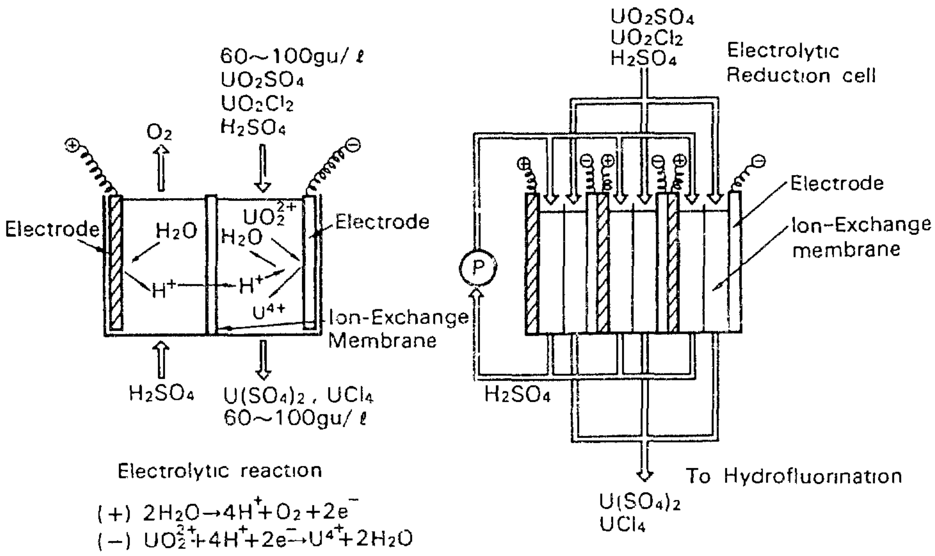

Fig-4 ELECTROLYTIC REDUCTION

Hydrogen ion produced at anode passes through the membrane and reduces UO_2SO_4 into $U(SO_4)_2$ at cathode.

④ Hydrofluorinating precipitation (See Fig-5)

Uranous Solution is precipitated to hydrated uranium tetrafluoride $UF_4 \cdot nH_2O$ with hydrofluoric acid in a reactor vessel of 8 cubic meter made of teflon coated fiber-reinforced plastic.

⑤ Dehydration (See Fig-5)

Hydrated uranium tetrafluoride $UF_4 \cdot nH_2O$ is dehydrated in a fluidized-bed reactor of 35cm diameter with N_2 gas.

⑥ Fluorine fluorination (See Fig-6)

Dehydrated UF_4 is converted to UF_6 gas with F_2 gas, and then UF_6 gas is cooled and trapped in cold traps.

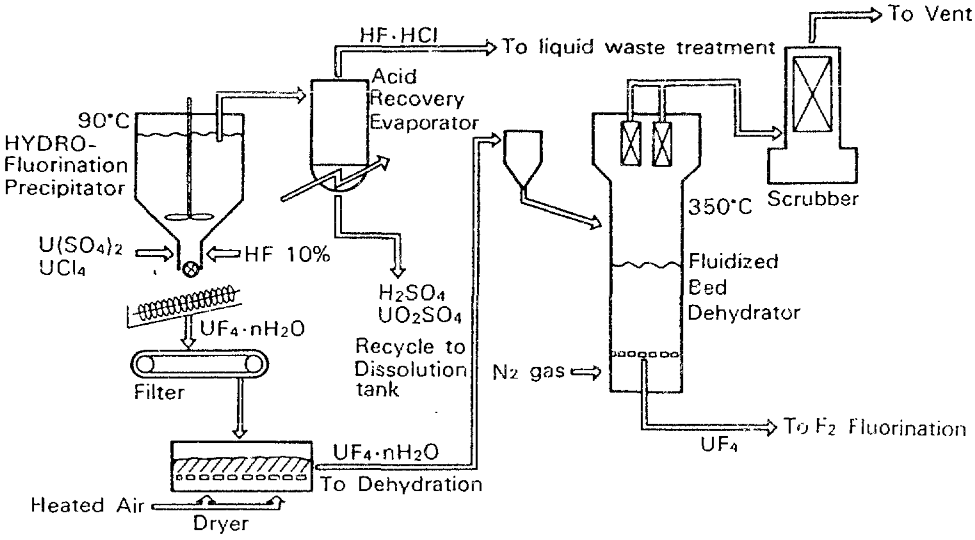

Fig-5 HYDROFLUORINATION AND DEHYDRATION

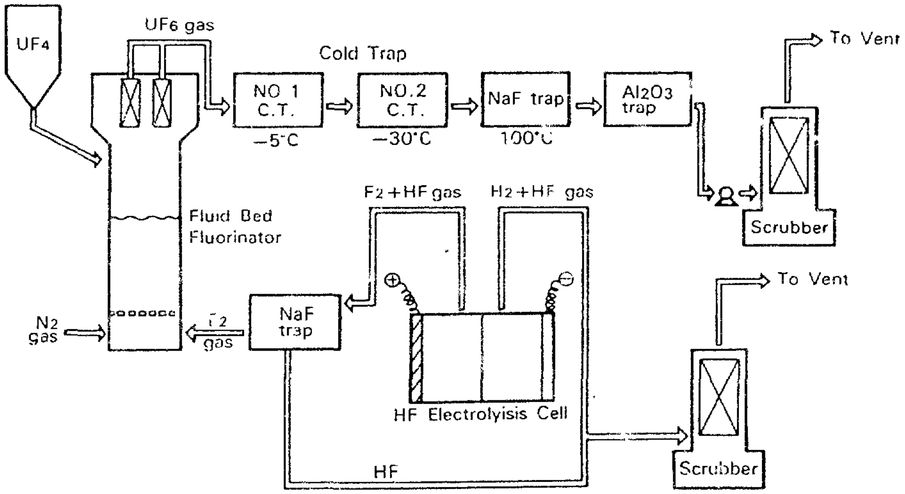

Fig-6 F2 FLUORINATION

The fluorinator is a fluidized-bed reactor of 40cm diameter.

⑦ Liquid waste treatment (See Fig-7)

The following liquid waste is discharged from the process.

1) Raffinate from amine extractor containing H_2SO_4 and impurities.

2) Solvent scrubbing waste containing Sodium carbonate Na_2CO_3.

3) Hydrofluorination waste containing H_2SO_4, HCl, HF and U.

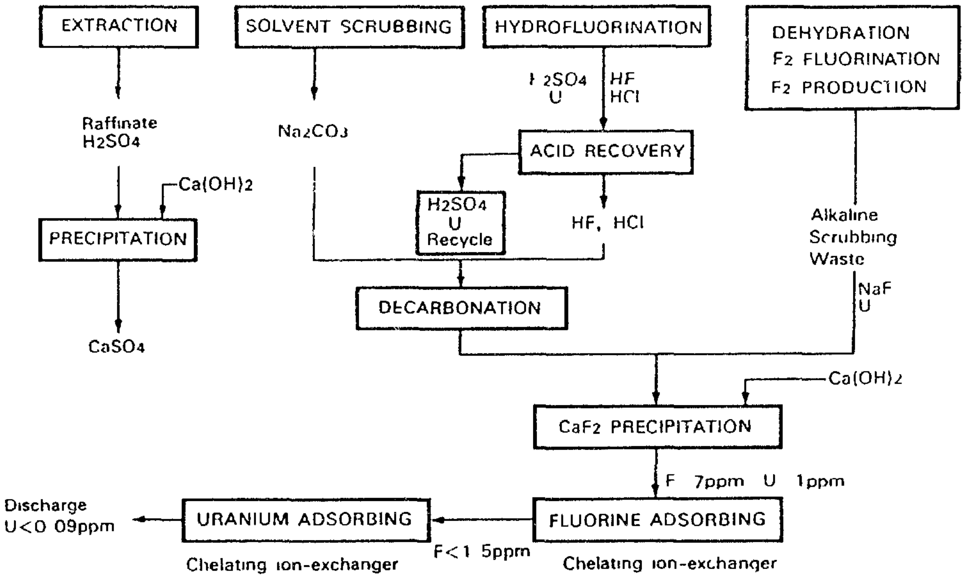

Fig-7 WASTE TREATMENT

4) Alkaline scrubbing waste in dehydration and F_2 fluorination process containing NaF and U

Raffinate is treated with $Ca(OH)_2$ to remove containing H_2SO_4 and impurities by precipitating as $CaSO_4$ etc

Hydrofluorinating waste is evaporated to recover H_2SO_4 and Uranium

Vapour containing HF and HCl is condensed and used to decarbonate the solvent scrubbing waste

The decarbonated waste and alkaline scrubbing waste is treated with $Ca(OH)_2$ to remove containing fluorine and uranium as precipitated CaF_2 roughly, then small amount of residual F, U in waste is removed by chelating ion-exchange adsorbing resin for discharging from facility

(2) Specification of impurities in uranium concenrate

The specification of impurities in feed uranium concenrate is determined by decontamination factor in erch process and DOE specification of product UF_6.

The PNC process has 3 purification steps as follows.

① Amin extraction ② UF_4 precipitation ③ F_2 fluorination.

The decontamination factors and uranium concenrate specification derived from them is shown in table-1

The elements which decrease the efficiency of electrolytic reduction are specified further strictly, but this is not fatal.

The limited impurities are noble metals of Cu, Ag, etc. and transition metals of Fe, Co, Ni, etc.

Since Co_3, PO_4, Cl disturb the amine extraction and As is strict regulated environ mental material, these materisls are strictly specified.

Table 2 and 3 show the impurities specification of converters in the world. [2].

Severe materials in the PNC process are PO_4, Cl, F, Mo, CO_2 and As.

Table-1 DECONTAMINATION FACTORS OF EACH STEP IN PNC PROCESS AND URANIUM CONCENTRATE'S (U C) SPECIFICATION

( ) estimated value

		Impurity elements	UF_6 Spec	Decontamination factor ① Extraction	 ② UF_4 Precipitation	 ③ F_2 Fluorination	Uranium Concentrate's Spec
		Sb	1 ppm/U	(1 400)	(100)	2ppm/U	NON
		Nb	〃	(8 000)	(100)	4	NON
		Ru	1 〃	(28 000)	(1 000)	3	NON
		Ta	1 〃	(8 000)	(100)	(1)	NON
		Ti	1 〃	1 200	1 000	(1)	NON
		Cr	10 7	30 000	(1 4)	(1)	NON
		Mo	1 4	2 7	1 200	(1)	4 500
		W	1 4	(3 000)	1 200	(1)	NON
		V	1 4	80	200	( )	96 000
		Ca	Total 300	21 000	4	70	NON
		Mg		650 000	445	3	NON
		Th		3 300	26	(100)	NON
		Zr		50	100	(100)	NON
		Na		1 800	20	20	NON
		K		1 800	50	60	NON
PROCESS DISTURBANCE	REDUCTION	Fe		28 600	2 000	00	NON
		Ni		878 000	400	(00)	NON
		Co		210	2 000	(100)	2 100
		Ag		1 000	1 300	100)	1 000
		Cu		51 200	1 300	(100)	25 000
	EXTRACTION	Br	5		(10 000)	1	10 000
		Cl	100		(10 900)	1	
		F	NON		1	1	0 000
		PO_4	50		(10 000)	1	10 000
		CO_3			(10 000)		15 000
OTHERS		As	NON	1 400	15 000	(1)	1 000
		B	8	4 200	4 000	( )	NON
		Si	00	37 800	100	( )	$SiO_2$15 000

Table-2 COMPARISON OF CONVERTERS' MAXIMUM ALLOWABLE SPECIFICATION LIMITS (MAXIMUM PERCENTAGES)

Constituent	PNC	Allied	Kerr McGee	BNFL	Comurhex	Eldorado
Vanadium (V)	9 6	0 75	0 85	0 70	0 30	0 85
Phosphorus (P)	1 0(PO_4)	1 00	0 70	1 00	1 00	0 70
Halogens (Cl Br I)	1 0	0 10	0 50	0 30	0 25	0 30
Flourine (F)	1 0	0 10	0 15	0 30	0 30	0 20
Molybdenum (Mo)	0 45	0 30	0 75	0 60	0 60	0 45
Sulfur (S)	——	12 00	4 50	——	——	——
Iron (Fe)	——	1 00	2 00	——	——	——
Arsenic (As)	0 1	0 10	2 00	2 50	2 50	2 00
Carbonate (CO_3)	1 5	0 50	3 00	4 00	3 00	3 00
Calcium (Ca)	——	1 00	1 50	5 00	5 00	1 50
Boron (B)	——	0 10	0 15	1 00	0 20	0 20
Silicon (Si)	8 0(SiO_2)	2 50	1 50	8 00	5 00	——
Magnesium (Mg)	——	0 50	1 50	——	——	——
Thorium (Th)	——	——	2 50	——	——	2 50
Zirconium (Zr)	——	——	0 50	0 50	2 00	——
HNO_3 Insoluable Uranium	——	——	——	——	0 10	0 10
Extractable Organic Material	——	——	0 10	——	0 10	0 10
Water (H_2O)	15 0	5 00	7 50	15 00	10 00	5 00
Sodium (Na)	——	7 50	——	——	15 00	——
Potassium (K)	——	3 00	——	——	——	——
Titanium (Ti)	——	0 05	——	——	——	——
Sulfates (SO_4)	——	——	——	——	10 00	10 50

Table-3 COMPARISON OF CONVERTERS' IMPURITY SPECIFICATION LIMITS WITHOUT SURCHARGE

(MAXIMUM PERCENTAGES)

Constituent	PNC	Allied	Kerr-McGee	BNFL	Comurhex	Eldorado
Vanadium (V)	1 0	0 10	0 10	0 20	—	0 10
Phosphorus (P)	0 3(PO_4)	0 10	0 35	0 50	—	0 35
Halogens (Cl Br I)	0 3(Cl^-)	0 05	0 25	0 10	—	0 25
Flourine (F)	0 3(F^-)	0 01	0 15	0 01	0 15	0 15
Molybdenum (Mo)	0 1	0 10	0 15	0 20	0 20	0 15
Sulfur (S)	—	3 00	3 50	—	—	—
Iron (Fe)	—	0 15	1 50	—	—	—
Arsenic (As)	0 05	0 05	1 00	1 00	1 00	1 00
Carbonate (CO_3)	0 5	0 20	2 00	2 00	2 00	2 00
Calcium (Ca)	—	0 05	1 00	1 00	1 00	1 00
Boron (B)	—	0 005	0 15	0 20	—	0 15
Silicon (Si)	4 0(SiO_2)	0 50	1 00	4 00	—	—
Magnesium (Mg)	—	0 02	1 00	—	—	—
Thorium (Th)	—	—	2 00	—	—	2 00
Zirconium (Zr)	—	—	0 50	0 10	0 20	—
HNO_3 Insoluable Uranium	—	—	0 10	—	—	0 10
Extractable Organic Material	—	—	0 10	—	—	0 10
Water (H_2O)	10 0	2 00	7 50	10 00	—	5 00
Sodium (Na)	—	0 50	—	—	1 00	—
Potassium (K)	—	0 20	—	—	—	—
Titanium (Ti)	—	0 01	—	—	—	—
Sulfates (SO_4)	—	—	—	—	—	10 50

(3) The purity of product UF_6

We converted the typical uranium concentrate in the world as follows

① Pingxiang refinary in china, UO_2 type.

② Ranger mine in Australaria, U_3O_8 type.

③ Key lake mine in Canada, U_3O_8 type

④ Akouta mine in Niger, MDU, SDU type

The impurities in these uranium concentrate is shown in table 4, and among these, the Akouta's uranium concentrate contains Mo and almost impurities the most.

So, the purity of UF_6 product converted from Akouta's uranium concentrate is shown in table 5, and it satisfies the DOE specification

Table-4 IMPURITY CONCENTRATE OF FEED URANIUM

(PPM)

Impurity	Spec		CHINA	Australia	CANADA	Niger
	Standard	Maximum	Pingxiang	Ranger	Key lake	Akouta
V	10,000	96,000	5	660	< 10	3,300
P	3,000	10,000	170	380	7	2,900
Cl, Br, I	3,000	10,000	7	30	2	1,500
F	3,000	10,000	7	1	7	140
Mo	1,000	4,500	30	10	250	2,400
S	——	——	——	3,700	43,000	——
Fe	——	——	70	1,100	100	3,900
As	500	1,000	1	<1	170	< 100
CO_3	5,000	15,000	——	——	——	——
Ca	——	——	100	1,000	110	2,000
B	——	——	10	3	3	990
SiO_2	40,000	80,000	60	1,500	2,200	5,800
Mg	——	——	5	1,000	23	2,900
Th	——	——	20	——	——	4
Zr	——	——	5	20	80	7,700
Na	——	——	0.4	170	230	15,200
K	——	——	10	400	13	1,000
Ti	——	——	< 1	<5	< 5	——

Table-5 IMPURITY CONCENTRATE OF PRODUCT UF_6

PPM/U

Impurity	Feed U (Akouta)	Dissolving Solution	Stripping Solution	UF_4	UF_6	DOE spec
Al	1,700	1,600	38.3	3.4	5.48	Total 300ppm /U
Ca	2,000	1,300	45.5	26.2	1.85	
Cd	<5	<1.0	<0.3	< 0.2	<0.2	
Cu	<5	7.7	<0.6	< 0.4	<0.2	
K	1,000	552	3.9	5.5	3.6	
Mg	2,900	3,100	12.2	0.2	0.52	
Mn	300	217	1.9	< 0.2	<0.2	
Na	15,200	19,700	495	1.51	1.21	
Ni	<10	3.01	0.66	2.3	0.33	
Pb	<10	6.7	0.56	< 0.2	<0.2	
Zn	56	16.9	5.6	0.38	4.4	
P	2,900	——	44	0.5	0.5	50
Si	5,800	——	0.2	< 0.2	<0.2	100
Ti	——	101	2.5	< 1.0	<1.0	1.0
Mo	2,400	1,800	800	< 1.0	<1.0	1.4
V	3,300	482	<5	< 4	<1	1.4

(4) Loss of uranium

The possible outlets of uranium from the PNC process are as follows.

① Raffinate in amin extraction

② Solvent scrubbing waste.

③ Hydrofluorinating waste.

④ Off gas from the UF_6 cold traps.

There is very few uranium loss from the extration process ①, ②.

Hydrofluorinating waste ③ contains 10% uranium which is recovered by an evaporator with H_2SO_4 to recycle to uranium concenrate dissolusion process.

Therefore there is no loss of uranium in this process ③.

UF_6 gas in off gas ④ is recovered by NaF chemical traps now, but NaF is expensive.

So we are now going to construct a water scrubber which absorbs UF_6 gas in off gas to recycle uranium.

(5) The process economy

The main expendetures on the present process are as follows.

① Steam for acid recovery

② Hydrofluorine

③ $Na_3\ CO_3$ for solvent's scrubbing

④ N_2 gas for fluidizing inert gas.

⑤ HCl for stripping.

⑥ NaF pellet for UF_6 recovery.

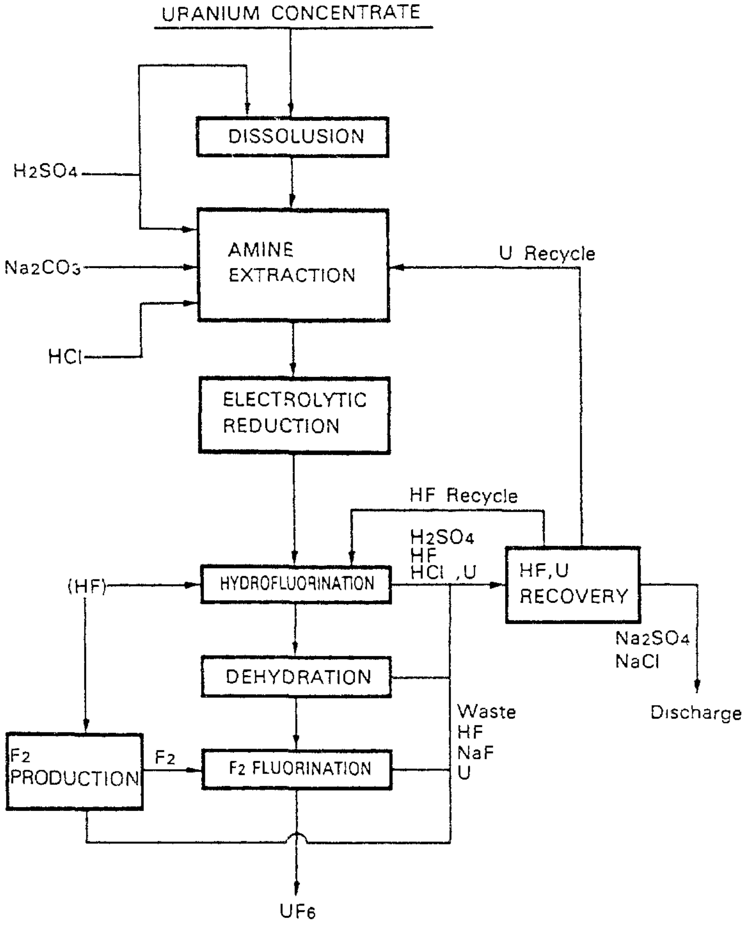

Fig-8 ADVANCED PNC PROCESS

Therefore PNC has developed the economical hydrofluorine and uranium recovery method which reduces the ①, ② and ⑥.

As shown in fig-8, this advanced process treats the waste containing F, Cl, SO_4, Na, U・etc and recovers HF and U by precipitation and dissolution and evaporation, therefore this process does not generate the solid waste which raises the cost by strage.

We will demonstrate this advanced process by the pilot plant in this year.

We are performing another improvements as follows.

① N_2 gas recycle

② UF_6 recovery by a water scrubber to replace NaF traps.

③ Impurities removal by ion-exchange resin to replace amine solvent extraction.

The concept ③ is derived from the merits of the PNC process which has an unique excess purification process that is UF_4 precipitation.

Therefore amine extraction can be replaced by more rough and cheap impurity removal method like ion exchange which removes only the impurities which can not be removed after and disturbs after process.

In the case of UF_6 convesion by the PNC process the concept of uranium extraction should be improved by the concept of small amount of impurities removal which leads to compact, cheap equipments and operation cost.

(6) Features of the PNC process

As describing above, the merits and demerits of the PNC process are summarized as follows.

(Merits)

① Triple purification

1) Amin extraction 2) hydrofluorinating precipitation

3) F_2 fluorination

② Easy to control the wet process until UF_4 precipitation because of homogenious low temperature system.

③ Active reactivity of UF_4 precipitate which simplifies the next F_2 fluorination process.

④ Easy to recycle the fluoride waste.

⑤ Easy to produce metal at mine site.

(Demerits)

① Large space occupation of the equipments with low concentrated solusion system.

② Many kinds of waste and large amount of waste.

We are developing the recycling system of waste and the compact equipments for wet process like pulse column extractor etc, and we will overcome these demerits in future.

4. The subjects of UF_6 conversion to commercialize in Japan.

[1] Needs

The commercializing plans of nuclear fuel cycle in Japan are as follows.

① Reprocessing plant (at Shimokita)

capacity : 800tU/year

start up : 1995

② Enrichment plant (at Shimokita)

Capacity up of 150TSWU, year by year. from 1991 to 2000.

The final capacity is 1500tSWU/year.

Therefore the demand of UF_6 conversion will grow large on near 1995.

[2] The problems in domestic industrialization

There are 5 commercial converters in the world with capacity of 52,290tU/year which is surficient to supply world's demands, and conversion price is cheap.

As shown in Fig-9, the conversion price depends on the plant scale largely.

The world's converter with the plant scale of about 10,000tU/year can afford the conversion service on the cheap price of 7 $/kgU (1.3 milliones yen /tU), but on the domestic case with the demand of 200 tU/year, the price will be 11.1 $/kgU (2.0 millions yen/tU) and it seems better to depends upon the

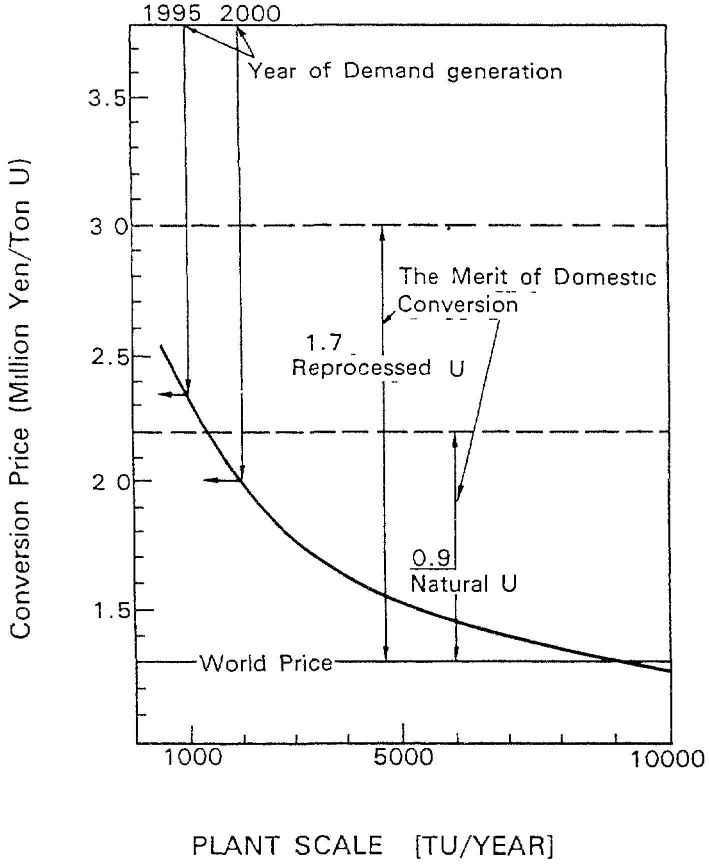

Fig-9 CONVERSION PRICE AND PLANT SCALE

world's converter's service.

But as shown below and Fig-10 the conversion price of uranium concentrate i is cheap and comparable with the transportation price or the interest of excess uranium preparation during UF_6 transportation etc.

	Terms	Price (million yen/tU)
①	Transportation of UF_6 to Japan	0.3
②	Transportation of reprocessed uranium from Japan to foreign converter's	0.8
③	UF_6 cylinder	0.3
④	The interest of excess uranium preparation during the period from conversion to enrichment (about 3 months)	0.3

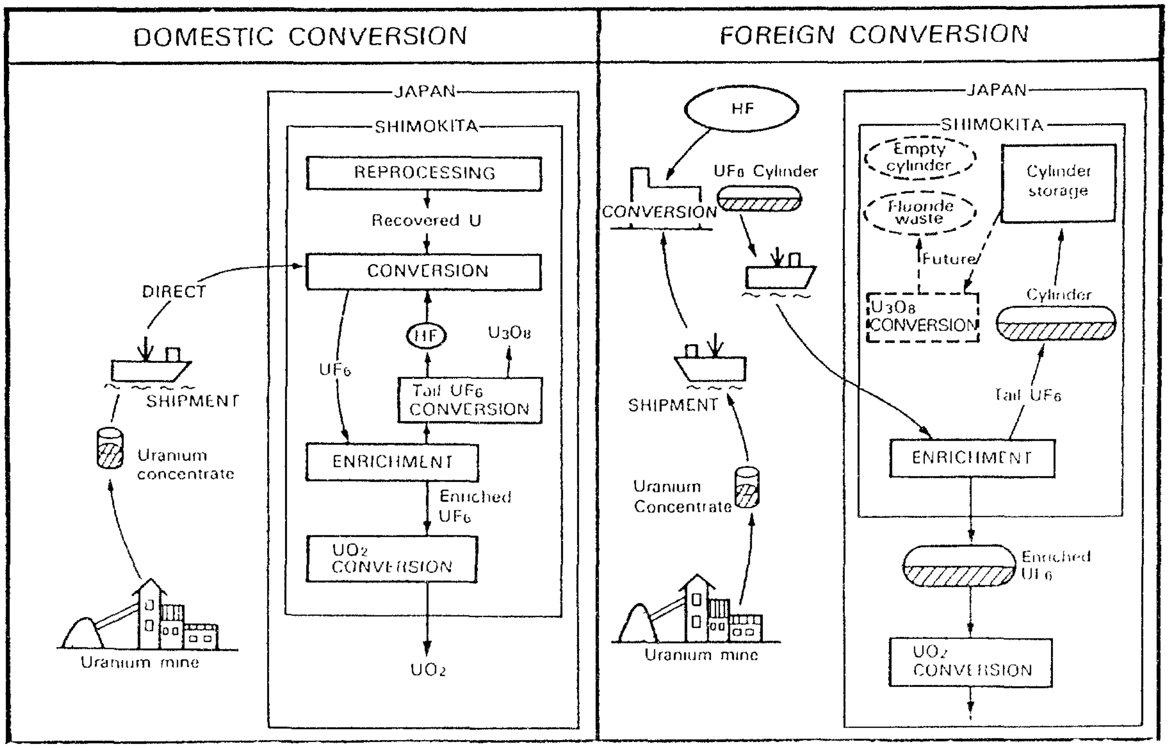

Fig-10

On the case of conversion of reprocessed uranium, there are no supplier in the world except COMURHEX with small capacity of about 250 TonsU/year and with about six times of natural uranium conversion.

On the case of domestic conversion, these expense can cut down and total economy can be achieved.

[3] The policy to commercialize the UF_6 conversion.

The following policy is necessary to commercialize the UF_6 conversion in Japan.

① Make a strong combination with enrichment to cut down

1) transportation cost

2) excess uranium preparation

3) excess time loss just like transportation period.

4) excess job like UF_6 analysis.

5) excess man power just like managemeut.

6) excess facility just like utility.

② Combine with the tail UF_6 conversion to recover the fluorine and the cylinders and cut down chemicals and material cost.

③ Combine also with UO_2 conversion of enriched uranium to cut down the same costs as ① and ②

④ Dilute the reprocessed uranium with the natural uranium to compensate the following demerits owing to the excusive conversion.

1) scale demerit

2) high γ-ray activity by U232 daughter

3) batch treatment by heterogeneous enriched uranium.

4) critical limitation by the enriched uranium over 1% U235

By the one pack construction of related planes as above, the following economy can be achieved, in the case of domestic UF_6 conversion.

Case	Saving cost (million yens/ton U)
① Natural Uranium	0.9
② Reprocessed Uranium	1.7

Therefore the establishment of the domestic conversion saves the total fuel cycle cost in Japan. (See Fig-9).

But these saving is effective only for the domestic demand.

The following technology should be developed to construct the economical conversion plant.

① Fluorine recovery from UF_6

② Mixed conversion of natural and reprocessed uranium.

If the AVLIS is industrialized in future, the merit of thePNC process for metal production will be recognized. scince almost mills at mine site can be exchanged the process easily to the PNC process because they have amine extraction process already.

But the following technology should be developed to reconstruct economical rifining plant of U metal at mine site.

① Hydrofluorine recovery from the process, UF_4 to metal.

② Economical fuel battery for electrolytic reduction.

PNC is developing the hydrofluorine recovery technololgy ① now, and fuel battery will be economical in future, so the mine-site PNC process may be hopeful in future.

5. Conclusions

The PNC process has been demonstrated by the pilot plant.

The purity of product UF_6 satisfied the DOE specification, even with the worst feed just like Akouta's uranium concentrate.

The uranium lose was negligible small, but uranium recovery systems like NaF traps are being improved to economical system like water scrubber.

We found that the non-sludge treatment of fluoride waste improves, the economy of chemicals, power and steam.

The more advanced process is being developed.

The mine-site PNC process will gain advantages in the future Laser enrichment system.

The conversion of reprocessed uranium by dry conventional process has been tested and the improved scale up equipments have been developed.

The domestic conversion plant will convert principally the reprocessed uranium.

To construct the economical conversion system in Japan, the UF_6 conversion plant should be combined with enrichment, tail UF_6 conversion and enriched UF_6 reconvesion plant, etc. and hydrofluorine recovering technology should be developed.

We are willing to contribute the world's UF_6 conversion industry by developing the latest technology.

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EXPERIENCE IN YELLOWCAKE REFINING AND ITS CONVERSION TO URANIUM TETRAFLUORIDE AT IPEN-CNEN/SP

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Abstract

This paper will focus the experience acquired during the operation of a pulsed columns solvent extraction pilot plant in the purification of a yellowcake produced from the industrial treatment of monazite sand. Special care was devoted to the rare earths elements, thorium and zirconium decontamination. Intermediate product is an uranium trioxide obtained by dewattering and thermal decomposition of diuranate and its conversion to uranium tetrafluoride.

The experience developed and the establishment of the quality control procedures to follow up all steps on both pilot unities as an important support to the technical work is emphasised.

1. INTRODUCTION

As contribution to the national program for developping atomic energy for peaceful uses, headed by the Brazilian Nuclear Energy Commission (CNEN), the Instituto de Pesquisas Energēticas e Nucleares (IPEN), S.Paulo, has given a great deal of effort concerning a systematic development of research for the establishment of the technology of uranium and thorium. The program is very much dedicated to the education and training of chemists and engineers, and to the production of some nuclear material for further metallurgic work and fabrication of fuel elements for research reactors.

In this paper we summarize the main activities on the purification of uranium raw concentrates and their conversion into nuclear grade compounds. The design and assemblage of pilot facilities for pure ammonium diuranate (ADU), uranium tetrafluoride and uranyl nitrate (UN) and its further denitration to trioxide are discussed.

The development and adaptation of analytical procedures and their applicability as an important support to the technical work and the quality control of the abovementioned nuclear grade materials is emphasied as well.

2. THE FIRST YELLOWCAKE

The first yellowcake that we work with since several years is a sodium diuranate (SDU) produced from the industrial processing of monazite sand [1]. The chemical treatment for breaking up monazite sand by alkaline process has been in practice in Brazil (S.Paulo) since 1948 on an industrial scale [2]. The production capacity is about 3000 metric tons of monazite per year for the production of thorium, rare earth chlorides (2000 tons) and phosphate as the main products. After decontaminated from radium and its descendents by coprecipitation with barium sulphate the rare earth chlorides are commercialized. Thorium is stocked mainly as a crude hydroxide (thorium sludge). Uranium is recovered as a by-produtct in the form of sodium diuranate.

The main impurities considered in this yellow cake are sodium, phosphate, silica, iron and, of course, thorium and rare earth elements (RE). Great concern was given to the decontamination of thorium and rare earths. In Table I is presented a representative composition of this SDU.

TABLE I - CHEMICAL COMPOSITION OF SODIUM DIURANATE

ELEMENT	%
U as U_3O_8	79.5
B	0.0002
Cu	0.001
V	0.004
Mo	0.0005
As	0.01
P as PO_4	0.3
S as SO_4	1.5
F	0.02
Halogens	0.015
Th as ThO_2	3.0*
Rare Earths	0.2
Sm + Eu + Gd + Dy	0.02 max.
Fe	0.1
Cd	0.007
Pb	0.0015
Ti	0.0015
Si as SiO_2	1.4
Na as Na_2O	9.2

* Variable from 0.3 to 8.0%

As the abovementioned SDU at the monazite plant is only dewatered at 110-120°C and usually contains some organic mater, as a not controlled impurity, before its dissolution the yellowcake is calcined at 450°C during two hours. This treatment was introduced in the flow-sheet to avoid evolution of NO_x gases. We worked with this uranium concentrate for several years, as it was the unique raw material at hand.

3. A NEW YELLOWCAKE

Recently a second yellowcake could be used. It came from the Poços de Caldas Industrial Complex, at Poços de Caldas, Minas Gerais State. This industrial plant is owned and operated by NUCLEBRAS. The yellowcake is an ammonium diuranate of very good quality. The unique difficulty we had to cope with is the presence of zirconium contamination. After its dissolution with nitric acid, the clear uranyl nitrate solution was treated for the removal of the great majority of zirconium. It is clear that this yellowcake could not be calcined, otherwise it will be convert into uranium oxide which solubilization will generate high evolution of NO_x gases and the installation is not ready to absorve them.

4. DISSOLUTION OF YELLOWCAKE

The initial step is the dissolution of the concentrate with nitric acid for the obtaintion of a clear uranyl nitrate. During the dissolution the gross amount of silica is removed by dehidration of silicious acid. The dissolution is accomplished into a stainless steel reactor of 300 L capacity in a batchwise fashion. The yellowcake is poured direct and slowly into the nitric acid. After all the yellow cake was introduced its digestion is made with 2M HNO_3 at 90-100^oC for the complete floculation of silica.

If zirconium is present, the uranyl nitrate is treated with controlled amount of phosphoric acid. Both silica and zirconyl phosphate are separated together. The hot pulp is filtered into a canvas filter and the residue thoroughly washed for the removal of soluble uranyl nitrate. The filtered uranyl nitrate solution has a concentration of 475 g U/L and after cooled is adjusted to 300 g U/L and 1M HNO_3 previously to the solvent extraction. Sodium or ammonium nitrate, not less than 1M used as salting out agent is formed during the dissolution. In the case of the SDU produced from the monazite sand the troublesome presence of Th and RE is minimized by the controlled addition of sodium sulfate [3,4].

5. TBP EXTRACTION PILOT PLANT FOR PURIFICATION OF URANIUM

A pilot plant facility set up for the purification of uranyl nitrate is based on the conventional liquid-liquid extraction technique using three pulsed columns for the extraction, scrubbing and stripping, respectively. The facility and its equipment, operational flow-sheet, performance and gained experience were published [5,6]. The facility comprises a section for the safety opening of the drums and for the dissolution of the yellowcake. The organic phase is a (v/v) 35% TBP-varsol. The three columns have perforated plates of about 23% area. The extraction is accomplished in coutercurrent using an organic to aqueous ration of 2.2 to 1. The loaded organic phase containing 135 g U/L leaves the extraction column and is admited to the scrubbing columnn where it is scrubbed with 0.2M HNO_3 in an organic/aqueous phases ratio of 1:1. The washed organic phase

(110-115 g U/L) is stripped with water using and aqueous/organic ratio of 1.6 to 1, resulting an uranyl nitrate solution of 70-105 g U/L. The third column can be steam heated and operated at 40-60°C resulting in an uranyl solution of mean 100 g U/L value. This solution is filtered through a celite layer for the coalescence os small droplets of TBP and then forced into a layer of pure diluent to remove the last traces of TBP.

6. PRECIPITATION OF AMMONIUM DIURANATE (ADU)

The pilot plant is equipped to perform the precipitation in a batchwise way, into a 500 L reactor, and as continuous operation as well. The pure uranyl nitrate solution (100 g U/L) is heated to about 60°C and the ADU is obtained by bubbling undiluted anhydrous NH_3 gas. The final pH can be controlled to values raging from 4,0 to 7,5 for ADU to be send to the UF_4 unity or to pH about 10 (excess NH_3), if the ADU is directed to ceramic grade UO_2 pellets. For the batchwise precipitation the ADU is dewatered into a vacuum canvas filter and has an umidity ranging from 45 to 50%.

In the continuous precipitation using one step reaction the reactor (Ø27 cm x 100 cm, 56L) is fed with uranyl nitrate at a rate of 1.2-2.0L/min, heated at 60°C, and NH_3 bubbled at a rate of 60-80 L/min. The final pH is usually about 10 (excess NH_3) . The slurry of ADU is deposited in the bottom of the continuous filter and is sucked by Vacuum into the rotating drum. The cake leaves the drum with about 50% umidity, the thickness of the layer ranging from 2.5 to 3.5 mm.

7. TRIOXIDE FACILITY

A facility for the conversion of ADU to UO_3 cumprises a continuous, electrically heated, belt furnace. The ADU is fed directly from the rotating filter to the stainless steel conveyor belt moving inside the furnace with zones having different temperatures, the gradient ranging from 110° to 500°C. The final product is an UO_3 oxide used as feeding material for the tetrafluoride plant or sent to further conversion to ceramic grade dioxide. The residence time during the dewatering is 2-3 hours.

8. TREATMENT OF AQUEOUS EFFLUENTS

The uranium purification pilot plant gives rise to some solutions containing uranium, thorium, rare earths, iron and titanium, the main stream coming from the extraction column. All effluents are collected and treated with sodium hydroxide. The precipitate is filtered out and returned to the dissolution section with nitric acid and sent to the extraction again.

9. TETRAFLUORIDE PILOT PLANT

After some previous work [7,8] a pilot plant facility to acquire the necessary technology on the UF_4 production for futher uses in the reduction to U metal and preparation of UF_6 was set up [9]. The establishment of this unity had the collaboration and technical assistance from the International Atomic Energy Agency (IAEA).

The starting material is UO_3, reduced to UO_2 by cracked NH_3 and the use of anhydrous hydrogenfluoride for the conversion to UF_4. During some operation of this pilot the process of obtaintion of UO_3 was changed in the sense that the ADU precipitate at pH 7.5 for ceramic grade was calcined to UO_3 in the continuous belt furnace and then pellotized in spheres of about 4-6 mm, dried again and used as feed material in the L reactor. This new type of UO_3 exhibeted excellent mechanical properties. Nowadays we changed once more to the use of directly UO_3 produced as flakes of 3-4 mm thickness by filtration of ADU in the vacuum rotating filter and dried and calcined in the moving belt conveyor. This type of UO_3 exhibeted excellent mechanical properties. This trioxide is contacted with anhydrous hydrogen fluoride for the conversion to UF_4. The green salt produced is of good quality, assessing a minimum of 95% UF_4.

10. WET WAY UF_4 PREPARATION

A bench scale facility for preparation of uranium tetrafluoride via aqueous conversion of UO_2 powder with hydrofluoric acid is under experimental test. The dioxide is obtained in the dry moving bed reactor that has been in operation also for the UO_2 production as well. The UO_3 is reduced again by hydrogen generated by ammonia cracking. A second UO_2 type is produced by direct reduction of ADU in a moving belt furnace with hydrogen.

The conversion of both type of UO_2 with hydrofluoric acid is quite simple and effective, the tetrafluoride being filtered using a vacuum canvas filter and dried stepwise, first at 110-120°C and then at higher temperature. The quality of this green salt for uranium reduction or hexafluoride preparation is under investigation, the first results being promissor.

11. DENITRATION OF URANYL NITRATE

Development studies on a fluidized bed process for conversion of uranyl nitrate solution to uranium trioxide and recovery of nitric acid is under investigation. A pilot plant is being set up comprising an unity for concentration of uranyl nitrate solution from 100 g U/L to about 900 g U/L, followed by denitration of the melteded uranyl nitrate to UO_3. This new unity has the first test scheduled for second semester 1986.

12. QUALITY CONTROL

Mention will be made for some procedures specially developed to assist the pilot plant work. A rapid routine determination of uranium content in uranyl solution is done by gamma-ray spectrometry [10], using the ^{235}U 185 Kev photopeak. A procedure was outlined for the direct determination of U content of uranyl nitrate-TBP-organic phase [11]. The thermogravimetric behavior of ADU samples, and specially the pyrophoricity grade of UO_2 powders and their O/U ratio in UO_2- powder and pellets was developed [12]. The analytical control of UF_4 was made by sequential analysis of the most probable products existing with the tetrafluoride [13]. The determination of microquantities of

B in highly pure uranium and thorium compounds is done through the extraction of the colored complex of BF_4^--monomethyl thionine [14,15].

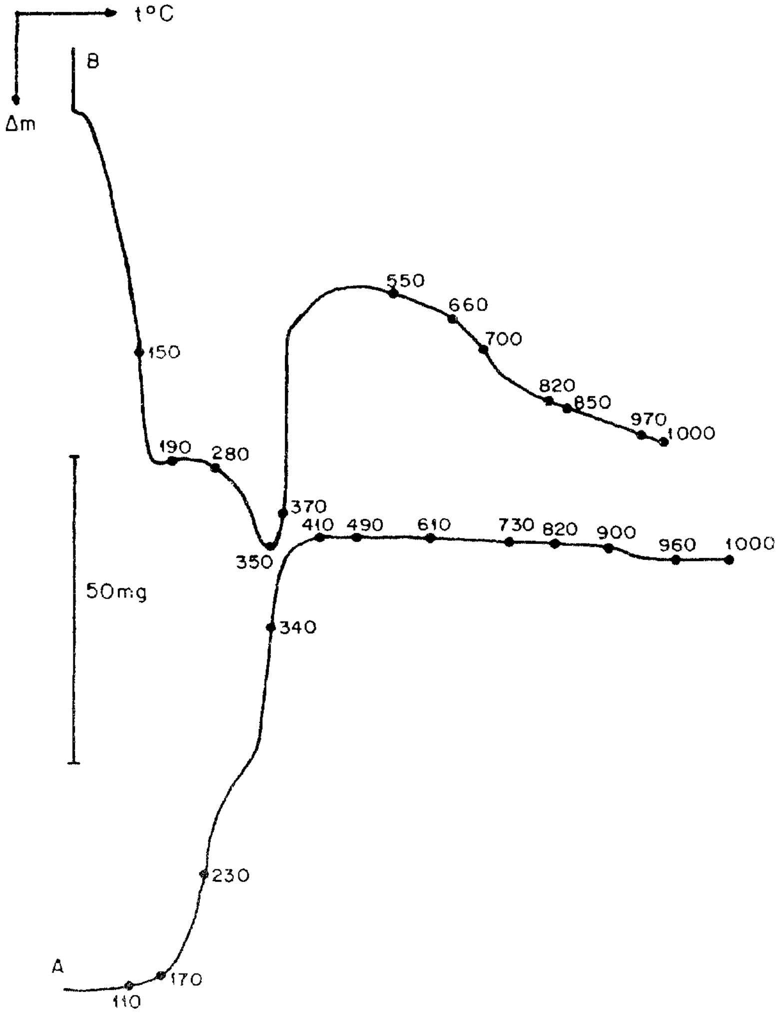

FIG. 1 THERMOGRAVIMETRIC CURVES OF URANIUM DIOXIDE [12]

(A) UO_2 (normal) obtained by reduction of U_3O_8 in H_2 at 770°C.

(B) UO_2 (pyrophoric) obtained by direct reduction of ADU in H_2 at 770°C.

A procedure for the separation and concentration of extremely low amounts of thorium and rare earths from uranyl solutions was developped based upon the sorption of those elements from solutions containing 0,3M HF into a small column of alumina [16]. Using this technique the individual RE have been analysed by emission spectrography [17]. A semiquantitative routine spectrometric method was outlined for the direct determination of 18 elements in uranium compounds, including UF_6, using gallium oxide and sodium fluoride. Vanishing small amounts of RE in uranium are determined by fluorescende spectrometry after separation into an alumina column [18]. Zirconium is analysed by direct spectrofluorimetric determination in uranyl chloride using morin [19] and spectrophotometrically with chloroanilic acid [20].

Procedures for the determination of the composition of the cell electrolyte were developed based on the alkalimetric determination of HF and the total determination of free hydrofluoric acid liberated after percolation on a strong cationic ion-exchange resin, H-form, and on the determination of melting point of the mixture. The presence of residual HF in uranium hexafluoride is determined after its hydrolysis and measurement of total uranium and total hydrofluoric acid.

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CONVERSION OF NON-NUCLEAR GRADE FEEDSTOCK TO UF_4

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Abstract

The South African Conversion route is based on the direct feed of ammonium di-uranate produced by any one of a number of different mines. The physical and chemical characteristics of the feedstock can thus vary considerably and influence the conversion rate as well as the final UF_6 product purity.

The UF_4 conversion reactor is a Moving Bed Reactor (MBR) with countercurrent flow of the reacting gas phases.

Initial problems to continuously operate the MBR were mostly concerned with the physical nature of the UO_3 feed particles. Different approaches to eventually obtain a successful MBR are discussed. Besides obtaining UO_3 feed particles with certain physical attributes, the chemical impurities also have an effect on the operability of the MBR.

The influence of the feedstock variables on the reduction and hydrofluorination rates after calcining has largely been determined from laboratory and pilot studies.

The effect of chemical impurities such as sodium and potassium on the sinterability of the reacting particles and therefore the optimum temperature range in the MBR is also discussed.

Confirmation of the effect of sodium and potassium impurities on the conversion rate has been obtained from large scale reactor operation.

1. INTRODUCTION

1.1 General

The South African process is based on the conversion to UF_4 of the sulphate ADU produced by the mines, followed by a UF_6 flame reactor and subsequent purification of the UF_6 by distillation.

In this paper the history of the conversion steps is traced, the present experiences and development regarding the impure feedstock is discussed and the future development outlined.

1.2 The four nuclear sectors

Four independent groups are responsible for the various aspects of nuclear material production.

These four are:

i) the gold producing mines that produce sulphate ADU as a by-product,

ii) the Nuclear Fuels Corporation of SA (NUFCOR) which produces Uranium Oxide Concentrates for export and also handles the transport of ADU slurry to the Atomic Energy Corporation of SA, Limited (AEC),

iii) the AEC which converts ADU to UF_6 and then enriches this material, and

iv) the Electricity Supply Commission (ESCOM) which generates electric power and also operates the Koeberg Nuclear Power Station.

A few comments regarding each activity will clarify the AEC's responsibility.

Up to 17 uranium extraction plants are operated by various gold mines. The processing of the uranyl sulphate and subsequent ADU precipitation and filtration is dependent on the specific mine's requirements [1].

The clearing house of ADU is NUFCOR and the NUFCOR plant has produced uranium oxide concentrates for export since 1953. A wealth of experience has been built up at this plant, which has made a significant contribution to the AEC conversion plant.

1.3 The AEC operations

The AEC is sited at Valindaba and produces enriched uranium. A pilot plant has been used for initial UF_6 production and development work but this will be shut down during 1986.

A bigger UF_6 conversion plant for the production of suitable UF_6 for the AEC enrichment plant has been built and will be commissioned during 1986.

The raw material inputs to the plant are ADU from the mines, CaF_2 and sulphuric acid for HF and the subsequent F_2 production. The ADU to UO_3, the UO_3 to UF_4 the UF_4 to UF_6 followed by UF_6 distillation steps then produce a suitable UF_6 for the enrichment plant. (See Figures 1 and 2).

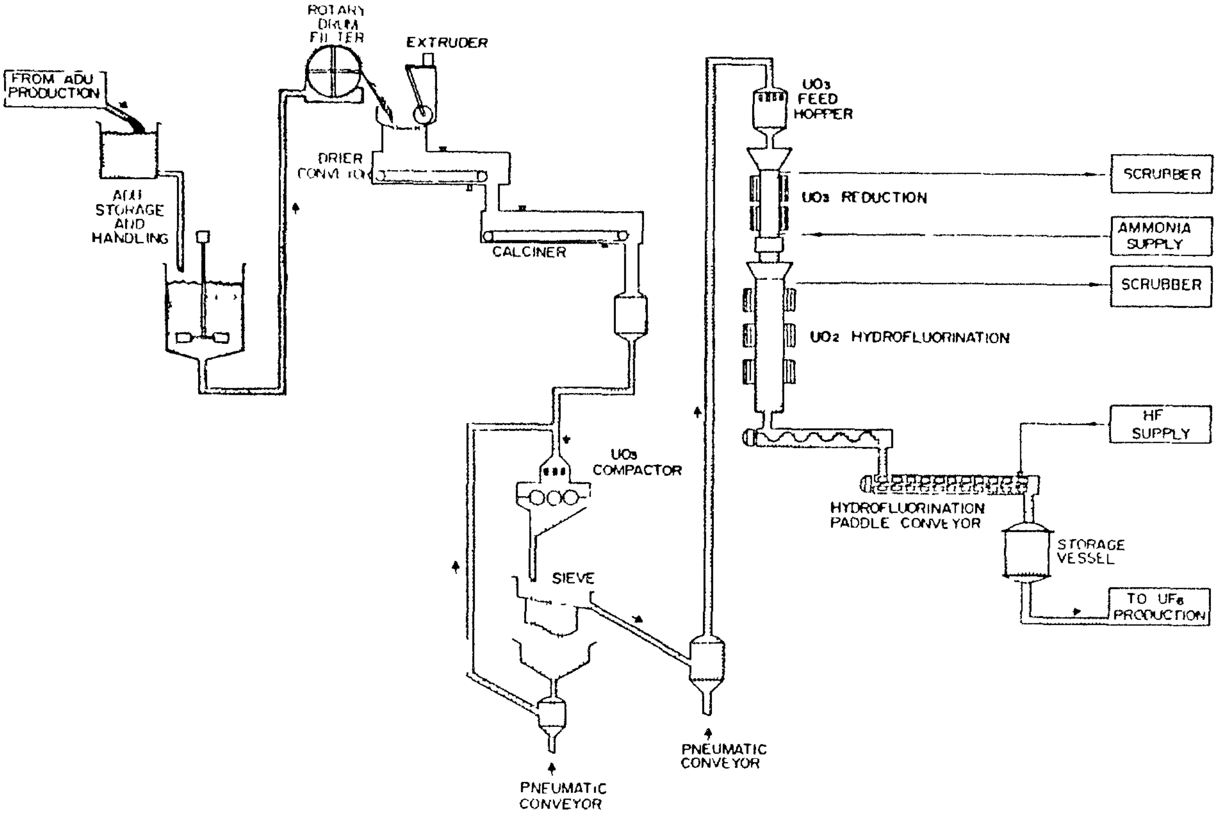

Fig. 1 Schematic representation of ADU to UF_4 production.

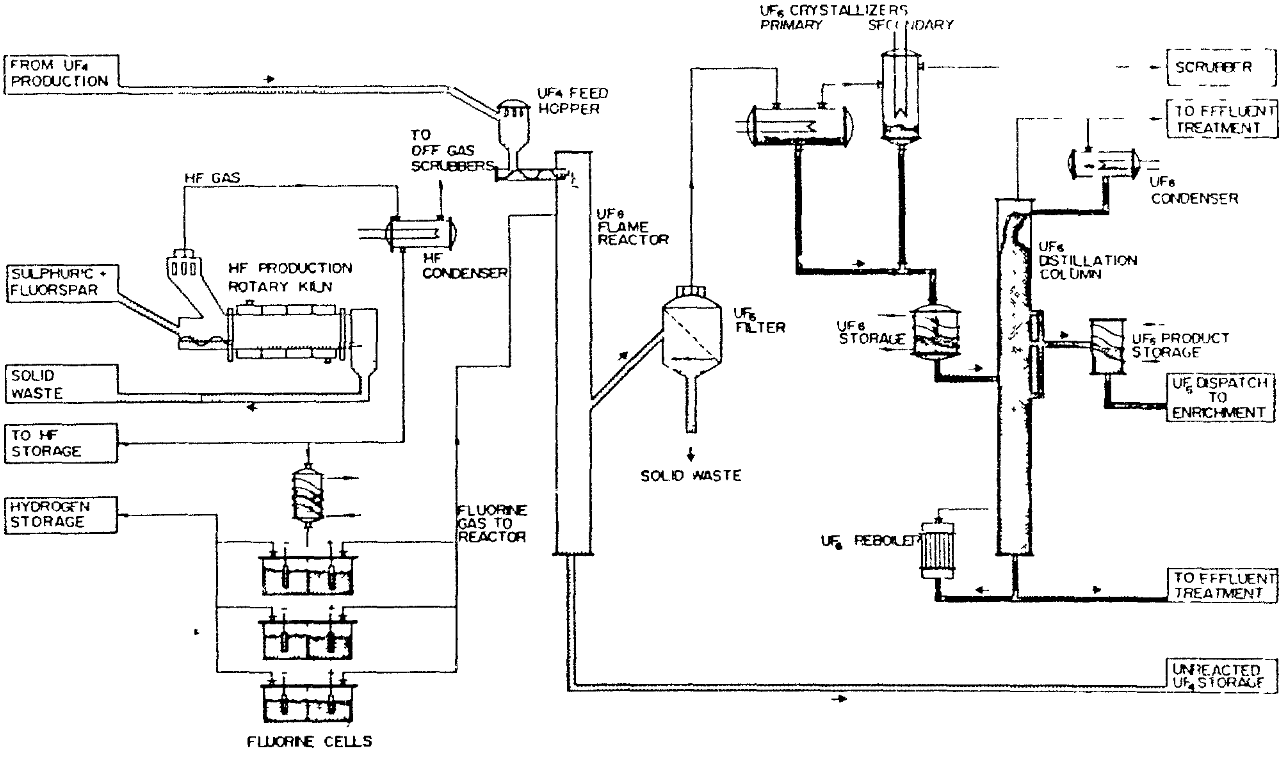

Fig. 2 Schematic representation of UF_4 to UF_6 production.

This paper emphasizes the ADU to UF_4 process steps, although the restrictions or requirements set by the ADU properties or UF_6 specifications are also mentioned.

2. UF_4 CONVERSION HISTORY

2.1 Initial objectives

The AEC utilizes a moving bed reactor (MBR) for the conversion of UO_3 to UF_4. In the first section of the reactor UO_3 is reduced to UO_2 by means of NH_3 and in the second the UO_2 is hydrofluorinated to UF_4 by means of HF. The gas and solids flow countercurrently in the reactor.

The following description of how the process was developed must be seen in the light of the non-nuclear grade ADU and thus the impure UO_3 used as feedstock. It was known that successful commercial conversion had been obtained with a MBR but with nitrate based and nuclear pure feedstock. It was not always clear during development work whether adverse effects such as sintering or unreactivity were caused by certain impurities (say Na, K, Ca, etc.) or by the sulphate content.

It was at first thought that the initial purification steps of ADU were expensive and that simple UF_6 distillation at the tail-end was more cost effective. Environmental factors relating to effluent treatment of a possible TBP plant for ADU purification also influenced the initial decision to opt for tail-end purification. However, as the cost of the UF_6 is high, any processing steps must minimise UF_6 losses.

In order to obtain UF_6 suitable for enrichment at the AEC distillation is utilized to reduce the volatile fluorides such as MoF_6.

2.2 Process development

The South African UF_4 conversion background can arbitrarily be divided into four periods.

2.2.1 The first period (- December 1972)

NUFCOR originally carried out feasibility studies to determine whether South African material could be converted in a MBR. During these initial studies emphasis was placed on the ADU preparation conditions such as precipitation pH, precipitation temperature and precipitation rate, as well as the allowable sulphate content. A limit of 4 % sulphate in the ADU was specified and ADU preparation conditions were established. Since the ADU precipitation particle size determines the success of conversion to UF_4 the specification requires that 50 % of the particles be greater than about 5 - 10 μm. Precipitation conditions at the mines are therefore as follows: a temperature between 30 and 40 °C, a uranium concentration in the mother liquor of between 7 and 9 g/ℓ, a residence time of about 17 to 24 minutes and a pH between 7,0 and 7,4.

Furthermore the filterability prior to drying and calcining is important and the ADU slurry density is specified to be between 1300 and 1450 kg/m^3 at delivery.

Additional studies to correlate the ADU precipitation particle size, specific surface area of the UO_3, UO_3 powder bulk density and operational conditions such as temperature were unsuccessful.

However about 20 tonnes of UF_6 was successfully produced by NUFCOR and it was decided to proceed with this process.

2.2.2 The second period (1973 - December 1982)

During this period a pilot UF_4 reactor was constructed and commissioned at the AEC. Empirical studies to correlate thermogravimetric analysis with reactor operation were unsuccessful.

The feed UO_3 was material as produced by the drier-calciner. Various configurations to the ADU extruder were made in an attempt to produce acceptable UO_3 feed particles. Also various mechanical devices were introduced into the UF_4 reactor to aid bed movement but the effect of the mechanical aids was to cause powdering of the UO_3/UO_2 particles with subsequent unpredictability of bed movement.

Although the reactor runs were unsuccessful, valuable experience was gained in the operation of drier-calciner during this period.

2.2.3 The third period (1983 - July 1985)

At the beginning of 1983 it was apparent that the UF_4 reactor required UO_3 feedstock of a better physical (mechanical) quality.

A compactor (pelletizer) was acquired to obtain UO_3 feed particles with a predictable sieve analysis.

Table I shows a typical sieve analysis. It can be seen that about 90 % of the UO_3 feed has particles greater than 4,75 mm.

Also, all mechanical aids to bed movement were removed and the reactor converted to a conventional MBR.

TABLE I

Typical UO_3 feed particle sieve analysis for UF_4 reactor

Size (mm)	>9,5	6,7 - 9,5	4,75 - 6,7	3,35 - 4,75	2,36 - 3,36
Mass (%)	20	48	23	7	2

In addition to the acquisition of the compactor, a detailed semi-empirical laboratory study was undertaken to investigate the effect of sodium and potassium on the sintering characteristics of the UO_3 - UO_2 - UF_4 particles.

During the pilot reactor runs from April 1985 to July 1985 the compacted UO_3 feed was used and the Na and K content checked. In addition, some of the previously unsuccessful operating conditions were changed. The reduction temperature was kept to about 700 °C and the hydrofluorination temperature profile in the reactor limited to about 600 °C at the exit where 100 % HF was introduced. The HF was not diluted with nitrogen, as had previously been the case to counteract the high reactivity of the sulphate material.

TABLE II

Summary of UF_4 pilot reactor runs for April to July 1985

Total runtime to shutdown - 1562 hours
Operating time - 80 %
Downtime - 20 %
UF_4 produced - 63 tonnes

UF_4 content (%)	>90	80 - 90	70 - 80	60 - 70	50 - 60	40 - 50	<40
Amount of material (%)	5	26	39	15	3	4	8

Typical results of these runs are presented in Table II. From this table it can be seen that about 70 % of the material had a conversion of greater than 70 % to UF_4. Additional discussion follows in Section 4.

2.2.4 The fourth period (August 1985 -)

The pilot reactor runs established the required UO_3 particle size distribution and the correct reactor operating procedures. Together with knowledge obtained from empirical laboratory studies on "good" ADU feedstock the commercial conversion plant reactor could be re-evaluated and modified.

Whereas the pilot reactor had a throughput of about 45 kg/h (UO_3) the production reactor's throughput is approximately 175 kg/h. Typical residence times are 11 and 7 hours respectively.

The reactor is constructed of two materials: the reduction section of Stainless Steel 309 and the hydrofluorination section of Monel 400.

The reactor is equipped with vibrators that are intermittently switched on to facilitate bed movement.

The production reactor was successfully commissioned and has produced UF_4 similar in quality to the pilot reactor.

3. RESEARCH AND DEVELOPMENT

There are two main requirements for a MBR to operate successfully for high UF_4 yields.

Firstly the solid bed must move consistently without blocking or channelling. To satisfy this requirement the feed UO_3 particles must comply with the specified sieve analysis.

Secondly the individual particle must be porous, reactive, have low sinterability, have a wide operating temperature range and must not powder easily.

The ADU feed and drier calciner operating conditions determine the feed characteristics of the UO_3 compactor. The UO_3 compactor operation determines to a large extent the particle characteristics.

Laboratory investigations were principally aimed at the ADU calcining conditions to obtain UO_3 with low U_3O_8 and NH_4^+ content. In addition, detailed investigations were carried out into the effects of the impurities Na and K on the reactivity and consequently on the temperature range which the UO_3-UO_2-UF_4 particle could withstand. Reduced reactivity can be caused by a reduced specific surface area (sintering by forming of a low melting point NaF eutectic or collapsing of pore structure) or by formation of sodium or potassium fluorides on which the product gases such as water adsorp more strongly, preventing a higher reaction rate.

The relative contributions of these factors to reduced reactivity has not yet been established and thus cannot be quantified at present.

3.1 UO_3 production

3.1.1 Plant operation

In order to obtain UO_3 with a low U_3O_8 and ammonium content the operating conditions presented in Table III are normally used.

TABLE III

Typical drier-calciner operational conditions

UO_3 production rate		160kg/h
Drier	- air inlet temperature	290 °C
	air outlet temperature	65 °C
	residence time	1 hour
	ADU thickness on belt	30 mm
	air flowrate	2,4 ton/h
Calciner	- air inlet temperature	410 °C
	air outlet temperature	290 °C
	residence time	1 hour
	UO_3 thickness on belt	30 mm
	air flowrate	2,4 ton/h

Typical ADU properties from 6 mines are given in Table IV. The resultant UO_3 has properties as shown in Table V. From this table it can be seen that the UO_3 feed particle typically has a porosity (ε_p) of about 60 % with a specific surface area (SSA) of about 20 m^2/g.

These tables form the basis of further discussions.

TABLE IV

ADU Properties of materials investigated

Material	pH	Moisture	SG	D_{p50}	Total SO_4^{2-}	Total U
Mine		(%)		(μm)	(%)	(%)
1	7,6	35,0	1,30	9,6	3,74	71
2	7,5	34,4	1,40	8,6	2,60	73
3	7,0	27,8	1,28	9,2	1,93	74
4	7,6	40,2	1,37	6,4	0,81	73
5				2,0		
6				4,0		

TABLE V

UO_3 Properties of materials investigated

Material	Total U	SO_4^{2-}	U_3O_8	Na	K	Na+K	$\rho_p \cdot 10^{-3}$	ε_p	SSA
Mine	(%)	(%)	(%)	(µg/gU)	(µg/gU)	(µg/gU)	(kg/m^3)		(m^2/g)
1	80	3,10	2,4	30	11	41	2,01	0,67	18,3
2	80	2,43	1,1	72	140	212	2,10	0,57	19,0
3	81	1,97	6,1	151	356	507	2,05	0,66	17,3
4	81	1,04	4,4	256	558	814	2,06	0,66	18,3
5	79	1,26	3,7	1200	177	1277	1,99	0,53	18,7
6	78	0,59	6,5	220	7066	7286	2,08	0,65	9,2
7	81	0	8,4	97	168	265	2,08	0,63	17,7
8	82	0,5	5,6	523	328	851	2,21	0,57	20,8

3.1.2 Thermal decomposition of UO_3

Since the thermal history of feedstock UO_3 determines the amount of other oxides, and therefore reactivity characteristics it is necessary

(a) during plant operation to keep operating conditions closely controlled, and

(b) for investigation purposes to have repeatable characteristics.

A typical mine-produced material (Mine 8, Table V) with medium-high Na+K was thermally decomposed in air for periods of one hour to obtain equilibrium with atmospheric oxygen.

Figure 3 (curve A) shows the fourfold reduction in specific surface area (SSA) between 500 and 700 °C. The accompanying curve B shows the oxygen to uranium ratio (O/U) change. At an O/U ratio of about 2,7 a phase change occurs and the SSA change coincides with this change.

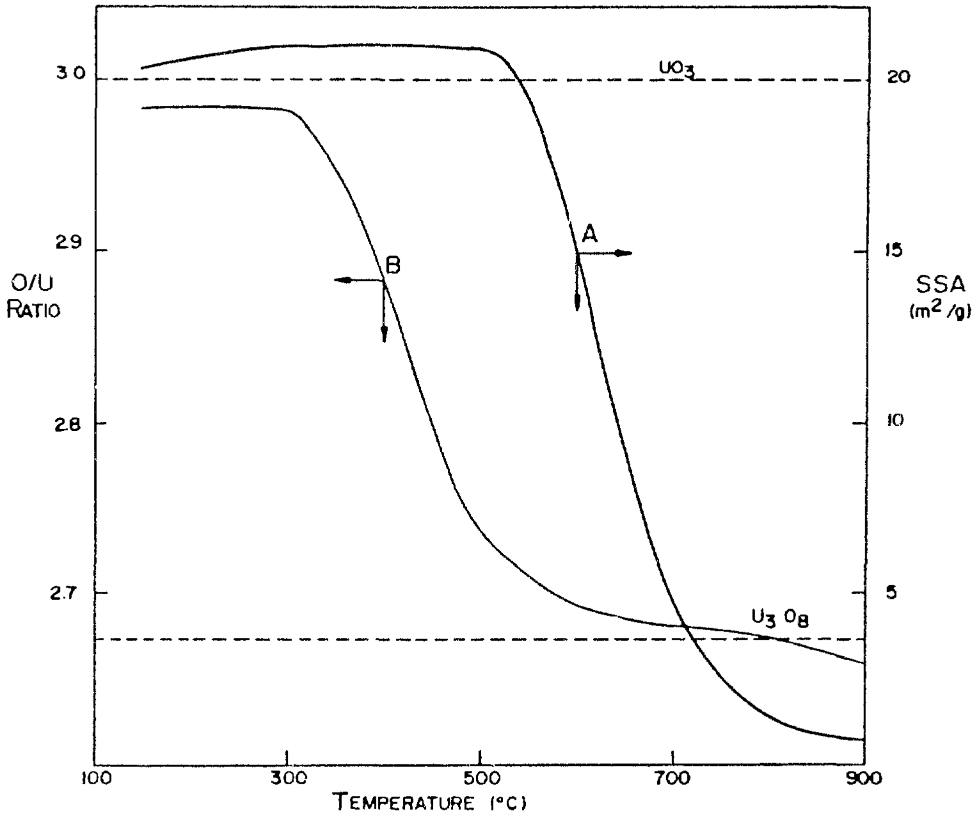

Fig. 3 Thermal decomposition of UO_3 in air.

A few comments pertaining to curve A are relevant.

It is known that the reduction rate is directly proportional to the feedstock SSA [2]. Therefore feedstock UO_3 which has been heated to about 700 °C prior to reduction will have substantially lower reactivity.

Further, if rapid reduction occurs on the outer crust of large non-porous particles in the reactor, inner particle temperatures will rise, leading to decreased SSA with subsequent more difficult reduction at later stages in the reduction zone.

The loss of SSA is an indication of sintering and is independent of the gas composition but is a temperature sensitive phenomenon.

Preliminary tests in a nitrogen atmosphere indicate that the SSA first increases between 400 - 500 °C before decreasing at higher temperatures.

Similar curves are being drawn up for materials containing different quantities of Na+K, and also in an inert atmosphere.

3.2 Particle reactivity investigation (Na+K)

It is known that sodium and potassium have deleterious effects during reduction [3] and hydrofluorination [4]. Laboratory studies were and are being conducted on two levels. Firstly empirical tests were developed to check material for possible plant conversion, primarily to determine the effects of different Na+K contents.

Since "good material" conversion characteristics are known both from the plant and the laboratory, the results of these tests are then used for comparative rather than quantitative purposes.

Secondly, reaction rate kinetic studies are being conducted with both thermogravimetric analysis and small static beds in order to obtain rate equations for development of a reactor model. The reactor modelling is based on solving the reaction kinetics differential equations for the particles without sintering effects (Appendix). Later studies will include the sintering effect followed by full modelling of the entire reactor.

3.2.1 Static bed tests - method

In order to obtain comparative results on widely differing materials the following empirical method was developed for laboratory use.

A sample of sieved UO_3 with a mesh size between 2,36 and 3,36 mm is obtained from the plant compacted material. The sample of about 5 g is spread as a single layer of particles on a grid contained within a tube. The tube is heated in an oven to obtain the required bulk reaction temperature.

For all the reduction and hydrofluorination tests the UO_3 is first converted to U_3O_8 in a nitrogen atmosphere at 650 °C for 60 minutes. The sample is then taken to the reduction temperature for NH_3 reduction followed by the hydrofluorination temperature for hydrofluorinating with HF.

3.2.1.1 Reduction tests

After the sample is taken to the test reduction temperature from the 650 °C level, it is reduced with NH_3 for only 6 minutes. Since the determination of the UO_2 content is difficult to establish directly the sample is then hydrofluorinated at 550 °C for a period of 20 minutes to ensure complete hydrofluorination of all UO_2. The amount of UF_4 formed is then an indication of the UO_2 obtained during reduction.

This test is carried out for a specific material at the following reduction temperatures: 600, 620, 640, 660 and 680 °C.

This series of tests is then repeated for the other materials.

The results of the reduction tests are presented in Figure 4.

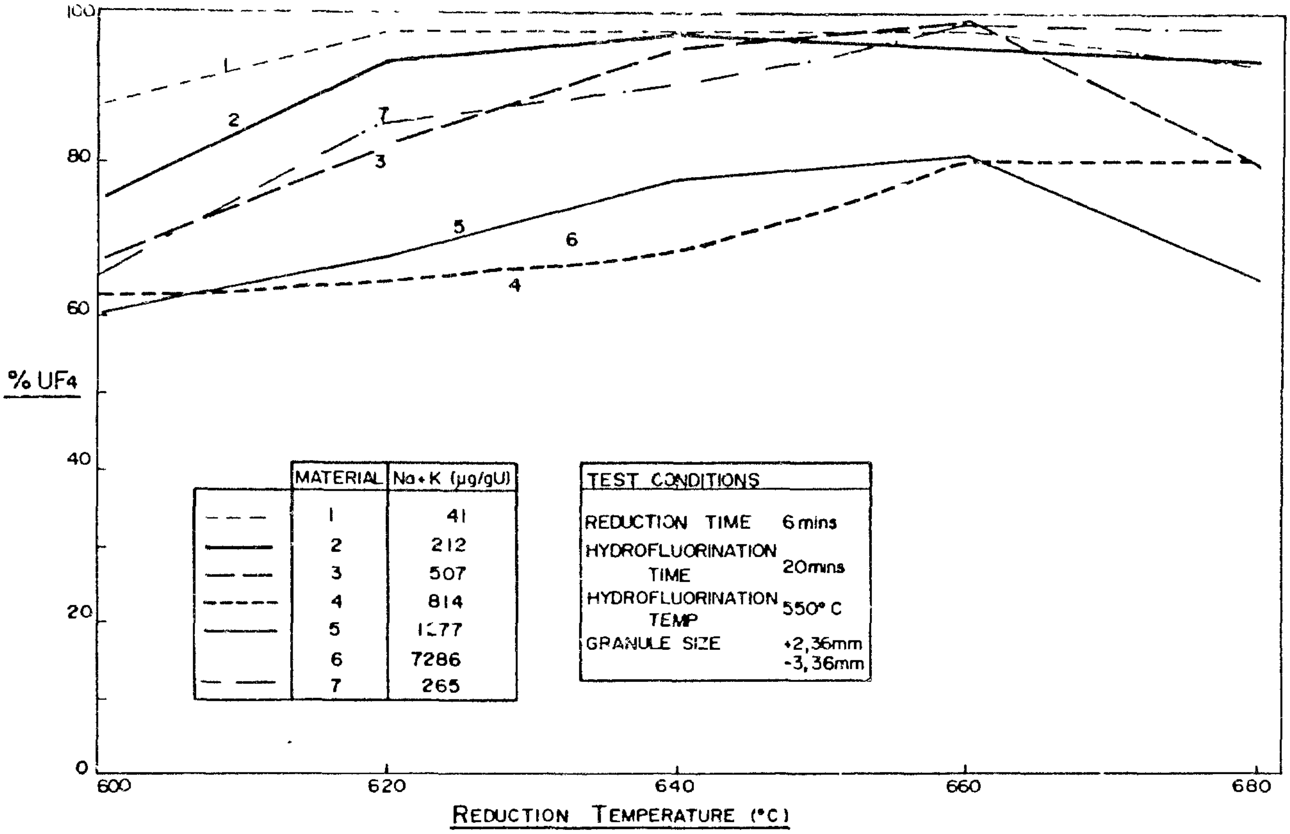

Fig. 4 Optimum reduction temperature.

3.2.1.2 Hydrofluorination tests

These tests were similar to the reduction tests except that complete reduction without sintering was ensured by reducing at 600 °C for a longer period (30 minutes).

Subsequent hydrofluorination is then carried out for a shorter period (10 minutes) at 450 °C. To obtain a curve for a specific material the test is repeated with fresh samples at 500, 550, 600, 650 and 700 °C to obtain an "optimum" temperature profile for hydrofluorination. The entire sequence is then repeated for another material.

The results are shown in Figure 5.

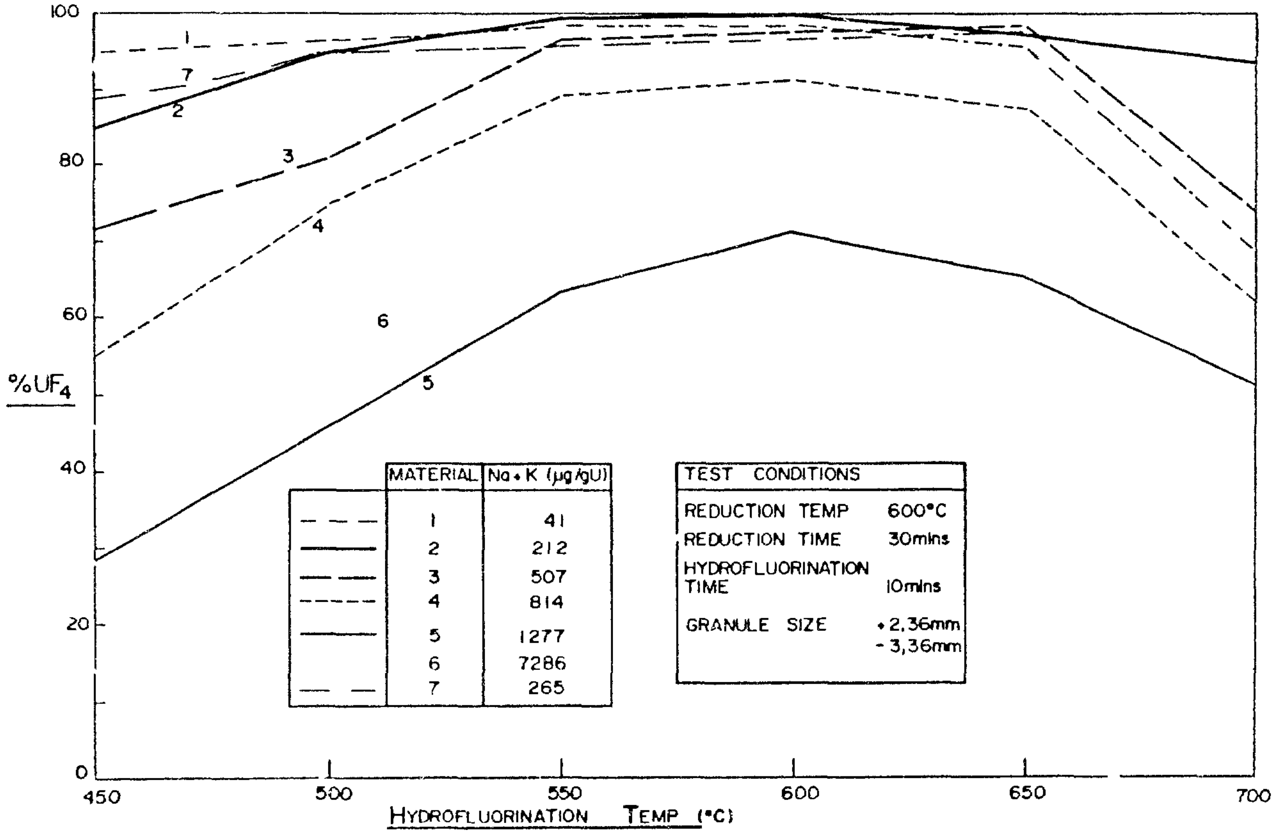

Fig. 5 Optimum hydrofluorination temp.

3.2.2 Static bed tests - temperature dependence

3.2.2.1 Reduction

Two main conclusions emerge from the temperature conversion curves for the different materials (Figure 4).

The materials with a low Na+K content have a wider temperature range in which reduction can occur and will therefore convert more easily in a MBR with moderate channelling.

The materials with a high Na+K content have a lower conversion and narrower effective temperature range.

It must be pointed out that these temperatures are average oven temperatures and cannot be related directly to reactor bed measured values.

3.2.2.2 Hydrofluorination

Hydrofluorination temperature curves (Figure 5) indicate a similar pattern to that of the reduction tests. Materials with a low Na+K value have both a wider temperature range (450 °C to 650 °C) and higher UF_4 conversion (80 % to 100 %).

The materials with a high Na+K value (5, 6) have a narrow temperature range (550 °C to 650 °C) and a low UF_4 yield (60 % to 70 %).

3.2.2.3 Preliminary conclusions

For both figures 4 and 5 the increasing UF_4 yield at low temperatures result from kinetic considerations. At the high temperatures the particle reactivity decreases due to increased sintering and/or a decrease in available surface area.

Table IV shows that the difficult materials (5, 6) have a low ADU precipitation particle size (2 - 4 µm), whereas the better materials have a 50 % precipitation particle diameter greater than 6 to 10 µm.

Besides this complicating factor, Table V indicates that the materials with higher Na+K have a lower sulphate content.

Increased reactivity during reduction and hydrofluorination of materials with low sulphate levels (up to 700 ppm) is known [4].

A test material (number 7) was prepared to check if the same Na+K with zero sulphate would behave in accordance with sulphate or Na+K rankings. This material (Na+K = 265 µg/gU) behaved very similarly to material 2 (Na+K = 212 µg/gU). See Table V and Figures 4 and 5.

At the higher temperatures the UF_4 yield for all the materials decreased. (Figures 4 and 5).

This decreased reactivity due to increased Na+K is known [4], but the main problem in laboratory tests is to obtain data which can be reliably used for interpretation of plant operations.

From a MBR point of view the wider and higher the temperature conversion profiles, the better the material which will be converted in the plant (Figures 4 and 5).

This means that materials 3 and 4 would reduce better than material 6 which has a high Na+K content.

Furthermore, these temperature conversion profiles give an indication of the temperature excursions the reactor can sustain. This indication of an allowable temperature excursion is, of course, more pertinent in the reduction reaction, since the hydrofluorination reaction is reversible and is conducted countercurrently, and has a reasonable residence time.

3.2.3 Particle reactivity - Na+K rate dependence

In order to compare the effect of Na+K, the rates of hydrofluorination of the different materials at the "optimum" hydrofluorination temperature of approximately 550 °C were determined for an average particle size of 2,86 mm.

The rate constant fits a first order reaction rate and is shown in Figure 6.

It can be seen that the increased amounts of Na+K reduce the reaction rate considerably.

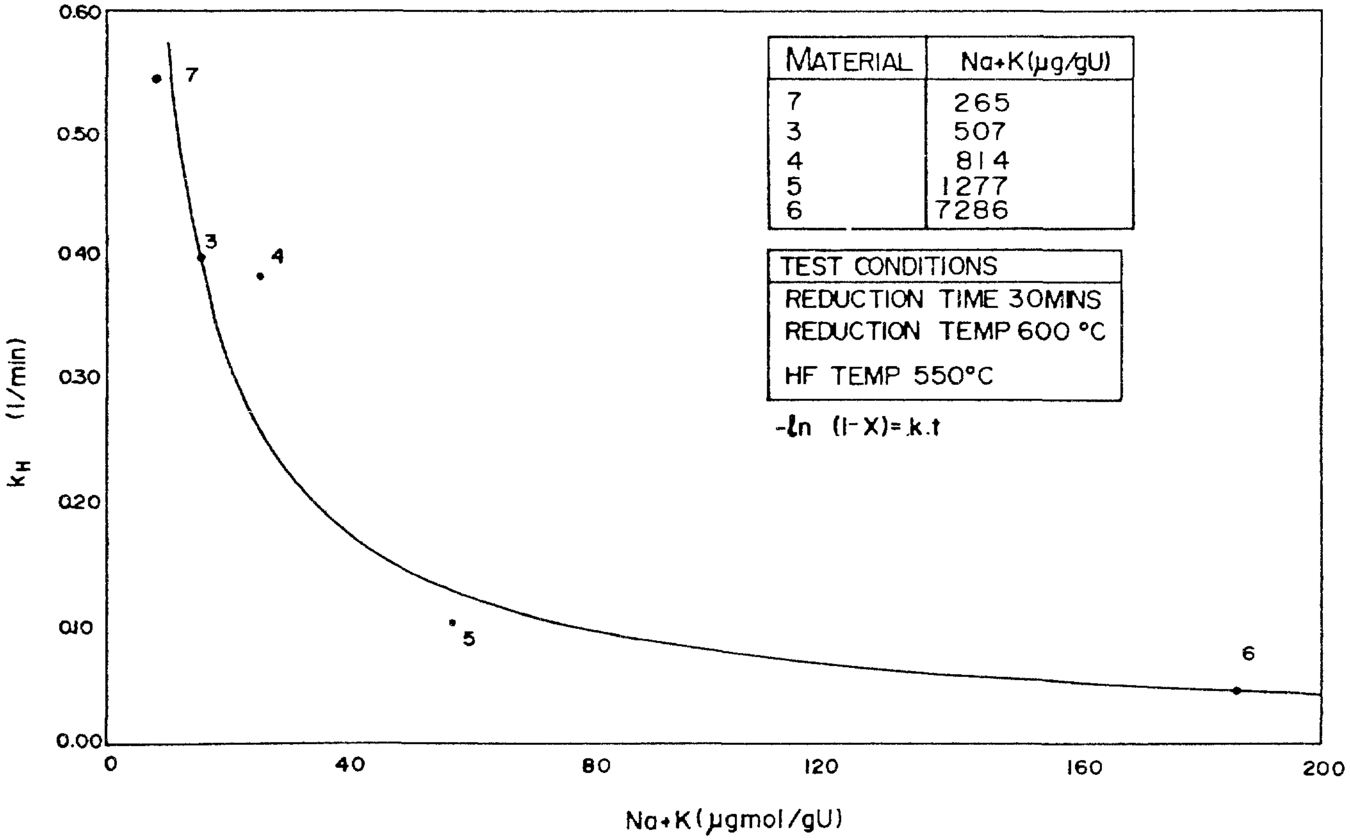

Fig. 6 Hydrofluorination rate as a factor of Na + K.

3.2.4 Particle reactivity - size dependence

Figures 4 and 5 were obtained from tests carried out on material of about 2,86 mm particle size.

Preliminary results on the zero order rate constant for reduction show the particle size dependence in Figure 7.

The bulk of material in the reactor feed has a size greater than 5 mm (Table I) and experimental data will be obtained in this particle size range.

It appears from Figure 7 that the preliminary results from the thermobalance give far higher reaction rates. The static bed test parameters are being checked to obtain better ammonia circulation and closer temperature measurement of the layer.

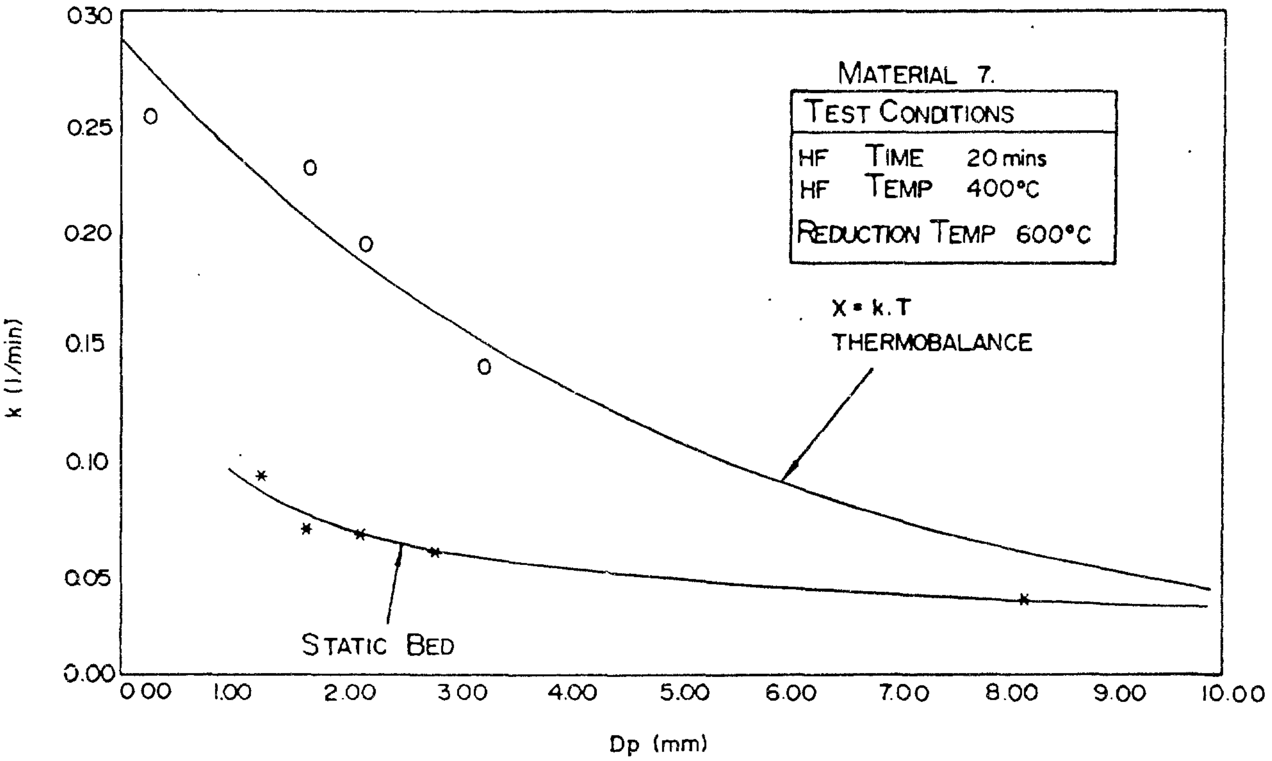

Fig. 7 Reduction rate on thermobalance and static bed.

Since a thermobalance run is comparatively fast, it would be useful to correlate these results with the static bed and finally with plant operating conditions.

The particle size dependency of the hydrofluorination reaction must still be carried out.

4. UF_4 REACTOR RUNS

As indicated in an earlier section and Table II the UF_4 pilot reactor runs were relatively successful in terms of reactor availability and UF_4 yield.

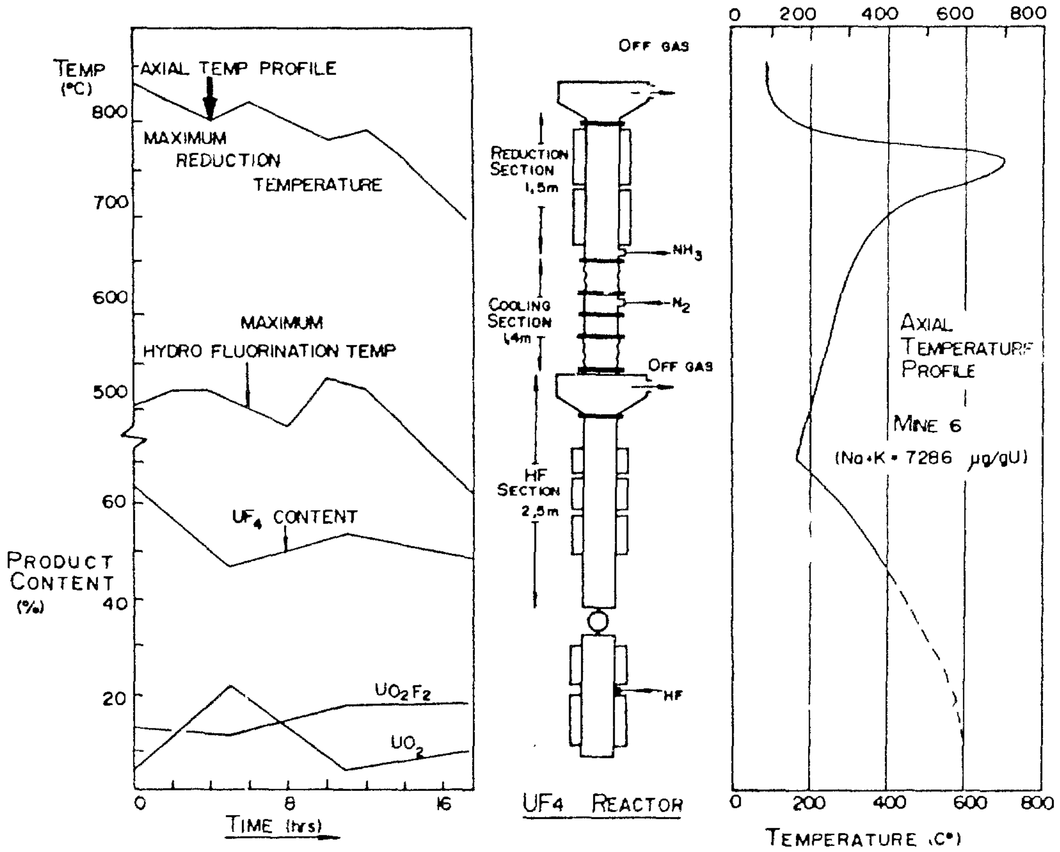

Fig. 8 Pilot reactor run with high Na + K (Mine 6).

The reactor run with material 6, high in Na+K, (7286 µg/gU) is depicted in Figure 8.

From the static bed tests (Figure 4) for material 6 it is clear that sintering or loss of reactivity during reduction will set in at 650 - 700 °C. This is borne out by the fact that the reduction temperature could not be sustained in the reactor (Figure 8). Note also that the UF_4 conversion was low and the high UO_2F_2 content indicates incomplete reduction.

Also shown in the figure is a typical reactor temperature profile at a given moment. The typical sharp reduction temperature vs reactor length indicates a narrow reaction front.

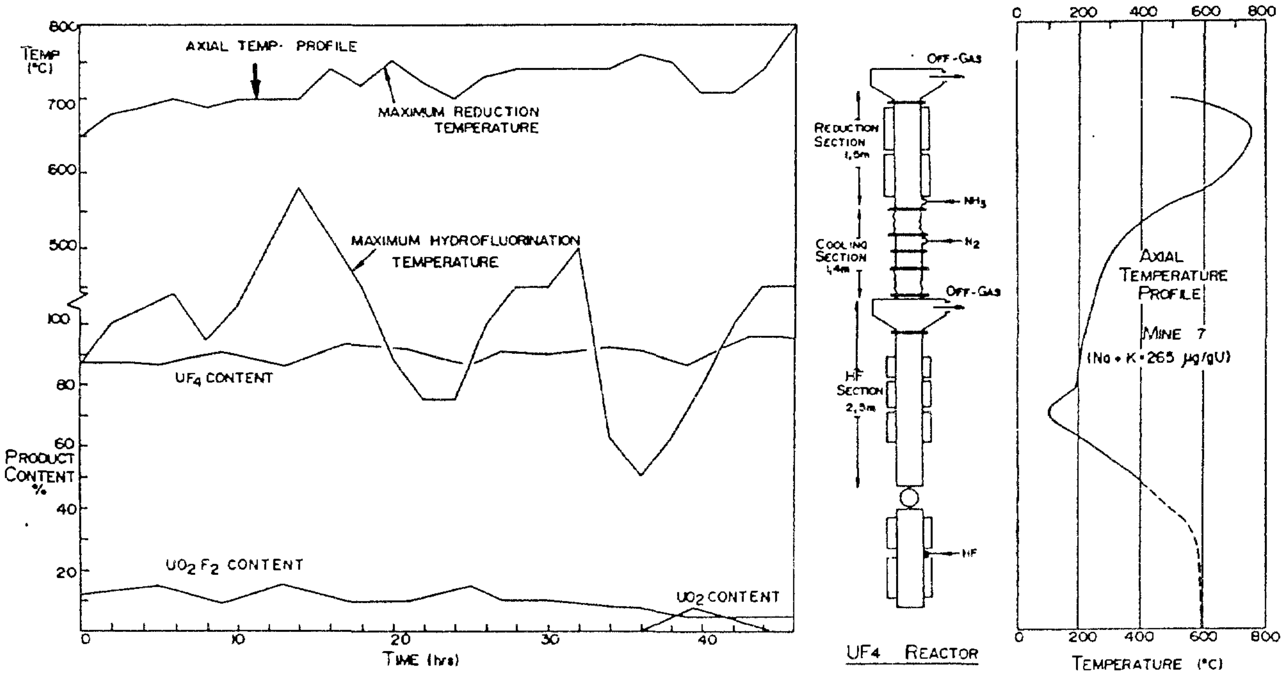

Fig. 9 Pilot reactor run with low Na + K (Mine 7).

In contrast, a reactor run with material low in Na+K (Mine 7) is shown in Figure 9. Despite a varying maximum reduction temperature, a high yield of UF_4 was obtained. A typical reactor temperature profile is also given. In this case the broad reduction temperature front is in contrast to the sharp reduction reaction zone seen in materials containing high Na+K.

5. UF_6 FLAME REACTOR AND PURIFICATION

The UF_4 material produced thus far at the AEC has been of a variable quality and the operating requirements for the flame reactor have to a reasonable extent been determined.

After the UF_4 powder has reacted with F_2 the UF_6 is filtered and condensed. These steps reduce the non-volatile fluoride impurities. Typical changes in impurity level obtained so far are reflected in Table VI.

TABLE VI

Typical impurity levels of non-volatile fluorides in UF_6 produced from UF_4 before distillation in comparison with the Enrichment Plant feed Specification.

Element	Compound	Bpt	UF_4	UF_6	Enrich= ment Spec
		(°C)	(µg/gU)		
Cu	CuF_2	>1000	48	<0,4	5,40
Mn	MnF_2	>1000	33	<0,2	3,60
Ni	NiF_2	>1000	250	<0,6	7,10
Co	CoF_2	>1100	11	<0,6	0,64
Fe	FeF_2	>1100	1260	20,0	50,00
Pb	PbF_2	1293	4	<1,0	4,00
Zn	ZnF_2	1500	29	0,3	14,00
Mg	MgF_2	2260	182	14,0	3,60
Ca	CaF_2	2500	1054	54,0	14,00

TABLE VII

Typical flag element impurity levels in UF_6 produced from UF_4 before distillation in comparison with the Enrichment Plant feed Specification

Element	Compound	Bpt	UF_4	UF_6	Enrich= ment Spec.
		(°C)	(ug/gU)		
B	BF_3	-100	-	-	0,11
W	WF_6	18	3	0,7	7,10
Mo	MoF_6	35	16	5,5	11,00
V	VF_5	111	24	1,2	0,11
Cr	CrO_2F_2	200	23	16	14
Th	ThF_4	200	-	-	0,71
Bi	BiF_3	1000	3,5	0,5	0,21
K	KF	1500	390	0,3	-
Na	NaF	1700	470	30	-

Since the more volatile fluorides such as WF_6, MoF_6 and VF_5 flow with the UF_6 a distillation step is required for purification.

These impurities have been used as flag compounds for distillation design. Typical values of these compounds are shown in Table VII. It must be noted that these results, which were obtained during development of the distillation, are not consistent. However, it can be seen that in general the UF_6 is close to enrichment feed material quality.

6. CONCLUSIONS AND FUTURE DEVELOPMENT

The compilation of an ADU specification ensuring that a high UF_4 conversion is obtained with minimum distillation of the resultant UF_6 product is in progress.

To convert mine-produced ADU, the contributory effects of specific surface area, impurity levels of sodium, potassium and sulphate must be quantified. A reaction kinetic modelling study of the UF_4 reactor has been commenced to achieve these goals.

7. ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the AEC for the opportunity of submitting this paper, and also to the operations and analytical staff for their contributions to the work. Special mention is made of J F Kruger, R Viljoen, D Mitchell, B J Steynberg, Dr A G M Jackson and Dr W A Odendaal. (Appendix)

APPENDIX

MODELLING OF THE REDUCTION AND FLUORINATION OF URANIUM PARTICLES

1. SIMULATION APPROACH

(a) From the pore size distribution (PSD), assuming ideal cylindrical pores, the catalyst particle is discretized into groups of pore geometries. (Fifteen for this example).

(b) The behaviour of each of these groups of pores are simulated and the global conversion of UO_3 to products calculated.

(c) The finally reduced particle is simulated similarly for the more extensive fluorination reaction.

(d) The mechanism of sintering is fairly ill described in literature and experimental data (to be collected) will be employed to define the relationship between the particle temperature and the sintering activity.

2. MODEL

2.1 Reduction reaction

(a) The reaction is assumed to take place in the pore according to

$$k \cdot A_{UO_3} = \int dC_{NH_3}$$

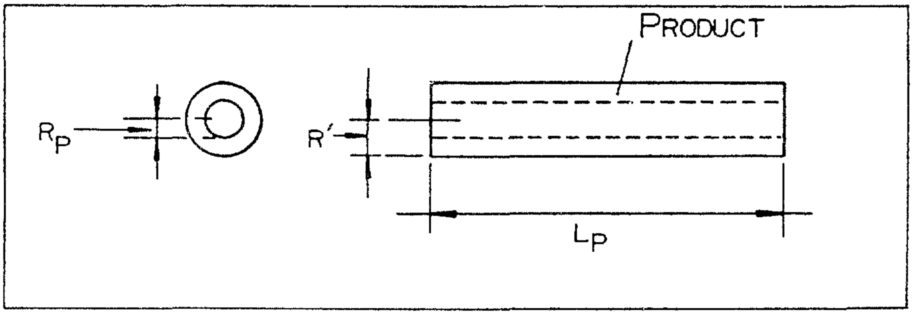

Fig. 10 Definition of pore parameters.

(b) The differential equation describing the reduction reaction in the pore is shown in Figure 10.

$$\frac{d^2\theta}{ds^2} = \frac{2\cdot A_{RL}^2\cdot\phi_p^2\cdot\rho\cdot\theta}{1+\phi^2 s\cdot\rho\cdot(\rho-1)}$$

with

$$\theta = \frac{C_{NH_3}}{C^o_{NH_3}} \; ; \; s = \frac{z}{L_p} \; ; \; A_{RL} = \frac{L_p}{R_p} \; ;$$

$$\phi_p = \frac{k\cdot R_p}{D_p} \; ; \; \rho = \frac{R'}{R_p} \; ; \quad \phi_s = \frac{k\cdot R_p}{D_u}$$

and the boundary conditions

$\phi = 1$, $s = 0$ and $\phi' = 0$, $s = 1$.

(Side reactions are not included in this brief note).

2.2 Fluorination reaction

The more simple model for the equilibrium reaction in the particle, postulates the pore reaction model as

$$\frac{d^2\theta}{ds^2} = A_{RL}^{\ 2} \cdot \phi^2 \cdot [\theta - \frac{1}{K_c} \cdot \frac{C_{H_2O}^{0,5}}{C^o{}_{HF}} \cdot \frac{S_{UF_4}}{S_{UO_2}}]$$

with $A_{RL} = L_p/R_p$

$\phi^2 = R_p{}^2 \bullet k \bullet S_{UO_2}/D_p$

$\theta = C_{HF}/C^o HF$

S_i = surface area of i

K_c = equilibrium constant

and $\theta = 1, s = 0$ and $\theta' = 0,\ s = 1.$

(This differential equation is solved for the HF reaction only and the other side fluorination reactions are evaluated on an ad-hoc basis according to the kinetic data available.)

3.0 PRELIMINARY RESULTS

Based on kinetic data obtained from Harrington and Ruehle and also Gmelin, the differential equations were solved for two particle sizes but no compensation was made for the sintering effect. The results are depicted in Figure 11.

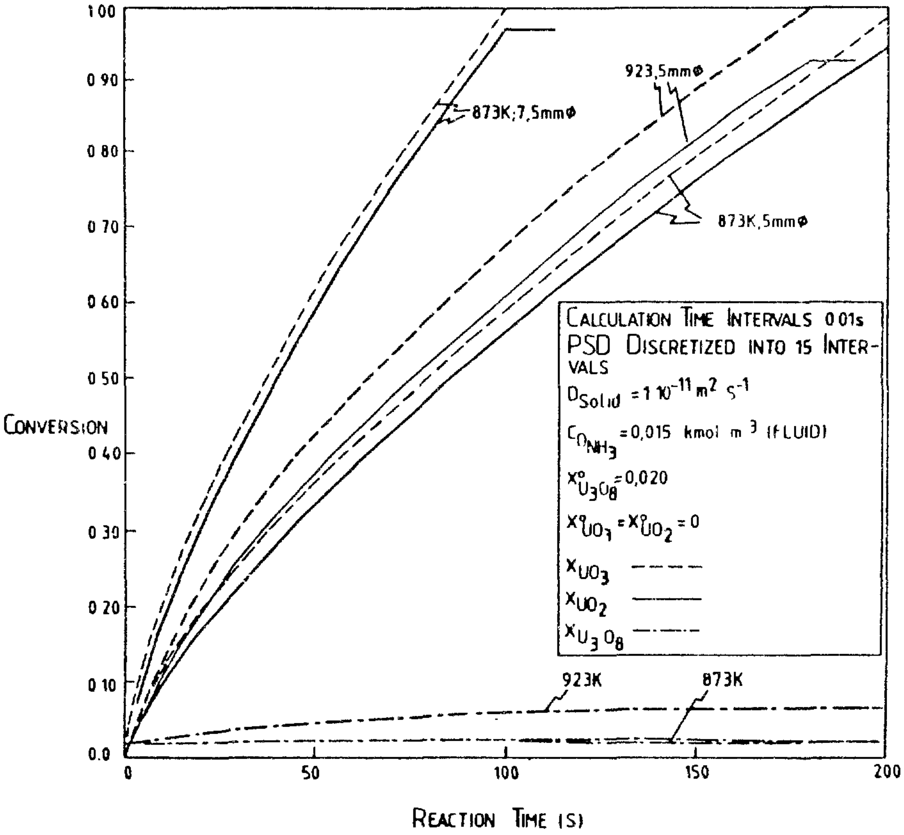

Fig. 11 Conversion profile for UO_3, UO_2, U_3O_8.

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THE CONVERSION FROM URANIUM TETRAFLUORIDE INTO HEXAFLUORIDE IN A VERTICAL FLUORIZATION REACTOR

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Abstract

Experiments conducted in a vertical fluorization reactor of 200 mm. diameter for converting uranium tetrafluoride or tri-uranium octa-oxide into uranium hexafluoride are reviewed. A brief acount of the process flow sheet, major equipments employed and operations procedures is presented. The advantages of such a reactor are discussed.

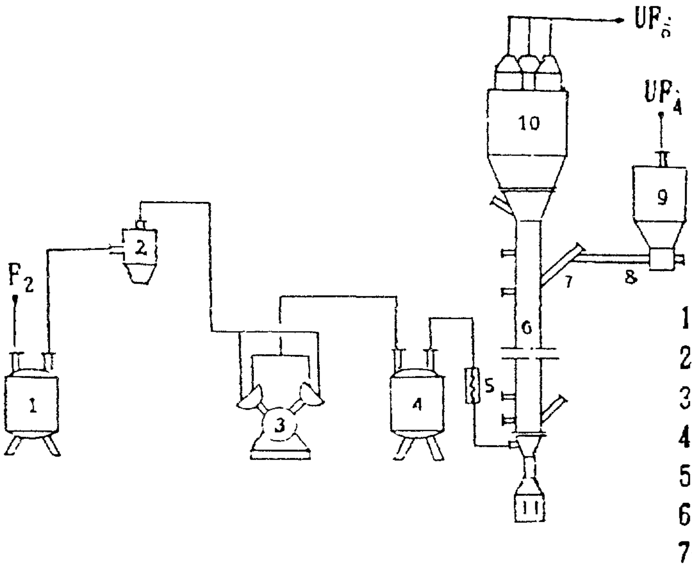
It is concluded that such a vertical fluorization reactor posesses certain advantages over conventional fluorization equipments. It can be employed not only for the conversion of uranium tetrafluoride into uranium hexafluoride, but also for the direct transposition of tri-uranium octa-oxide into uranium hexa-fluoride. Even tri-uranium octa-oxide with low concentration of ^{235}U can be effectively converted into hexafluoride by using this technique. It is hereby claimed that the vertical reactor in question can serve as a commercial fluorization reactor with good adaptability.

Introduction

The production of uranium hexa fluoride is a very important link in the processing and conversion of nuclear fuels. Fixed bed reactors, horizontal agitating reactors, fluidization reactors, flame reactors etc. have been employed for this purpose, with fluidization reactors and flame reactors being currently used in many nuclear fuel plants. Selection of the appropriate reactor for the production of uranium hexafluoride from uranium tetrafluoride and/or tri-uranium octa-oxide depends very much upon the charact-eristics of the reaction as well as upon the safety measures demanded. In general, the fluorization of tri-uranium octa-oxide is usually carried out in a series of small-sized horizontal agitating reactors. For years, as a result of continuous experimentation and innovation, a new model vertical fluorization reactor, specially designed to envelope the major advantages of most conventional reactors mentioned above, has eventually come into existence. Experimental results of the conversion of uranium tetrafluoride and/or tri-uranium octa-oxide into uranium hexafluoride in a vertical fluorization reactor of 200 mm diameter has proven that the productivity of the reactor is comparatively high, with excellent direct yields of metal and comparatively low residue. Furthermore, the reactor itself is structurally simple, relatively low cost, easy to operate and easy to maintain. It is also observed that the vertical reactor is adaptable to most raw materials, adaptable to the conversion of uranium tetrafluoride into uranium hexafluoride as well as to that of tri-uranium octa-oxide into hexafluoride.

Description of Flow Sheet and Process Equipments

Preheated and pressurized fluorine gas is passed into a gas distributor located at the bottom of the vertical reactor. At the same time, uranium tetrafluoride or triuranium octa- oxide is fed into the reactor through a feeder and a feeding pipe. The gas and the solid feed meet countercurrently inside the reactor and the feed is converted into uranium hexafluoride. The outer shell of the reactor is electrically heated to provide the temperature needed for the reaction to proceed. A continuous stream of compressed air is introduced between the shell wall of the reactor and the electrical heating device to cool down the wall temperature. Functioning of the electrical heating device and cooling system is automatically controled through necessary instrumentation. Reactor gas,



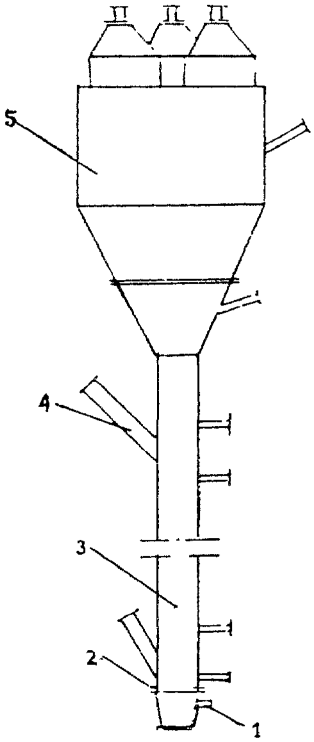
1—Buffering Tank;
2—Cleaner;
3—Pressurizer;
4—Buffering Tank;
5—Preheater;
6—Vertical Fluorization Reactor;
7—Feeding Pipe;
8—Feeder;
9—Hopper;
10—Filtering Trap;
11—Slag Collector

Fig.1 Flow Sheet of Fluorization

composed of UF_6, F_2, N_2, O_2, HF etc, is directed into the filtering trap to remove solid dust entrapped and proceeds to the condensing system (not shown in Fig. 1) , where entrained uranium hexafluoride is recovered. The filtering trap is periodically blown with flourine gas to effect a lowering in its resistance to flow. Slag formed during the reaction accumulates at the bottom of the reacting zone and is dumped into the connecting slag collector by inverting the turnable gas distributor. Reactor gas is monitored and analysed by automatic gas chromatography.

Referring to Fig. 1, it will be noticed that the major pieces of equipments employed in the experimental system are as follows:vertical fluorization reactor, pressurizer, feeding device for solid feeds, electrical heating device and filtering trap.

The vertical reactor of 200 mm diameter (Fig. 2) is made of Monel alloy. Five temperature measuring tappings, with thermocouples inserted, are located along the length of the reactor body to register the temperatures at the corresponding sections of the reactor . The pressurizer is fundamentally a diaphragm compressor. The feeding system for solid raw material is composed of a hopper, a feeder and feeding pipe. The feeder is driven by a variable speed motor, allowing remote and automatic control of feeding rate in the central control room. The reactor gas filtering trap is of inserted design, so that it may be installed at the top of the reactor to allow direct dropping of the blown dust into the main body of the reactor for further reaction. The electrical heating device is divided into five different sections of



1--Inlet for Elemental Fluorine ;
2--Gas Distributor;
3--Main Body of reactor;
4--Feeding Pipe;
5--Filtering Trap.

Fig. 2 Vertical Fluorization Reactor

equal power supply. A gas distributor is located at the bottom of the reactor to ensure even distribution of the gas stream within the reactor. Its distributing plate is made from Monel alloy. Elemental Fluorine is pressurized through the diaphragm compressor before entering the reactor.

The operation procedure begins with the switching on the electrical heating elements to allow the temperature within the reactor to rise to a pre-set value. Then, elemental fluorine is introduced for a few minutes. After that, switch on the feeder motor, letting in a pre-set amount of uranium tetrafluoride or tri-uranium octa-oxide intermittently, to initiate 'ignition' for the chemical reaction. As soon as the temperature of the reactor body reaches a certain value, feed in uranium tetrafluoride or tri-uranium octa-oxide continuously, and the system will be directed to continuous processing. During the course of continuous operation,the rate of flow of flourine gas in respect to the amount of uranium tetrafluoride or tri-uranium octa-oxide fed is closely adjusted in accordance with indications of analytical results shown by the gas chromatograph.

Results and Discussions

1. Raw Materials

The two species of feed are used in the experiment one is refined uranium tetrafluoride and the other tri-uranium octa-oxide. The tri-uranium octa-oxide is a purified product from waste containing uranium in uranium enrichment plants. Evidently, the two species are different in their respective physical and chemical properties, hence different technological parameters have to be employed for their processing. yet the resulting products obtained are both of extremely high quality. For uranium tetrafluoride, the direct yield of metal is over 99.5% with 0.02—0.05% residue; and, for tri-uranium octa-oxide, the respective figures are above 97% and 0.5%. Evidently, such a vertical fluorization reactor proves to be very well adapted to the processing either raw materials, with steady proceedings. Hence, it is hereby claimed that such a vertical fluorization reactor can be used for the two different purposes advantageously.

2. Reaction Temperature

Reaction temperature is, of course, one of the important parameters for the reaction of urlanium tetrafluoride or tri-uraium octa-oxide with elemental fluorine to form uranium hexafluoride, as it is well acknowledged that the reaction rate of any chemical reaction depends very much on its reaction temperatore. At room temperature, uranium tetrafluoride reacts rather slowly with elemental fluorine. It is found that only at temperatures over 250°C. would the reaction proceed at a significantly faster rate. In the temperature range of 250 -600°C., the rate of fluorization is apparently independent of reaction temperature. It is pointed out that at 250°C. the interaction of tetrafluoride and elemental fluorine is a very complex process. Intermediate products such as U_4F_{17}, U_2F_9, UF_5 etc. are formed. Further fluorization of these indtermediates leads to the formation of uranium hexafluoride. It is suggested that such intermediate products are most unstable and tends to 'sinter' within a certain temperature range. Further heating , such intermediate products can occur dismutation reactions, forming uranium tetrafluoride and uranium hexafluoride. The rate of dismutation holds a linear relationship with reaction temperature. Consequently, a higher reaction temperature not only would favor an increase in the rate of fluorization but also would promote the rate of dismutation. This would mean less intermediate products formed, shorter existence of such intermedite products in the reaction and elimination of their 'sintering' . As a matter of fact, it is observed that at temperatures above 350°C., 'sintering' of intermediate products can be essentially avoided.

However, it must be pointed out that though an increase in reaction temperature does favor the processing of the fluorization, too high a temperature is regarded as inappropriate. This is particularly true dealing with the fluorization of tri-uranium octa-oxide, which is highly exothermic, otherwise unforeseen' operating problems may come into existence. Furthermore, extremely high temperatures are capable of accelerating corrosive effects to the reactor, and are deterious to the life of the reactor.

The principal rule for the choice of reaction temperatures for the fluorization of uranium tetrafluoride and /or tri-uranium octa-oxide in a vertical reactor should be as follows: select the lowest possible temperature but be sure that the rate of fluorization reaction is comparatively high at this chosen temperature. Experimental results has indicated that when appropriate temperatures are chosen, the rate of fluorization can be optimized and 'sintering' of intermediate products can be avoided. Furthermore, the exothermic behaiour of the fluorization of tri-uranium octa-oxide can be kept under control, thus eliminating possible operating problems. With appropriate temperatures under control, the operating process with proceed steadily and keeping the reactor wall temperature will not be of any problem. It is observed that with appropriate reaction temperature chosen, the experimental reactor does not shown any significant corrosion during an extended period of repeated experimentation. This happens to be a prominent advantage for employing a vertical fluorization reactor, which is seldom attained by a flame reactor or a horizontal agitating reactor.

3. Loss of Elemental Fluorine

In a vertical fluorization reactor, the solid feed drops down from the top of the reactor and elemental fluorine enters the reactor at its bottom part through a gas distributor. Solid feeds of uranium tetrafluoride or tri-uranium octa-oxide fall down the main body of the reactor by gravity and follow a comparatively evenly distributed path. At the same time, elemental fluorine flows up countercurrently and evenly distributed by passing through the gas distributor. Consequently, better mutual contact between the two phases within the reactor can be materialized. Furthermore, excess elemental fluorine will be able to have contact with fresh uranium tetrafluoride at the feeding system located near the top of the reactor. This would mean that a vertical reactor can operate efficiently with minimum excess elemental fluorine. It has been proven in our experiments that only about 5% excess elemental fluorine is necessary for the smooth operation of a single vertical fluorization reactor to ensure excellent conversion of uranium tetrafluoride. for tri-uranium octa-oxide, the corresponding figure is around 7%. Evidently, this can never be achieved with a flame reactor, which calls for an excess elemental fluorine of over 25%. The same goes true with a single fluorization reactor, which requires more than 10% excess fluorine. Less fluorine lost is therefore claimed to be another advantage for vertical fluorization reactors.

4. Amount of Slag and Productivity of the Reactor

It has already been mentioned before that the conversion of uranium tetrafluoride and tri-uranium octa-oxide into hexafluoride in a vertical reactor gives slage of 0.02 0.05% and not any more than 0.5% respectively. With a flame reactor of the same diameter, slag formed would amount to 1-2%. The amount of slag formed during the reaction process would unavoidably be reflected in the direct field of metal attained, and is an important indication of the operational efficiency of a reactor. In this respect, it is conspicuous enough that vertical reactors prove to be highly advantageous.

Low slag formation in a vertical reactor is credited, first of all, to the structural design of the reactor. Countercurrent flow of solid feed and elemental fluorine provides excellent conditions for better and thorough reaction to be taken place. Unconverted intermediate products would fall onto the the gas distributor at the bottom and are reacted upon by freshly introduced elemental fluorine; further promotion of its conversion into hexafluoride is hence effected. Of course, steady operation for an extended period is another reason for low slag formation.

With this innovative structural design, handy to operate and easy to get steady operation, the reactor claims to have rather high productivity. For a 200 mm diameter reactor of this design, 4000-5000 kg/m^{2} .h. of uranium hexafluoride can be attained.

The achievement of higher productivity can be explained as follows. First, the structural design of the vertical reactor can conduct out reaction heat from the reactor under predetermined conditions and allows handy and steady operation. Secondly, increasing the rate of gas flow is possible with such a design. Furthermore, solid feed of appropriate particle size reacts rapidly with elemental fluorine at the bed temperature to form intermediate products, which would further react with elemental fluorine to give uranium hexafluoride, concurrently with the dismutation reactions at high temperatures. It is noticed that intermediate products react with elemental fluorine during their fall onto the bottom distributor, and since the particle size and the specific gravity of such intermediate products are much greater and higher than the original solid feeds, higher rates of gas flow are allowd. Of course, the rate of gas flow should be controlled to be greater than that required for the fluorization of the original solid feed, but below that which would cause entrainment by the gas. An increase in the rate of gas flow within the reactor would mean an increase amount of elemental fluorine inside the reactor body, which in turn would bring about an increase in productivity for the reactor.

5. Special Features Concerning the Fluorization of U_3O_8.

There are certain special problems that should be taken care of when dealing with the fluorization of tri-uranium octa-oxide. Extensive heat of reaction formed during the fluorization of tri-uranium octa-oxide must be conducted out of the system otherwise the reactor body will be ruined. Furthermore, since tri-uranium octa-oxide is a recovered by-product from uranium enrichment. It involves ^{235}U of various enrichment, Safety measures must be attended to during its fluorization. Both of these problems have been successfully attended to in our experiments.

Conclusion

Experimental results attained prove that converting uranium tetrafluoride or tri-uranium octa-oxide into uranium hexaflouride in a vertical fluorization reactor under pre-determined conditions is highly adventageous in many respects. Low loss in elemental fluorine, low slag and high direct yield of metal, comparable to those attained with horizontal agitating reactors, are claimed. High productivity comparable to flame reactors is also evidenced. Simple structural design, handy to operate, easy to maintain, less floor space occupied, low capital cost, excellent adptability for processing different raw materials are other additional advantages claimed. Vertical fluorization reactors are more advanced than horizontal agitating and fluidization reactors, and they comparable to flame reactors.

Extended periods of repeated experimentation has proven that the technique of converting uranium tetrafluoride or tri-uranium octa-oxide into uranium hexafluoride in a vertical fluorization reactor is most reliable. The reactor itself and its operation are technically proven. The technique can be successfully transplanted in commercial practice.

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THE SOLVENT-CONTAINING RESIN FOR REMOVING URANIUM FROM EFFLUENT OF REFINING PROCESS

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Abstract

Two types of solvent-containing resin (CL-5209 and CL-5401) have been prepared by suspension polymerization of monomers in the presence of active components. The active components are dialkyl alkyl phosphonate (for CL-5209) and trialkyl phosphine oxide (for CL-5401) respectively. Uranium in dilute nitric acid or acidic nitrate solution can be adsorbed selectively and efficiently with these resins. Losses of these active components in water are less than 4 ppm. Because of these characters, these resins can be used to remove uranium from effluents of refining process, such as the raffinate from TBP extraction stage, the filtrate from precipitation stage, etc. The concentration of uranium in the raffinate treated with CL-5209 or CL-5401 column is lower than 0.05 mg/L. Ammonium carbonate solution can be used as eluant for loaded column. Water may also be used for elution of loaded CL-5209. Uranium in the eluate may be recovered by precipitation or by recycling the eluate into the feed solution of TBP extraction stage.

The chemical concentrates produced by uranium ore processing plants and the various uranium-containing wastes from the production of metallic uranium fuel elements and uranium dioxide ceramic fuel elements contain so many impurities that it is necessary to refine these materials. TBP extraction process is commonly used for refining. The waste liquor from this refining process consists mainly of the raffinate of the TBP extraction stage and the filtrate from the precipitation stage. This effluent contains about 0-3 $\underline{N}$ H^+, 5-200 mgU/L, 0.1-3 $\underline{N}$ NO_3^- and many different impurities. In general , uranium in this effluent should be removed at first. The uranium concentration can be decreased to a value of less than 0.05 mg/L by neutralizing the effluent with ammonium hydroxide followed by adsorption with silica gel. The disadvantage of this procedure is that a highly radio-active solid waste containing uranium is produced. Anion exchange resins are incapable of adsorbing uranium from dilute nitric acid solution. Cation exchange resins have a poor selectivity for uranium. So these ion-exchangers are unsuitable for the treatment of the effluent mentioned above. It is well known that some neutral esters of the acids of phosphorus, also phosphine oxides, can extract uranium from nitric acid solution selectively and effectively. However, the uranium concentration in the effluent is so low that solvent extraction technique cannot be used economically for removing uranium. R.Kroebel and A.Meyer reported that a solvent-containing resin was prepared by adding an extractant to a mixture of monovinyl and polyvinyl compounds and by carrying out the suspension polymerization in the presence of the extractant. They called the resin obtained by this way as Levextrel resin and took example by a TBP-containing Levextrel type resin to describe its characteristics [1-7]. A detailed description of the structure and characteristics of the Levextrel resin was given by H.W.Kauczor and A.Meyer [8]. Some authors have investigated the possibility of applying the TBP-containing Levextrel resin to nuclear fuel reprocessing [9-11]. A TBP-containing resin CL-TBP similar to Levextrel resin was prepared in our research institute and its ability to adsorb uranium was determined. The results showed that this resin had a saturation capacity of 148 mgU/g resin in a solution of 5 N nitric acid and 3.8 gU/L. As the concentrations of nitric acid and uranium were lowered, however, the saturation capacity of the resin for uranium decreased considerably. The active component in the resin, TBP, shows a high solubility in water (about 400 mg/L), so this resin is unsuitable for the treatment of the effluent from refining process. It is known that dialkyl alkyl phosphonate and trialkyl phosphine oxide exhibit a much higher ability to extract uranium from nitric acid solutions than that of trialkyl phosphate. Moreover, the solubility of these compounds in water decrease considerably with the increase of their molecular weights. Based on these facts, two types of solvent-containing resins were developed in our research institute and named as CL-5209 and CL-5401 respectively.

1. PREPARATION AND THE CHARACTERISTICS OF CL-5209 AND CL-5401

The so called 5209 is a dialkyl alkyl phosphonate, in which the total number of the carbon atoms in the three alkyl groups is no less than 22. 5401 is a trialkyl phosphine oxide, in which the alkyl group is C_6-C_8, mainly C_7. They both were synthesized in our research institute.

An organic phase of styrene, divinylbenzene, initiator and the extractant (5209 or 5401) was added to a polyvinyl alcohol solution. The mixture was heated with stirring for 30 min. to a temperature of 80°C, left at this temperature for a period of 10 hours. After cooling, the aqueous phase was seperated off and the resulting bead polymer, i.e. solvent-containing resin, was washed with water and dried at 60°C.

The properties of the solvent-containing resin are dependent on the dosages of divinylbenzene and extractant. When the amount of divinylbenzene is less than 10% of the total amount of the monomers, considerable amount of the extractant can swelled into the matrix of the styrene-divinylbenzene copolymer, resulting in decreasing adsorption rate. It is evident that the content of the extractant in the resin should be as high as possible so as to obtain a solvent-containing resin with high capacity. Too much extractant in the resin, however, would give rise to decrease the mechanical stability of the resin.

The general characteristics of CL-5209 and CL-5401 are shown in TABLE 1.

TABLE 1. General Characteristics of Solvent-containing resins

	CL-5209	CL-5401
Active component	5209	5401
Active component content, wt%	60	50
Particle size, mesh	20-60	20-60
Bulk density, g/mL	0.58	0.55
Specific gravity	less than 1	

2. BEHAVIORS OF CL-5209 AND CL-5401 IN URANIUM ADSORPTION AND ELUTION

2.1. Adsorption rate

0.5 g of solvent-containing resin and 50 mL of uranium solution (1.16 gU/L, 1 N HNO_3) were added into a 100-mL ground-glass stoppered flask and the flask was shaken vigorously. Samples were taken at different contact time of 10, 30, 60 and 120 min., respectively. The remaining uranium concentration in these samples were analysed. Thereby the uranium adsorption capacity of the resins at different contact time could be calculated. The adsorption curves of CL-5209 and CL-5401 for uranium are shown in FIG.1 by plotting the uranium adsorption capacity of the resin against the contact time. FIG.1 indicates that both of the resins have a high adsorption rate for uranium.

2.2. Relationship between uranium adsorption capacity of the resin and uranium concentration in aqueous solutions with different concentrations of nitric acid

20 mL of uranium solution (1 gU/L, 1 N, 0.5 N or 0.1 N HNO_3) and a certain amount of resin were added into an 100-mL of ground-glass stoppered flask. After shaking for two hours,samples were taken from the solution to determine the remaining uranium value. That is the uranium concentration in

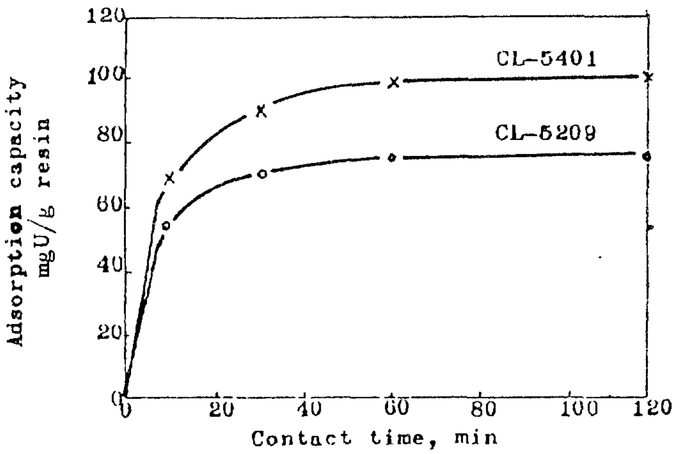

FIG.1. Adsorption curves of solvent-containing resins

the aqueous solution in equilibrium. Thereby the uranium adsorption capacity of the resin could be calculated. FIGs.2, 3 and 4 show the relationship between the uranium adsorption capacity of CL-5209 and the uranium concentration in the aqueous solution (1 N, 0.5 N and 0.1 N HNO_3) in equilibrium respectively. Some results with CL-5401 and CL-TBP are also given in FIGs.2 and 4 for comparison.

FIG.2 indicates that CL-TBP cannot adsorb uranium effectively from an 1 N HNO_3 solution. On the contrary, CL-5209 and CL-5401 exhibit a high ability to adsorb uranium in such a solution.

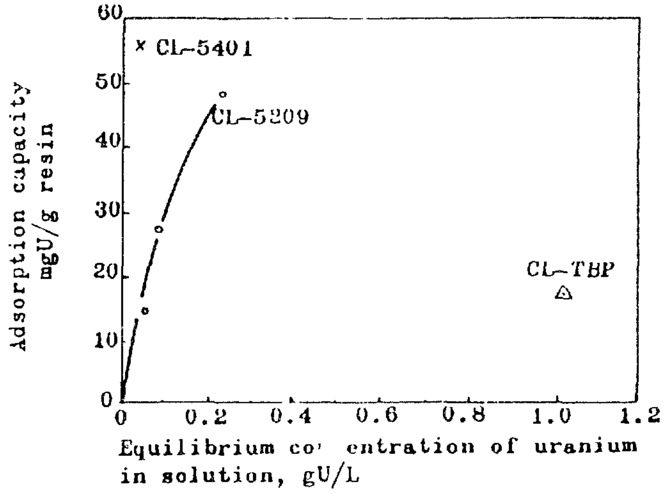

FIG.2. Relationship between adsorption capacity of the resin and equilibrium concentration of uranium in 1 N HNO_3 solution

FIG.3 indicates that CL-5209 can adsorb uranium effectively from 0.5 N HNO_3 solution.

FIG.4 indicates that CL-5209 is no longer effective for adsorption of uranium from 0.1 N HNO_3 solution. However, CL-5401 is still a good adsorbent for uranium in such a dilute nitric acid solution.

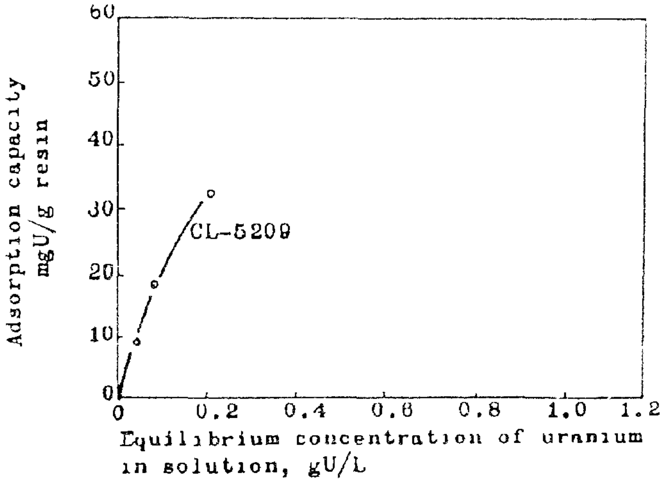

FIG.3. Relationship between adsorption capacity of the resin and equilibrium concentration of uranium in 0.5 N HNO_3 solution

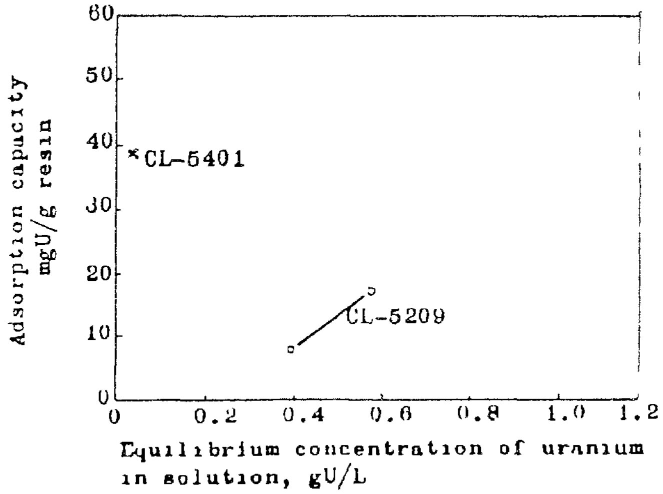

FIG.4. Relationship between adsorption capacity of the resin and equilibrium concentration of uranium in 0.1 N HNO_3 solution

2.3. Elution of uranium from loaded resin

The uranium-loaded CL-5209 could be eluted with water. 8 bed volumes of eluant were needed to complete elution at a flow rate of 1-1.5 bed volumes per hour. In this case, tailing was somewhat observed. When a 5% ammonium carbonate solution was used to elute the uranium-loaded CL-5209, no tailing was found.

Water was ineffective for eluting uranium from CL-5401. A 5% ammonium carbonate solution was used for this purpose. 5 bed volumes of eluant were needed to complete the elution.

2.4. Treatment of uranium-bearing effluent

The effluent (200 mgU/L, 2 N HNO_3) from refining process was treated with a column loaded with 20 kg CL-5401. A total of 12 m^3 of effluent was passed through this column. After this treatment the uranium concentration in the raffinate was less than 0.05 mg/L. A 5% ammonium carbonate solution was used as eluant. Uranium in the eluate obtained could be recovered by recycling the eluate into the feed solution of the TBP extraction stage or precipitated as uranium carbonate by boiling the eluate. After filtration or decantation, uranium carbonate so obtained was recycled to TBP extraction stage.

3. LOSSES OF THE ACTIVE COMPONENT

CL-5209 resin was contact with water thoroughly. Then 5209 concentration in the aqueous phase was analysed by gas-liquid chromatography. The result indicated that the loss of 5209 in water was 4 mg/L.

Put 0.5 g CL-5401 into 10 L of water and made them contact each other thoroughly. Then the uranium adsorption capacity of the resin was determined with uranium saturation method. The result showed that the uranium adsorption capacity of the resin so treated was only 6.7% less than the value of the untreated resin. According to this result the loss of 5401 in water could be calculated as 1.7 mg/L.

Based on the characteristics described above, we suggest that CL-5209 and CL-5401 should be applicable to the removal of uranium from effluents of refining process.

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WASTE MANAGEMENT IN THE REFINING AND CONVERSION OF URANIUM IN CANADA

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Abstract

Eldorado Resources Limited has operated uranium refining facilities at Port Hope, Ontario, since 1942. It was not, however, until 1955 that solvent extraction was used to produce nuclear grade uranium trioxide. In 1958 the production of uranium dioxide was commenced to provide fuel for the domestic CANDU reactors. Conversion facilities were added in 1970 to produce uranium hexafluoride for export.

In 1975 a decision was made to build a new refining and conversion facility in the Port Hope area. The outcome was, however, that a new refinery was built at Blind River in northern Ontario (some 500 km north of Port Hope) and a new uranium hexafluoride plant built at the existing Port Hope facility. The Blind River refinery came on-stream in 1983, and the Port Hope conversion plant in 1984.

Today, in Canada, uranium yellowcake is refined at Blind River and the uranium trioxide produced is shipped 500 km south to Port Hope where it is converted to uranium dioxide and uranium hexafluoride.

Process wastes from the Port Hope facility have been since 1956 and continue to be buried in a licenced waste management site some 16 km from Port Hope. There is no waste management site available to the Blind River refinery, nor is one planned.

Because of the increasing need to better manage process wastes, and to reduce their production, Eldorado embarked on a major program to reduce the amount of waste produced, to reduce the amount requiring burial, and to maximise recycle and reuse of these materials.

This paper addresses the approach, the successes or otherwise, that Eldorado has had in this endeavor. Since its inception, the program has resulted in achieving more than an 85 percent reduction in the wastes requiring burial, through the recycle of materials to other industries and by instituting process modifications which limit waste production. Initiatives to reduce still further the need for burial are being actively pursued.

1. INTRODUCTION

Process wastes arising from the refining and conversion of uranium yellowcake to uranium hexafluoride and uranium dioxide fuels have, in the past, been buried at two waste management sites near to Port Hope. The first site is at Welcome, some 2 km from Port Hope, and was used between 1948 and 1955. The second site is at Port Granby, some 16 km west of Port Hope. This site has been used since 1956, and is still in use today. Both sites are licenced, and are maintained and operated in accordance with the requirements of the Atomic Energy Control Board.

Over the last 5 years or so, Eldorado has developed a major program to both reduce the amount of waste produced in its operations and to recycle as much of the waste as possible. To date, the program has achieved over 85 per cent reduction in the wastes requiring burial, by recycling wastes to other industry and by instituting a number of process modifications which limit waste production.

TABLE 1

TYPICAL CHARACTERISTICS OF RAFFINATE

Constituent	Concentration (g/L)
Uranium	2
Thorium	6
Nitrate (as N)	11
Ammonia (as N)	4
Phosphate (as P)	17
Sulphuric acid	450
Silica (as SiO_2)	19
Organics	0.5
Iron	2
Aluminum	15
Copper	0.1
Density	1600
Radium-226	150 pCi/L

2. WASTE GENERATION

2.1 Raffinate

The major waste produced by Eldorado results from the refining of yellowcake to nuclear grade UO_3. The refining process consists of digesting the yellowcake in concentrated nitric acid and purifying the resultant solution by solvent extraction (SX), using tributyl phosphate in a kerosene solution. Uranium is selectively transferred to the organic phase in the extraction step while the impurities in the yellowcake remain in the aqueous phase. This is heated with sulphuric acid to drive off the nitric acid which is recovered and re-used.

The concentrated waste, called raffinate, is an inevitable waste product of uranium refining. It is produced at a rate of about 500 kg per 1000 kg of uranium refined. A typical analysis of currently produced raffinate is given in Table 1.

Since 1955, when UO_3 production began at Port Hope, Eldorado has used a number of raffinate disposal methods. Initially, a neutralized and filtered solution was discharged into Lake Ontario. This practice ceased in 1968 and was replaced by disposal of neutralized raffinate at a licenced waste management site. More recently, the burial of liquid waste was halted and a dry limed raffinate was buried at the waste management site or stored in drums at the refinery. All these three disposal methods had major shortcomings. Consequently, development work was carried out on the recycle of raffinate to a uranium mill for the recovery of the residual uranium and use of the sulphuric acid in the mill process. This recycle had the added advantage of consolidating the waste from milling and refining at one site.

2.2 Calcium Fluoride

Most of the UO_3 produced in the refining process is converted into uranium hexafluoride (UF_6), the feed material for uranium enrichment plants. About 78 per cent of the uranium refined by Eldorado is converted to UF_6. Since the Canadian nuclear program uses natural uranium, all UF_6 production is exported. Figure 1 shows a simplified flowsheet of the UF_6 conversion process currently employed at Port Hope.

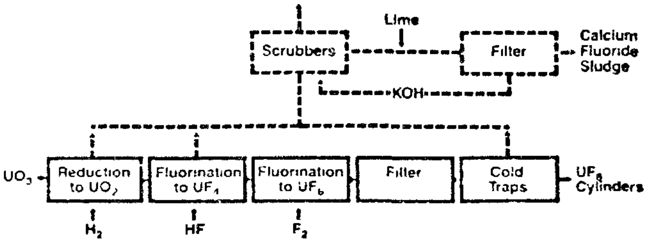

FIGURE 1: CONVERSION OPERATIONS

Pure UO_3 is first reduced to UO_2 with hydrogen. The UO_2 is then fed to aqueous reactors where it is reacted with aqueous hydrogen fluoride to produce UF_4. Reactor off-gas, containing uranium and hydrogen fluoride, is scrubbed in packed tower columns with a potassium hydroxide solution. UF_4 from the hydrofluorination reactors is dried and reacted with fluorine to produce UF_6. The gaseous UF_6 is filtered before being cooled and condensed as solid UF_6 in cold taps. Off-gases are collected and scrubbed with KOH. Finally, the UF_6 is melted and transferred to 9- or 13-tonne shipping cylinders.

All gases leaving the UF_6 conversion process are scrubbed with KOH solutions to reduce HF and other gaseous and particulate constituents to levels below emission guidelines. The KOH solutions from the scrubbers are reacted with lime to convert potassium fluoride to KOH and to precipitate the fluoride as insoluble calcium fluoride. Filters remove the calcium fluoride, producing a sludge of about 35% moisture. This calcium fluoride sludge is the major waste product from the UF_6 conversion process. It is produced at a rate of about 500 kg for each 1000 kg of uranium converted to UF_6. A typical composition of the sludge is given in Table 2.

TABLE 2

TYPICAL COMPOSITION OF CALCIUM FLUORIDE SLUDGE

Constituent	Concentration (% by weight)
H_2O	35
CaF_2	26
KOH	11
$CaCO_3$	5
$Ca(OH)_2$	23
Uranium	0.02

Since UF_6 production began in 1970, the calcium fluoride sludge has been transported to a licenced waste management site for burial in trenches.

2.3 Ammonium Nitrate

Eldorado also converts refined uranium into ceramic grade uranium dioxide (UO_2) powder. The powder is shipped to Canadian fabricators to produce fuel pellets for use in CANDU reactors. About 22 per cent of the uranium refined by Eldorado is converted to UO_2.

Refined uranium is converted to ceramic UO_2 by precipitating ammonium diuranate (ADU) from a solution of uranyl nitrate with aqueous ammonium hydroxide at about 80°C. The ADU is separated from the ammonium nitrate solution by filtration or by a centrifuge system. This ammonium nitrate solution is the major waste product from UO_2 conversion. The ammonium diuranate is first dried and then reduced to UO_2 in rotary kilns. The waste ammonium nitrate solution is concentrated by evaporation. About 800 kg of ammonium nitrate solution are produced for each 1000 kg of uranium converted to UO_2. A typical chemical analysis of the solution is given in Table 3.

TABLE 3

TYPICAL CHARACTERISTICS OF AMMONIUM NITRATE SOLUTION

Constituent	Concentration
Nitrogen	255 g/L
pH	8.3
Uranium	0.003 g/L
Radium-226	1 pCi/L
Density	1250 g/L

When UO_2 conversion first began in 1962, and until 1974, the ammonium nitrate waste solution was disposed of with the raffinate from the solvent extraction refining process. Between 1974 and the fall of 1977, the ammonium nitrate solution was disposed of at a licenced waste management site, separately from the raffinate.

2.4 Garbage

In addition to process wastes (raffinate, calcium fluoride and ammonium nitrate), the refining and conversion of uranium produces miscellaneous garbage. This consists of non-combustible wastes which are contaminated or have the potential for low levels of radioactive contamination.

All garbage is currently buried at a licenced waste management site. The amount of garbage buried annually is about 500 tonnes.

Combustible garbage is reduced to ash in an incinerator which was installed at Port Hope in 1979. Ash production is about 25 tonnes annually, and all ash is buried at the waste management site.

2.5 Scrap Metal

Refining and conversion operations at Port Hope have resulted in substantial quantities of scrap metal. This scrap metal consists of carbon steel, stainless steel, copper and aluminum. The material is in the form of piping, sheeting and fabricated items. Past disposal practice for scrap metal was burial with other contaminated garbage at the licenced waste management area.

In 1980, however, Eldorado developed a proposal which would allow scrap metal to be recycled through conventional channels.

Stringent requirements are enforced on the recycling program, namely:

- no visible uranium exists on the scrap metal,
- all scrap metal has a radiation level of less than 500 µRem per hour on contact; and
- the scrap material is transported directly from Eldorado to the mill facility where remelting occurs.

3. WASTE MANAGEMENT PROGRAMS

3.1 Waste Minimization

Eldorado's primary objective with respect to waste management is to reduce the amount of wastes which require burial at a waste management site. Significant progress has been made since 1975 in achieving this goal, despite expansion of the facilities which will almost triple the company's processing capacity.

The systematic decrease in wastes buried during the period 1977-1985 is shown in Figure 2.

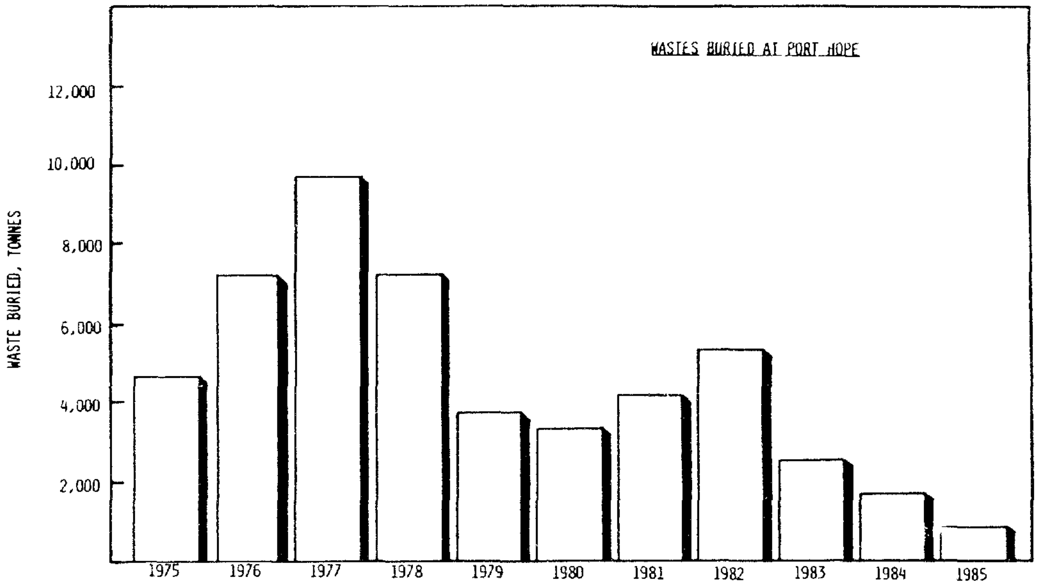

FIGURE 2

Ammonium nitrate burial ceased after 1977, when it was sold as a fertiliser in the local area.

Raffinate recycle to uranium mills was begun in 1978 with a trial program, and continued thereafter.

For the last four years a program to recycle calcium fluoride waste to steel mills, as a fluxing agent, has been underway. Problems have been encountered with respect to the amount of uranium in the waste (<200 ppm). Thus while the federal regulatory body (AECB) considers <200 ppm uranium to be recyclable to a steel mill, the provincial regulatory agency considers this to be too high. Process modifications are being developed to reduce the uranium content to allow recycle as a flux material. If this can be achieved, the only requirement for waste management at Port Hope will be for non-combustible garbage and incinerator ash. Currently, the calcium fluoride is sent for burial at a licenced waste management site.

The overall progress in reducing waste quantities is shown in Figure 3 where the total amount of wastes buried is expressed as a proportion of the uranium processed at the refinery. In 1977, over 2 kg of waste was buried at the Port Granby waste management site for each kilogram of uranium processed. This has been reduced to about 0.5 kg/kg U. Continued operation of recycling and minimization programs could further reduce this to 0.05 kg/kg U.

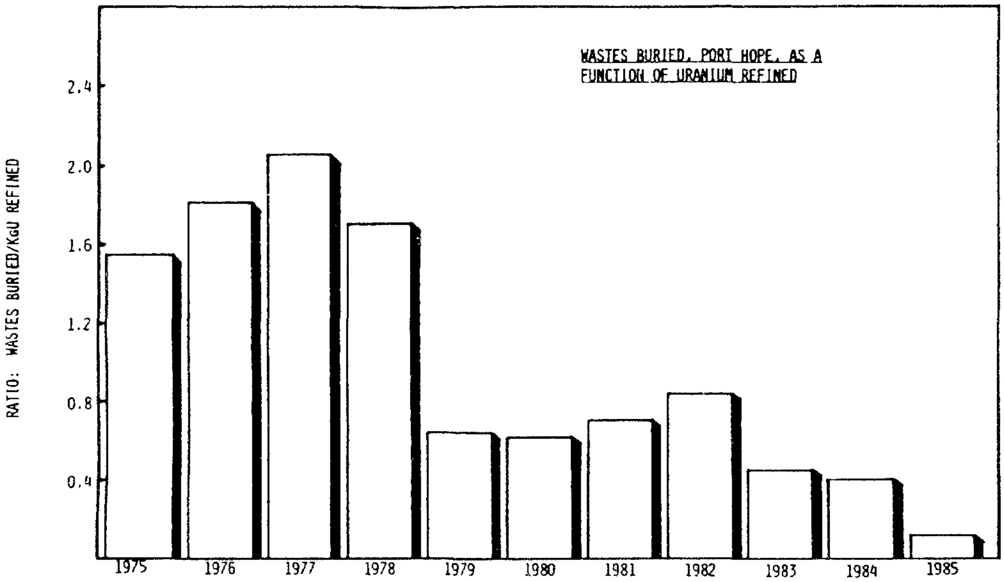

FIGURE 3

The successful reduction in the amount of wastes requiring burial has been achieved by vigorous pursuit of two waste management strategies, namely:

- develop new processes which minimize waste production; and
- identify uses for process wastes which allow their recycling to other industries.

3.2 Process Modifications

Development of new processes which minimize or eliminate waste generation is the preferred waste management strategy.

The new UF_6 processing method, called the "wet-way" process, uses aqueous hydrofluoric acid to produce UF_4 from UO_2 in place of gaseous HF in the original process. This provides for a more efficient use of HF and also allows process off-gases to be scrubbed with water instead of KOH solution. The dilute HF solution, which results from water scrubbing, can be recycled to the "wet-way" process. (In the original process, water scrubbing was not practicable because there was no use for dilute HF solutions.) Some KOH scrubbing is still necessary with the "wet-way" process, but because most of the HF is removed during the water pre-scrub, the volume of calcium fluoride is reduced by at least 75 per cent to less than 100 kg per 1000 kg UF_6, compared to the previous "dry-way" process.

Since conversion of UO_3 to UF_6 first began at Port Hope in 1970, fluoride emissions have been controlled by scrubbing process off-gases with KOH. The scrubbing process results in the need to dispose of a calcium fluoride sludge. Figure 4 shows the increasing amount of sludge produced in 1979-82 as a function of the corresponding UF_6 production. Over this period there was an increase in sludge production above what might be expected because of increased UF_6 production. In fact, the increased calcium fluoride sludge generation is a result of improvements in air emission control. Figure 5 shows the relationship between the amount of sludge and ar arbitrary air quality index over the period from 1975 to present. (The higher the air quality index the greater the fluoride emissions.) The improvement in air quality in recent years has been at the expense of an increase in calcium fluoride sludge generation.

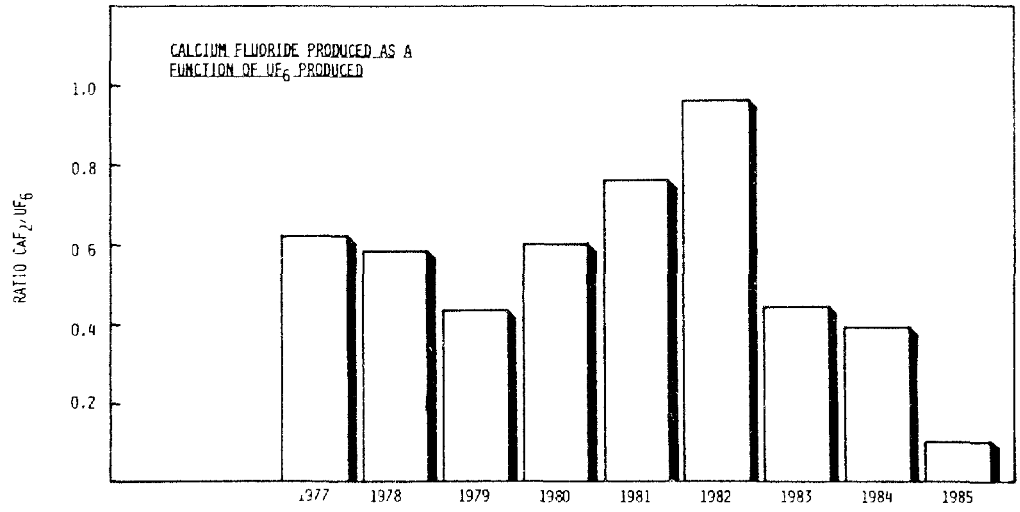

FIGURE 4

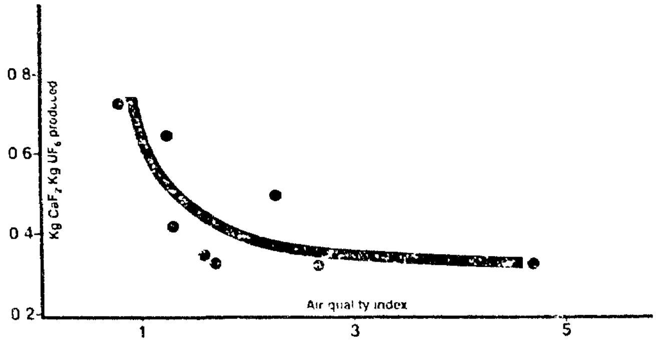

FIGURE 5:

RELATIONSHIP BETWEEN WASTE PRODUCTION AND AIR QUALITY

3.3 Waste Recycling to Other Industries

Where it is not possible to eliminate a particular waste, recycling to other industries avoids the need to bury waste at a licenced waste management site. Three wastes - ammonium nitrate, raffinate and scrap metal - are currently being recycled.

The substantial increase in the amount of wastes being recycled is shown in Figure 6. The recycling program began with the local use of ammonium nitrate as fertiliser in 1978. The program has been so successful that the demand exceeds the supply. Eldorado's fertiliser contains less uranium and radium than most commercial fertilisers.

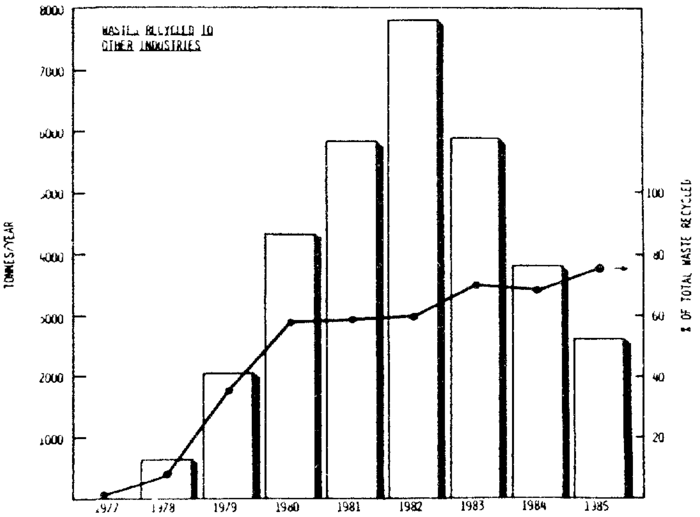

FIGURE 6

The recycling of raffinate to uranium mills in Ontario began with two test programs in 1978 and 1979. Currently, all raffinate produced at Blind River is recycled to uranium mills in Elliot Lake.

3.4 Summary

Over the past 5 years or so, the amount of waste from Eldorado's refining and conversion operations requiring waste management (burial) has been reduced by almost 80 per cent. Once the objective of recycling calcium fluoride is in place, over 95 per cent of what were previously considered wastes will have become by-products, used commercially in other operations.

THE REGULATION OF URANIUM REFINERIES AND CONVERSION FACILITIES IN CANADA

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Abstract

The nuclear regulatory process as it applies to uranium refineries and conversion facilities in Canada is reviewed.

In the early 1980s, Eldorado Resources Limited proposed to construct and operate new facilities for refining yellowcake and for the production of uranium hexafluoride (UF_6). These projects were subject to regulation by the Atomic Energy Control Board. A description of the Atomic Energy Control Board's comprehensive licensing process covering all stages of siting, construction, operation and eventual decommissioning of nuclear facilities is traced as it was applied to the Eldorado projects. The Atomic Energy Control Board's concern with occupational health and safety, with public health and safety and with protection of the environment so far as it affects public health and safety is emphasized.

Some regulatory difficulties encountered during the project's development which led to opening up of the licensing process to public input and closer coordination of regulatory activities with other provincial and federal regulatory agencies are described.

The Board's regulatory operational compliance program for U refineries and conversion facilities is summarized.

1. INTRODUCTION

In passing the Atomic Energy Control Act[1] in 1946, the Parliament of Canada declared atomic energy to be of national interest and therefore under the exclusive jurisdiction of the federal government. The Atomic Energy Control Board (AECB) was created to administer the Act which provides for the control and supervision of the development, application and use of atomic energy. Under the provisions of the Act, the Board issued the Atomic Energy Control Regulations[2] which determine the authorization and supervision regime

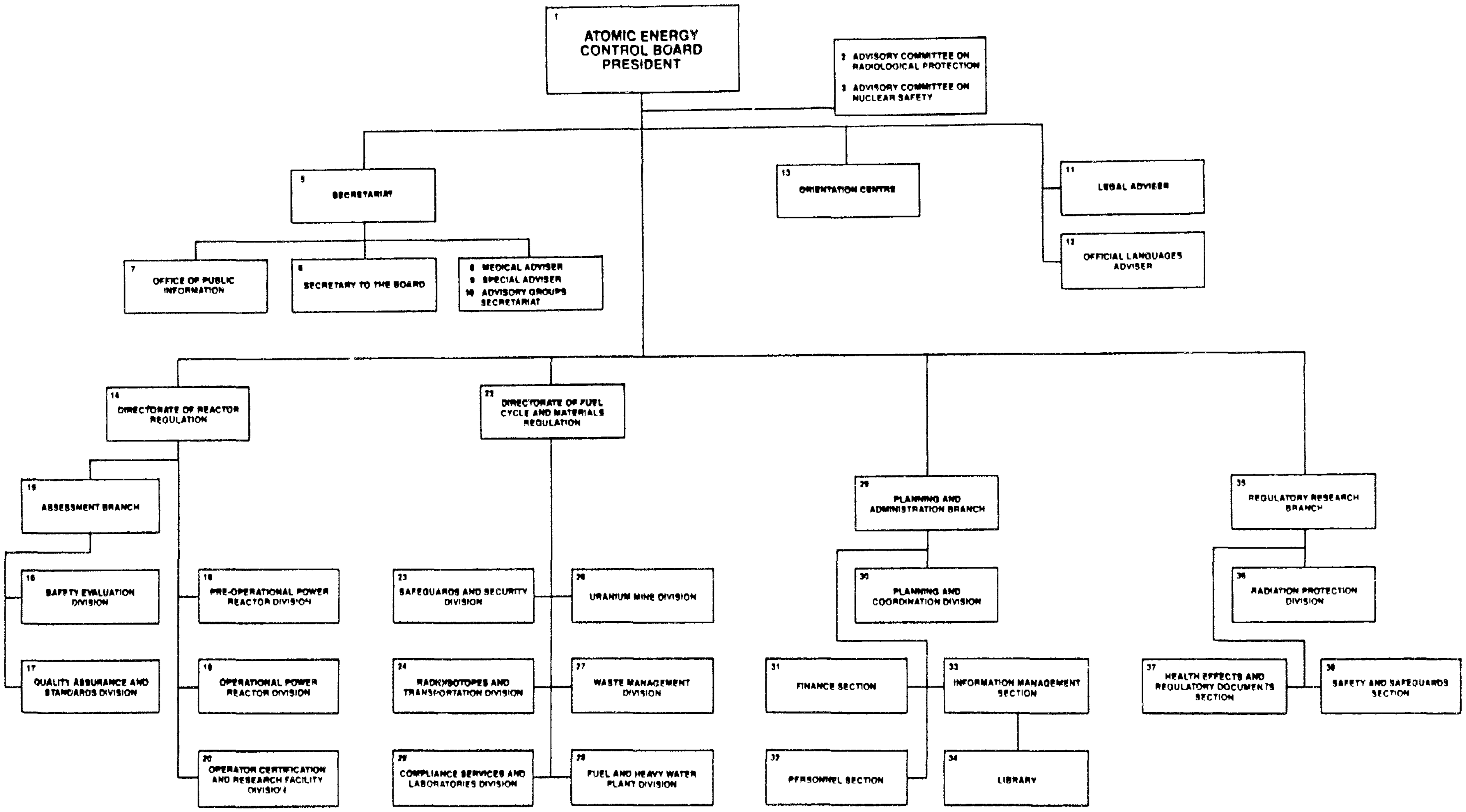

Fig.1. Atomic Energy Control Board - Organization Chart (1 January 1984).

applicable to all nuclear facilities. The Board has chosen to issue only general, skeletal regulations; specific regulatory requirements are applied through the licensing process.

2. STRUCTURE OF THE AECB

The AECB is an organization consisting of a Board of five members and a supporting technical and administrative staff of approximately 265 persons. In the following text, the "Board" means the five-member Board and the "AECB" means the organization and its staff. (See Figure 1).

Various Divisions of the AECB's Directorate of Fuel Cycle and Materials Regulation are responsible for regulating mines and uranium mills, refineries and conversion plants, fuel fabrication plants, heavy water plants, radioactive waste management facilities, transportation and packaging, and the use of radioisotopes. The Fuel and Heavy Water Plant Division (FWD) has responsibility for uranium refinery and conversion plant licensing and compliance activities. Most licensing assessment and review work and facility inspections are carried out by project officers of the FWD who are mainly "generalists". They are complemented by staff specialists in radiation protection, quality assurance and a variety of engineering disciplines.

Not involved in licensing but reporting separately to the Board are two advisory groups, the Advisory Committee on Radiological Protection and the Advisory Committee on Nuclear Safety.

3. SAFETY PRINCIPLES AND OBJECTIVES

Over the course of the AECB's existence safety principles and objectives have been developed that underlie its regulations and licensing practices. The Board's Advisory Committee on Nuclear Safety has produced a document[3], which was endorsed by the Board, on the safety objectives for nuclear activities.

The underlying concept is that the primary responsibility for achieving a high standard of safety resides with the licensee. The regulatory agency in turn is responsible for providing the objectives for nuclear safety and the guidelines for their application as well as for auditing industry's performance. This approach leads to the regulatory body having to determine how effectively the safety objectives are being achieved.

4. LICENSING PROCESS

The licensing process is the means by which the AECB gains assurance that a nuclear facility will be sited, designed, constructed, commissioned and operated in compliance with safety criteria and requirements established by the AECB.

This assurance is achieved by establishing communication with the applicant at an early stage in the project and maintaining surveillance over all safety-related activities in each phase of the project's development from the initial conceptual design of the facility through to its mature operation. The intent is to identify points of contention at as early a stage as possible to avoid situations where the applicant will find it economically difficult to make changes required by AECB staff.

4.1 Licensing Stages

For all nuclear facilities, the Board has established distinct administrative steps for the implementation of its authority. (See Figure 2). These consist of site acceptance which includes a public information program, approval to construct and a licence to operate. The applicant must convince the Board in detailed written submissions that the plant will meet the health, safety and security requirements of the Regulations. Details for these submissions are normally available in the form of guidelines.[4]

STEPS IN THE LICENSING OF A NUCLEAR FACILITY

1) PUBLIC INFORMATION PROGRAM

2) SITE ACCEPTANCE

3) CONSTRUCTION APPROVAL

4) LICENCE TO OPERATE (LIMITED PERIOD)

5) SITE CLOSURE

CHARACTERISTICS OF THE LICENSING PROCESS

1) APPROVAL IN STAGES

2) BURDEN OF PROOF ON THE APPLICANT

3) INSPECTION AT ALL STAGES

4) JOINT REVIEW BY REGULATORY AGENCIES

Fig. 2. Licensing stages.

Although the nuclear industry is subject to federal jurisdiction through the Atomic Energy Control Act, it has to be realized that a nuclear facility operating within a geographical location in a certain province of Canada, has some impact on that province and therefore provincial regulatory agencies do have a legitimate concern with regard to the operation of the facility.

In recognition of this joint interest, the Board has established a joint regulatory process. This means that the Board, as a lead agency, invites all regulatory agencies, federal and provincial, whose area of responsibility could be impacted on by the proposed nuclear facility to participate in a consultative regulatory process. This process ensures that legitimate concerns of any agency, federal or provincial, are considered in the regulatory process and are reflected in the licence in the form of a condition or requirement. Figure 3 outlines a Joint Regulatory Process chart as it might apply to a Site Assessment situation.

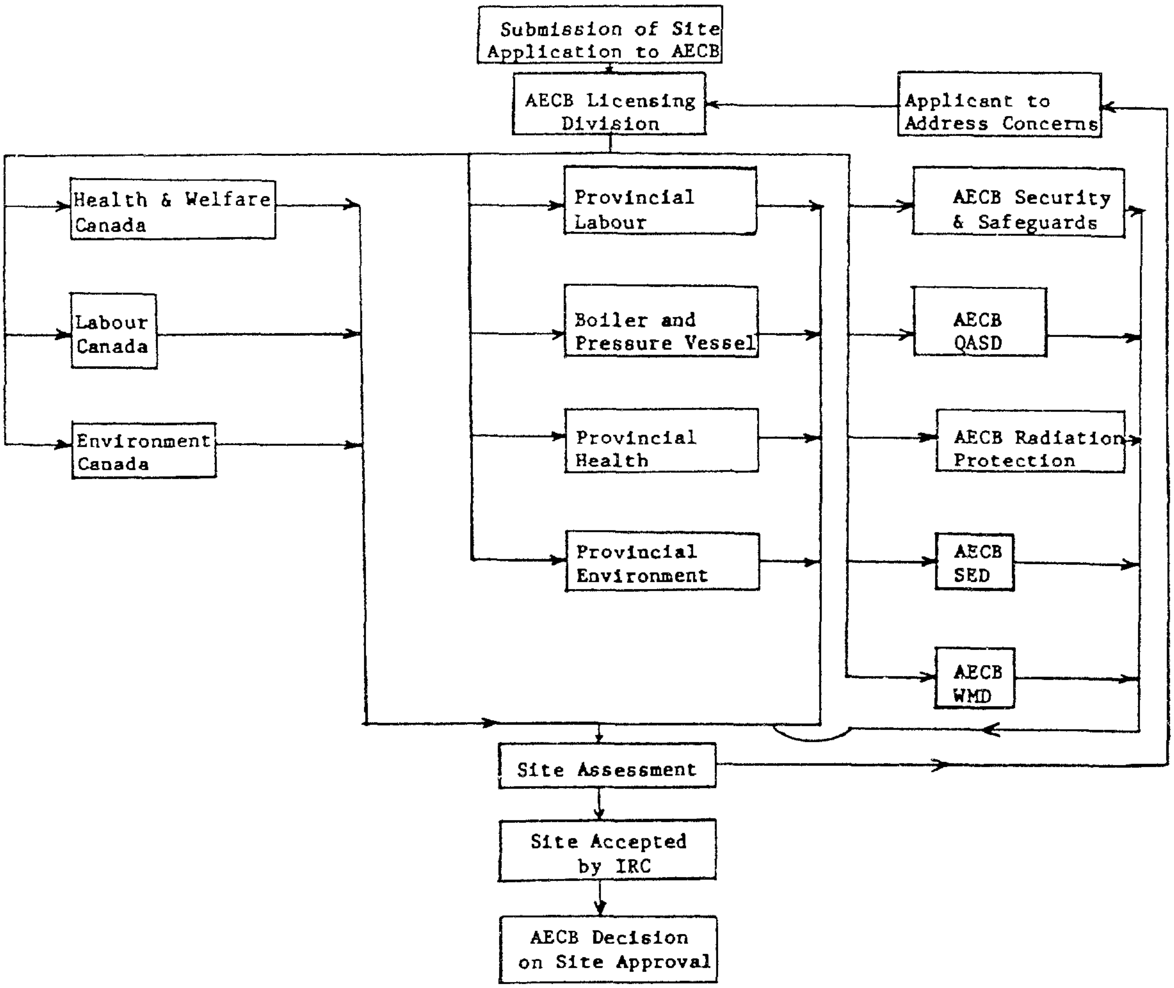

Fig.3. Joint Regulatory Process Chart.

In many cases, the applicant may be required by an environmental agency to prepare an environmental impact statement and submit it to a formal hearing or review process. The impact statement normally includes the type of information required by the AECB for site acceptance and can be submitted for that purpose. If a hearing is required by another agency the AECB withholds any site acceptance until the results of the hearing are available and evaluated.

4.1.1 Site Acceptance

The basic objectives at the Site Acceptance stage are to establish the conceptual design of the facility and to determine whether it is possible to design, construct, and operate the facility on the proposed site to meet the safety objectives and requirements established by the AECB. The primary documentation required is a Site Evaluation Report providing a summary description of the proposed facility and its impact on the environment including information on land use, present and predicted population, principal sources and movement of water, water usage, meteorological conditions, seismology and local geology.

During this phase of the licensing process, the applicant is required to announce publicly his intentions to construct the facility and to hold public information meetings at which the public can express its views and question the applicant's representatives.

4.1.2 Construction Approval

Prior to granting a Construction Approval the AECB must be assured that the design is such that the AECB safety principles and requirements will be met and that the plant will be built to appropriate standards. In order to do this, it is necessary that the design be sufficiently advanced to enable safety analyses to be performed and their results assessed.

Construction will only be authorized once the design and safety analysis programs have progressed to the point that, in the judgment of the AECB, no further 'significant' design changes will be required.

4.1.3 Operating Licence

Before issuing an Operating Licence the AECB must be assured, primarily, that the plant, as built, conforms to the design submitted and approved, and that the plans for operation are satisfactory. The requirements include submission of a Final Safety Report, completion of a previously approved commissioning program, and approval of operating policies and principles.

5. AECB LICENSING OF ELDORADO RESOURCES LIMITED FACILITIES FOR UO_3 AND UF_6 PRODUCTION

5.1 Background

Eldorado Resources Limited, a federal Crown corporation, has been mining and refining first radium and then uranium for 50 years. At present the Blind River refinery, in Blind River, Ontario, processes yellowcake concentrates from uranium mines in Canada and other countries to produce UO_3. In Port Hope, Ontario, the UO_3 is further processed to uranium dioxide (UO_2) fuel for CANDU reactors and also to uranium hexafluoride (UF_6) for export.

In light of a growing world-wide demand for UF_6 in the mid 1970s, Eldorado proposed to build a second uranium refinery in Ontario with a capacity of 9,000 tonnes per year of uranium as UF_6. Eldorado began the process of selecting a site for a new Ontario uranium refinery in 1975. By 1976, a long list of potential sites had been narrowed to four.

5.2 Environmental Review Processes

Of the four Ontario sites studied, the site at Port Granby (20 km from Port Hope) was chosen by Eldorado for development of a refinery. Over the following year a detailed Environmental Impact Statement (EIS)[5] was prepared and submitted to a panel set up by the federal government's Environmental Assessment and Review Process (EARP). Following technical and public review of the EIS, the Port Granby refinery proposal was the subject of two rounds of public hearings. The Atomic Energy Control Board participated in the hearings, providing technical analysis on Eldorado's proposal and explaining the Board's regulatory process to the panel. In early 1978 the panel concluded that the refinery itself and the refinery processes could be environmentally acceptable on an appropriate site if a number of conditions were met. The Port Granby site, however, was found to be unacceptable for a variety of reasons related to air quality, waste management, land use and social impacts.

Following the rejection of the Port Granby proposal, Eldorado identified potential sites in each of the Port Hope (Hope Township), Sudbury and Blind River areas of Ontario. The Hope Township site ranked highest in Eldorado's consideration. Following environmental hearings on all the sites, the Panel's report[6] was issued in February, 1979, concluding that all three sites could be acceptable for the project. In July, 1979, it was announced that the Federal Cabinet had concurred with Eldorado's selection of Hope Township as the preferred site for the Ontario refinery. Site preparation work began in early 1980 but was suspended when the Federal Cabinet (of a newly elected government) reviewed the earlier decision and determined that the refinery should be located at Blind River. Eldorado then proposed that the UO_3 production facility be sited at Blind River but that the UF_6 conversion facility be sited on the old Port Hope Plant property.

Eldorado publicly announced its proposals and the site applications for AECB approval of the Blind River refinery[7] and the Port Hope UF_6 conversion facility[8] were filed on September and October, 1980, respectively. With respect to the subject of environmental assessment, Eldorado chose not to submit the new proposal to the EARP process. The Board staff indicated that a specific environmental assessment process (non public hearing process) would be necessary and that this would be part of the Board's joint regulatory process.

The Blind River site although changed slightly from the original site proposed, did not present a problem to the AECB, the general area having been extensively reviewed by regulatory agencies and accepted by the EARP Panel. The Port Hope site, however, had not been subjected to any environmental assessment process and further, it did not provide for a "buffer zone", an area surrounding a nuclear facility which is under the control of a licensee.

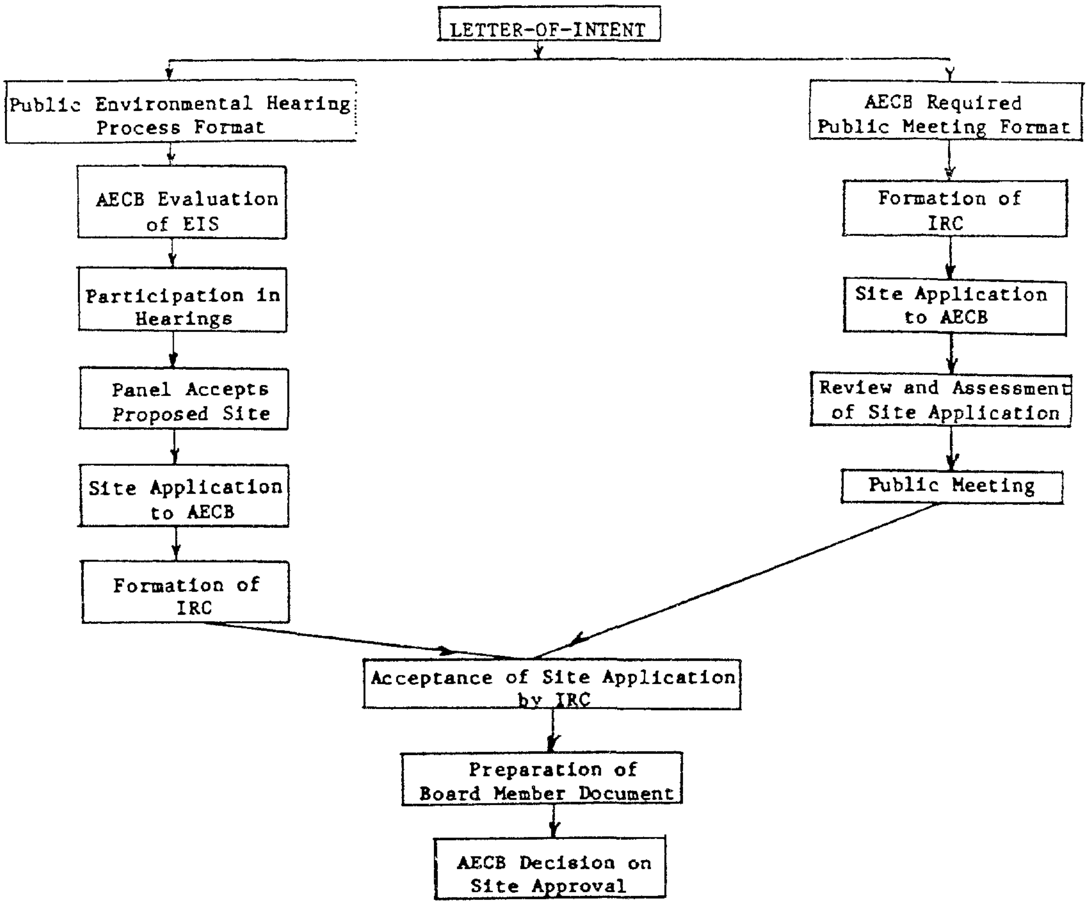

Fig.4. Site Approval Licensing Process Chart.

Figure 4 shows the difference in the two approaches (public environmental hearing vs AECB public meeting format with joint regulatory review).

5.3 Licensing of the Blind River Refinery

In September 1980, Eldorado applied formally to the AECB for approval to site the Blind River refinery on a 263 hectare site in the town of Blind River, Ontario. Board staff considered Eldorado's change from the original proposal.

5.3.1 Site Assessment

The regulatory reviews of the Eldorado Site Application[7] and other documents[7] presented to the AECB and the Interagency Review Committee, identified a number of deficiencies in the reports and requests for further clarification were submitted to Eldorado. Eldorado's responses to these requests were evaluated and considered acceptable by the AECB staff and IRC. The AECB staff recommended to the Members of the Board, in January, 1981, that site approval should be given.

5.3.1.1 Public Intervention

Following the government's decision that Eldorado establish a uranium refinery at Blind River, Ontario, some members of the public from the town of Blind River and surrounding area, claimed that the changes in Eldorado's planning warranted new public hearings. Conversely the Board staff believed that the change in site location was not sufficiently significant to require that a new public hearing be carried out.

In November, 1980, the Board received a submission from the Blind River and District Concerned Citizens Association reviewing Eldorado's site application. Although a number of their concerns had merit and were considered by Board staff in its evaluation, no new technical concerns were identified which would alter the Board staff position. At its January, 1981 meeting, the Board agreed to receive representatives from two groups. These groups were strongly opposed to nuclear energy in general and to the establishment of the Blind River refinery in particular.

After hearing the groups' presentations, the Board decided to defer a decision on site approval to allow staff an opportunity to study last minute submissions and to discuss the concerns in person with all groups in the Blind River area. The AECB attended a series of meetings with various public groups including local government elected officials. The AECB made presentations on the Board's mandate, the refinery licensing review procedures and the issues of air and water quality, radioactive wastes and radiation effects, as well as responding to questions and listening to public concerns. Following these meetings, the AECB staff concluded that no new information bearing on matters of health, safety, security or the environment had been presented which would alter its original recommendation that the site be approved for the purposes intended.

In mid-February, 1981, the AECB announced that it had approved Eldorado's application to site a uranium trioxide refinery near Blind River, Ontario.

Some details on the public participation and input during the course of the Blind River refinery site evaluation process is presented here to provide an indication of the extent to which the AECB's licensing process has become a more open one. In 1970, when an UF_6 Plant in Port Hope was licensed to operate almost no public information was made available on the AECB approvals and no public participation in the licensing process was contemplated.

5.3.2 Construction Authorization and Operating Licence

In February, 1981, Eldorado applied for Construction Authorization[9] to build the refinery. Information was presented to the AECB on facility design and layout, process description, safety programs, accident analysis, emergency procedures and quality control programs for design, procurement and construction. Eldorado's application and supporting information was reviewed by the AECB staff and by member agencies of the Interagency Review Committee. (See Figure 5).

It was noted that the refinery was designed to recycle as many wastes streams as possible and to minimize the number of discharge points. This design approach combined with monitoring and control programs proposed by Eldorado would enable detection and corrective action to be taken to limit the effects of upset situations to the environment.

A detailed accident analysis indicated that no credible scenarios were identified which did not have acceptable design features included to mitigate their consequences.

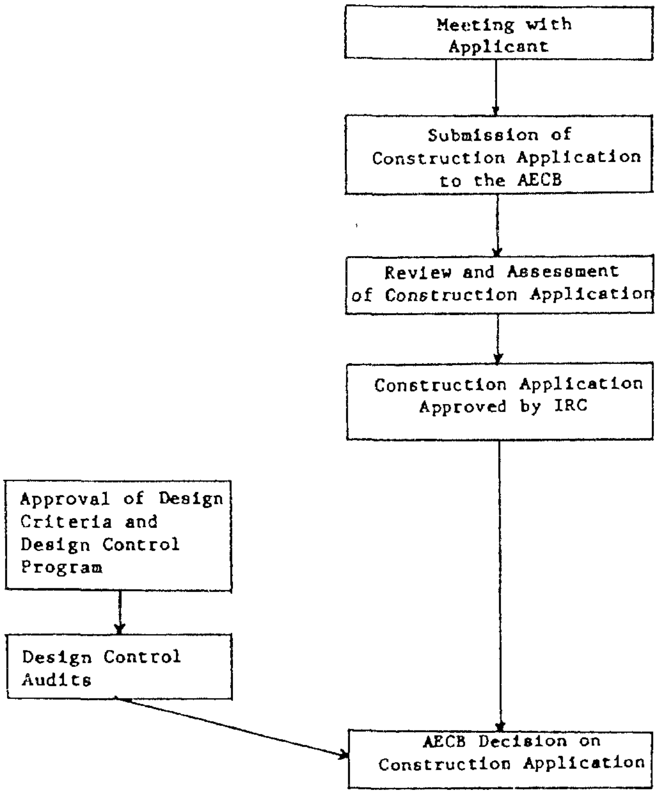

Fig.5. Construction Approval Licensing Process.

Construction Authorization for the construction of the uranium trioxide refinery in Blind River, Ontario, was granted by the Board in July, 1981.

In August, 1983, construction and commissioning of the refinery having been completed, the AECB granted Eldorado an operating licence. Leading up to this approval, the AECB staff had reviewed all the necessary commissioning reports on all major safety and environmental control systems and found the systems were in satisfactory condition for start-up. As well, radiation protection procedures for the plant were reviewed and some changes made as requested by the AECB staff. A Derived Release Limit (DRL) document was prepared by Eldorado and reviewed by the AECB staff. The plant design allows the plant to operate at less than 1% of the DRLs.

5.4 Licensing of the Port Hope UF_6 Facilities

In October, 1980, Eldorado applied formally to the AECB for approval to expand the uranium hexafluoride conversion facilities to include a new plant with an annual capacity of 9,000 metric tons of uranium, in the town of Port Hope adjacent to its existing Port Hope facility. An Interagency Review Committee, consisting of the AECB, Health and Welfare Canada, Environment Canada and the Ontario Ministry of the Environment, was formed to review Eldorado's application.

5.4.1 Site Assessment

A document "Application to the Atomic Energy Control Board for Site Approval - Port Hope UF_6 Facilities Expansion, October 1980"[8], was submitted to the AECB and IRC in support of the site approval application. The document was based on the AECB requirements and guidelines specified in the Atomic Energy Control Board licensing documents.[4]

Some of the significant issues identified are presented below.

1. The regulatory agencies agreed that if the proposed site was accepted, future approvals for the operation of the new UF_6 Plant would be contingent upon the existence of a clearly defined waste management plan.

Eldorado proposed to design the new facilities to reduce the quantity of wastes to a minimum. For example, a new process incorporated into the design of the new UF_6 facility allows recycle and recovery of hydrofluoric acid and an eight-fold reduction in CaF_2 generated. Eldorado had also made significant progress in the recovery and recycling of waste materials.

2. The lack of a large "buffer zone" was of concern to the IRC and therefore, the conceptual design of the facility was reviewed to ensure that appropriate design measures were proposed to compensate for the small buffer zone available and to ensure that the public would not be exposed to unacceptable levels of radiation and hazardous substances during normal and upset processing conditions.

Eldorado proposed to incorporate a number of technical features into the plant design which would give an increased measure of confidence in its ability to contain releases as follows:

- all effluent gas scrubbers and dust collectors will be installed inside the structure of the operating plant,
- secondary scrubbers will be installed to handle upset or emergency situations,
- all HF unloading from railcars will be carried out in an enclosed and ventilated building. No transfer of HF to the processing areas will take place without secondary containment,
- all liquid UF_6 handling (filling of shipping containers and sampling operations) will take place in autoclaves and inside the processing buildings,

- emergency electric power maintains the operation of key emission control systems.

Eldorado had designed additional environmental and engineering features into the proposed UF_6 facility to provide an adequate margin of in-plant safety systems, without reliance on the "buffer zone".

5.4.1.1 Public Information

Eldorado satisfactorily met the AECB's requirements for conducting a public information program. This program culminated with the holding of two public meetings in Port Hope in November and December, 1980. In general, the Port Hope public responded favourably to the idea of the Eldorado facilities being expanded in their town.

In July, 1981 the AECB approved the Port Hope site based on a recommendation from the AECB staff. The Board required Eldorado to carry out some further studies on the atmospheric dispersion modelling information presented in its application for site approval, as well as studies of groundwater flow on the site, as conditions of the approval.

5.4.2 Construction Authorization

In December, 1981, Eldorado submitted an application[10] to the AECB requesting approval to construct the proposed facility. The AECB staff and the IRC assessed the information presented by Eldorado to assure the reviewers that the design of the proposed facility would meet the safety and environmental requirements of the AECB and other regulatory agencies.

In April, 1982 Eldorado was granted partial approval to proceed with the plant construction. Eldorado was directed not to proceed with work on the HF unloading and storage area until further review on these facilities was carried out.

As well as the review of Eldorado's construction application[10] by the AECB and IRC, the AECB and Environment Canada contracted with engineering consultants to review Eldorado's proposed methods of bulk handling and storage of HF and NH_3 and to review the submitted accident analysis for possible omissions of significant events.

In May, 1982, after consideration of all of the information made available to it, the Board staff recommended that Construction Authorization be granted for all those remaining plant components which were not covered in the partial construction approval granted in April, 1982. The AECB agreed to grant this approval.

5.4.3 Technical Considerations of the Regulatory Review

5.4.3.1 Siting Considerations

A number of issues were identified in the review of Eldorado's Siting Application which required satisfactory completion or further studies to be carried out in order to obtain additional design information to allow for a complete evaluation of Eldorado's proposal to construct the facility. The following summarizes some of the more significant issues:

(a) The review of the atmospheric dispersion modelling used in the Site Application[8] led to the conclusion that the modelling may not be appropriate to the Port Hope site. Eldorado was requested to carry out validation tests and a sensitivity analysis to show that the atmospheric dispersion modelling information presented in the Site Application was valid for the Port Hope area.

Eldorado performed the requested work and Board staff concluded that the information contained in the study was adequate to satisfy the requirement of model validation and sensitivity analysis of the atmospheric dispersion modelling used.

(b) The Site Application[8] did not contain sufficient information to substantiate the claims that the groundwater flow from the proposed plant site was not in a southwest direction towards the Town of Port Hope's Water Treatment facility which contains a number of underground water storage chambers.

Eldorado was requested to conduct a further study to determine the groundwater flow direction.

The results of the study were used to determine whether additional containment facilities were required on the plant site and the type of contingency plans and monitoring programs to be developed for plant operation.

5.4.3.2 Construction Review

The Eldorado Construction Application was reviewed with particular emphasis placed on the design criteria, engineering design and proposed operation of those pieces of equipment and systems which have the greatest potential to cause significant releases of radioactive and toxic non-radioactive substances to the workplace and public environment. The plant safety systems were assessed to ensure that adequate design criteria were used in their design to mitigate the effects of normal and abnormal plant operations. Also, the Quality Assurance programs for the design, procurement and construction phases of the project were assessed to ensure that the necessary controls were being implemented.

The following is a brief summary of the major items reviewed:

a) The gaseous effluent treatment system for the new UF_6 facility consists of a series of large potassium hydroxide scrubbers and a number of dust collection systems. The scrubbing systems, designed for high efficiency fluoride removal, are arranged such that they can be operated in several series and parallel configurations to allow for plant upsets and to permit on-line preventative maintenance programs to be conducted.

In order to provide additional containment in the event of an accident, the HF storage building, F_2 cell maintenance area and the UF_6 product handling areas have separate, independent ventilation systems.

Eldorado had proposed an abatement system which should be able to adequately control air emissions.

b) The UF_6 product handling operations of the facility are located in areas physically segregated from the other plant processes. The UF_6 transport cylinders are filled in an area with its own emergency ventilation system and all sampling of hot UF_6 cylinders is done in autoclaves.

c) The design of the HF unloading and storage facility was a major review item for Board staff. Eldorado had proposed to build an HF facility which incorporates a structure to totally enclose two storage tanks, a below grade emergency storage tank and the rail car unloading station. This structure is ventilated and any HF emissions are scrubbed before release to the environment.

5.4.4 Operating Licence

By May, 1984 Eldorado had successfully commissioned all the utilities, major process areas of the plant, and safety systems and requested authorization to proceed with start-up of the plant to produce UF_6. A positive recommendation was made to the Board and the operating licence was approved. An operating licence containing nineteen conditions of operation was issued to Eldorado, on May 28, 1984, to operate the new UF_6 Plant in Port Hope.

5.4.4.1 Technical Considerations

(a) Board staff conducted a design audit of the process safety systems and considered them acceptable.

(b) During the construction phase, audits of quality assurance on the liquid HF, F_2 gas distribution and liquid UF_6 storage and handling system were carried out by the AECB staff and Ministry of Consumer and Commercial Relations (MCCR) staffs. All of these systems were jointly approved and accepted by the MCCR and AECB staff.

(c) AECB staff reviewed commissioning data and documentation related to all safety systems. A detailed review of environmental monitoring procedures was conducted and accepted by the Ontario Ministry of the Environment and Environment Canada staffs.

(d) Eldorado prepared detailed operational quality assurance manuals and procedures to control and maintain minimum standards on all safety-related aspects of plant operations. In addition, a program had been set-up for in-service inspection to minimize the probability of failure of piping and equipment.

(e) Detailed emergency procedures have been prepared by Eldorado and reviewed by Board staff and found to be acceptable.

(f) A derived release limit document was prepared and included data on the plant emissions and discharges. This was reviewed by Board staff and is considered acceptable. Eldorado was obliged, as a condition of licence, to maintain the airborne uranium emissions from the total Port Hope facility to less than 10% of the sum of the weighted DRL's, based on weekly averages. A gamma component was later added to the DRL control equation.

(g) Board staff reviewed the operator training program for the plant and considered it acceptable, including the training and operating procedure for the anhydrous HF acid storage area.

It was on the basis of this comprehensive review and assessment that the AECB staff recommended that ERL be permitted to commence operation of the plant to produce UF_6.

6. AECB Licensing Compliance and Surveillance

Compliance and surveillance of the licensee operations is carried out to determine whether the requirements of the Atomic Energy Control regulations and the conditions specified in the facility licence are being met. Issues and items relating to compliance are reviewed and assessed by the assigned project officer with assistance from specialists in other divisions within the AECB and outside agencies. Staff from provincial agencies may be, in some cases, appointed AECB inspectors for purposes of inspecting the licensees' facilities and for auditing the licensees' monitoring results. These inspections are done on behalf of these agencies themselves although reference may be made to the AECB licence. The AECB staff exercises a senior auditing function in cases where other agencies are involved.

Compliance reviews, assessments and recommendations by AECB staff and outside agencies are submitted to the AECB for consideration in taking regulatory action and as factors during licence renewal periods.

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CONVERSION OF URANIUM ORE CONCENTRATES AND REPROCESSED URANIUM TO NUCLEAR FUEL INTERMEDIATES AT BNFL SPRINGFIELDS

Part A: Uranium ore concentrates

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Abstract

Uranium processing has been carried out at the Springfields Works of BNFL for 40 years. During that time some 85,000 t U equivalent of uranium ore concentrate and in excess of 15,000 t U equivalent of uranium recovered from spent fuel reprocessing have been converted to nuclear fuel or nuclear fuel intermediates at Springfields. This paper describes how the conversion facilities have evolved in response to changes in factors such as market demand, feed and product specifications, industrial hygiene and environmental constraints, regulatory practices etc. Comments on the adaptation which will be necessary to deal with anticipated changes in the nuclear fuel cycle are provided.

1. INTRODUCTION

From its Headquarters at Risley, near Warrington, in the north west of England, British Nuclear Fuels plc (BNFL) co-ordinates the activities of its three operating divisions which between them provide a comprehensive range of nuclear fuel cycle services. The activities of the three divisions are summarised as follows:

i. The manufacture of nuclear fuel at the Springfields Works of BNFL near Preston in Lancashire is the responsibility of Fuel Division.

ii. The enrichment of uranium at the Capenhurst Works of BNFL near Chester is the responsibility of Enrichment Division.

iii. The reprocessing of irradiated fuel at the Sellafield Works of BNFL in Cumbria is the responsibility of Reprocessing Operations Division which is also responsible for operating two Magnox type nuclear power stations, one at Chapelcross and the other at Sellafield.

The aim of this part of the paper (Part A) is to describe current technology for converting uranium ore concentrates (UOC) to nuclear fuel intermediates at Springfields and to comment on recent or proposed changes in this technology. The conversion of reprocessed uranium at Springfields is dealt with in Part B.

In order to put UOC conversion technology into the context of Springfields site activities as a whole it is useful to summarise the main site activities which are:

1. Conversion of UOC to natural uranium tetrafluoride (UF_4).
2. Conversion of Magnox reactor depleted uranium (MDU) to reactor depleted UF_4.
3. Conversion of
    a. Natural UF_4 to uranium hexafluoride (UF_6) for enrichment at overseas enrichment plants or at Capenhurst
    b. Reactor depleted UF_4 to MDU UF_6 for enrichment at Capenhurst.
4. Reduction of
    a. Natural UF_4 to uranium metal for fabrication of Magnox fuel elements for UK, Italian and Japanese reactors.
    b. Tails depleted UF_4 to tails depleted uranium metal for non-nuclear applications.
5. Conversion of enriched UF_6 to ceramic grade uranium dioxide (UO_2) for fuel fabrication plants at Springfields and overseas.
6. Fabrication of oxide fuel assemblies for Advanced Gas Cooled Reactors (AGR) and Light Water Reactors (PWR and BWR).
7. Manufacture of cladding components for Magnox and AGR fuel elements.
8. Recovery of uranium values in residues recycled from uranium conversion and fuel manufacturing activities.

2. UOC CONVERSION PROCESSES. RECENT AND PROPOSED DEVELOPMENTS

Brief descriptions of the principal conversion processes as they now exist are provided in order to put recent developments into appropriate context.

2.1 Conversion of UOC to Pure Uranyl Nitrate

The uranium purification process at Springfields is based on continuous dissolution, filtration and solvent extraction in a nitric acid medium using counter current box mixer settler contactors and a 20% TBP/OK solvent. The existing technology has evolved over a period of 30 or more years by the replacement, refurbishment or stretching of equipment originally installed to meet the demands of the first UK civil reactor programme (Magnox). Since that time some 85,000 t U of uranium ore concentrates representing a wide variety of Yellow Cake types and origins have been processed through the purification plants. The flexibility of the process with respect to accommodation of the wide range in Yellow Cake quality has been and is still such as to provide little if any incentive for introducing fundamental changes.

2.2 Conversion of Pure Uranyl Nitrate to Uranium Trioxide

In all essential respects the Springfields process for producing natural uranium trioxide (UO_3) is similar to that which was later adopted at Sellafield for producing MDU depleted UO_3. A description of the Springfields process follows.

The physical and chemical properties of the uranium trioxide feed to the UF_4 production process have a crucial bearing on the performance of that process, and some comments on these properties and their origin is relevant.

UO_3 is prepared from pure uranyl nitrate by a two-stage continuous process comprising climbing film evaporation followed by fluidised bed denitration. The essential features of this process are summarised below.

The product of the purification stage, pure uranyl nitrate, is pumped to the tube side of the first of four long-tube natural circulation evaporation units in series. The liquor level in each of the four evaporator stages is maintained at approximately $^1/_3$ of the tube height by automatic control of the liquor flow into each stage. Discharge of concentrated uranyl nitrate product from the last stage, which operates under vacuum (~350 mm Hg abs), is automatically controlled so as to maintain a concentration of approximately 110% w/v 'U' using boiling point elevation to signal product strength. Variation of evaporator throughput is achieved by variation of the steam pressure applied to the first evaporation stage over the range 3-5 Kgm/cm^2.

Steam condensate from the first evaporation stage and the condensed vapour from the other three stages are used for pre-heating the feed liquor before the mixed condensates are recycled to the filtration and purification stages. The thermal conservation resulting from the four-stage evaporation and condensate/feed heat exchange is such that the amount of water evaporated is triple the quantity of steam used for evaporation.

The molten product of the evaporator is then denitrated in a fluidised bed reactor to give uranium trioxide in the form of a free flowing granular powder.

The denitration reactor is a vertical cylinder with a conical base through which protrude 21 fluidising air nozzles. The reactor charge, a bed of UO_3 fluidised on hot air, is maintained at 300°C by electrical heating elements in tubes through the cone base and in jackets around the walls of the cylinder. Molten uranyl nitrate is pumped into the fluidised bed via a spray gun located above the internal heating elements and 3' below the surface of the fluidised bed. The UO_3 particulates formed within the bed are removed continuously by the overflow from the surface and pneumatically transported to storage hoppers via a lift pot acting as a seal between the reactor and storage hopper. The fluidising air and gaseous reaction products, steam and oxides of nitrogen, are routed via sintered stainless steel filters to the nitric acid recovery plant which consists of a pre-absorption condenser and a series arrangement of six absorption towers stacked with stoneware rings. Water is fed to the last absorption tower at a rate calculated to produce a final acid strength of 40% w/w HNO_3 which is blended with purchased acid for use at the dissolution stage. The final traces of oxides of nitrogen are removed from the acid absorption plant exhaust by scrubbing in a tower irrigated by a 10% w/v solution of caustic soda.

The reliability and availability of the principal items of process plant in the UN to UO_3 sequence, most of which are constructed of AISI grade 321 stainless steel, has been such that all of these items are still in regular use after more than 20 years of operation. Over that time the production capacity of the denitration units has been stretched considerably in uprating exercises involving increase of bed height and heat transfer surface to allow for increase of electrical power rating from 300 Kw to 800 Kw. At the higher ratings the heat flux is such that precise and extensive monitoring and control of heat transfer surface temperature is required to avoid damage to the product or overheating of the reactor barrel.

The evaporation/denitration uprating exercise has now been completed to the stage at which the total Springfields capacity is 11,000 t U /year with an option to increase to 12,500 t U /year when justified by demand.

The product of the denitration stage, of which upwards of 100,000 t U has been made to date, is a free-flowing powder with properties typical of those listed in the following table:

Typical Properties of UO_3 Produced by Fluidised Bed Denitration

Crystalline form	γ or Type III oxide
Appearance	Aggregates of onion skin type particles
Mean particle diameter	130 microns
Tap density	4.5 g/cc
Angle of repose	40°
Specific surface area	0.1 to 0.2 m^2/g
Sodium content	10 ppm 'U' basis
NO_3^- content	0.5% w/w
Moisture content	0.05% w/w

2.3 The Rotary Kiln Uranium Tetrafluoride (UF_4) Production Process

For approximately 30 years fluidised bed technology was used at the reduction and hydrofluorination stages of uranium tetrafluoride manufacture, both natural and depleted, at Springfields. Following the successful introduction of rotary kiln technology in 1978 it was decided that the less economic and more hazardous fluidised bed plant should be phased out and replaced by a second kiln plant which is now under construction and scheduled for commissioning in 1987.

2.3.1 Hydration of Uranium Trioxide.

The volume expansion which occurs when a UO_3 particle is subsequently converted to UF_4 can create the situation where the rate of the hydrofluorination reaction is limited by the diffusion of gases to and from the $UO_2 \rightarrow UF_4$ reaction site unless the precursor UO_3 particle has sufficient innate open pore volume to accommodate the expansion. In the case of the high density, low surface area UO_3 particles prepared by fluid bed denitration, the required open pore volume is easily obtained by reaction of the UO_3 with water under conditions which lead to rapid and complete formation of the uranium trioxide dihydrate and a significant expansion in particle volume. Subsequent decomposition of the dihydrate then yields a particle with a lattice expanded sufficiently to accommodate the volume change in the conversion of UO_3 to UF_4.

UO_3 produced in the denitrator is transported pneumatically to one of a pair of feed hoppers from whence it is fed to the hydrator at a controlled rate co-currently with the stoichiometric quantity of water. The hydrator is a jacketed stainless steel trough agitated by an interrupted screw conveyor. Precise control of residence times and temperatures in specified sections of the hydrator ensures the formation of the required hydrate which discharges into the feed hopper for the next stage as a dry free-flowing powder with properties typical of those listed in the following table.

Typical Properties of Uranium Trioxide Dihydrate

Mean particle diameter	200 microns
Density	2.7 to 3.0 g/cc
Angle of repose	65°
Specific surface area (after decomposition at 450°C)	4 to 6 m^2/g

2.3.2 The Conversion of UO_3 to UF_4.

Early in the study of the dryway reduction and hydrofluorination reaction it became evident that temperatures high enough to cause sintering or solid surface modification could readily be attained at localised sites of the reacting solid. This effect occurs during the reduction reaction and in the initial stages of the hydrofluorination reaction. In either case the result can be incomplete conversion at the hydrofluorination stage due to what is frequently termed deactivation. Factors which have an important bearing on the deactivation process are the rates of heat release and heat removal from the reacting particle. The former is a function of factors which influence the rate of reaction, ie temperature, reactant concentrations, surface properties, etc, whereas the latter is dependant on heat transfer by conduction within the particle and by convection and radiation from the particle within the reacting mass. Interaction of these variables calls for very careful control of reaction conditions to ensure reproducible production of high grade UF_4, a level of control which has been achieved in the rotary kiln form of contactor.

2.3.3 Common Features of the Rotary Kilns.

Each rotary kiln system can be considered as comprising:

i. A powder feed and off-gas filtration hopper
ii. A rotating kiln barrel
iii. A powder discharge hopper

The powder feed hopper also contains the offgas filter clusters for removal of particulates from the exhaust before its discharge to the condenser and scrubber system. An automatic valve and fan sited in the exhaust gas line downstream of the scrubber controls the pressure in the kiln at $\sim$15 mbar g.

The kiln barrels are supported at each end on riding rings resting on roller bearings and can be driven at speeds in the range 1 to 8 rpm by one of a pair of electric motors, or, in an emergency, by a diesel powered motor.

Axial and radial movement of powder within the kiln is a function of rotational speed, kiln angle, volume throughput, the properties of the powder and the number, size and shape of the internal flights and dam rings. The influence of these and other variables such as reactant composition and temperature are optimised to ensure production of a product suitable in all respects for downstream processing. Control of the reaction temperature profile, which is of vital significance in this regard, is achieved by a combination of electrical heating, forced air cooling and comprehensive and precise monitoring of element, kiln wall and reactant temperatures.

Seal assemblies designed to prevent egress of the kiln contents are located at the powder feed and discharge ends where leak detection instrumentation is also sited. Continuous measurement of kiln alignment and seal condition is carried out to maximise seal life.

The contents of the powder discharge hoppers are periodically transported pneumatically on N_2 to the feed hoppers at the next stage of the process.

Kiln bed thickness by diametrical gamma scanning, and residence time distributions, by radioactive tracer injections, have been determined on both kilns for a variety of operating conditions. This type of information has been helpful in designing a dynamic simulation model which takes account of the major process variables and considers, in particular, reaction rates, powder transport mechanisms and all aspects of heat transfer and kiln temperature control.

2.3.4 Reduction of Uranium Trioxide.

Metered quantities of hydrogen and UO_3 hydrate are contacted counter-currently in a stainless steel rotary kiln and by precise control of the temperature and concentration of reactants complete conversion to UO_2 is achieved without loss of activity.

The hydrate feed rate is regulated by a screw feeder at the hydrate hopper outlet which maintains the hopper contents at a constant level to establish a positive seal between the kiln and the hydrator. The gas space in the hydrate hopper is continuously monitored to detect and respond to hydrogen levels about a preset value.

Exhaust gas from the reduction kiln, containing steam, excess hydrogen, nitrogen and traces of nitrogen oxides is discharged to atmosphere via a condenser, scrubber and flame arrestor.

The typical UO_2 product of the reduction kiln has an oxygen:uranium ratio of 2.02 and a specific surface area of 3 m^2/g.

2.3.5 Hydrofluorination of Uranium Dioxide.

Metered quantities of liquid anhydrous hydrofluoric acid are vaporised at ~20°C and fed into an inconel rotary kiln where it is contacted counter-currently with metered quantities of UO_2 to produce high grade UF_4 (>98% UF_4) at a high AHF usage efficiency (~95%). To prevent thermal damage to the basic particle leading to deactivation, incomplete conversion or in extreme cases, sintering of the bulk material, careful profiling of the reactant temperatures from the powder fed to the powder discharge ends of the kiln is essential.

The hydrofluorination kiln exhaust gas containing steam, nitrogen and excess HF is routed to a water cooled monel condenser and the condensate (10-15% w/w HF) collected in rubber lined mild steel tanks before on site blending for resale to the trade. The incondensibles are scrubbed with caustic soda solution before discharge to atmosphere.

The materials of construction for the main items of equipment at the rotary kiln hydrofluorination stage are mild steel, Inconel, Monel and rubber lined mild steel. Polyvinylidene fluoride pipework and valves are used for dilute hydrofluoric acid handling in the liquid phase. By comparison with the fluid bed route the elimination of the need for HF recycling and lower temperatures and pressures involved in the kiln route has virtually eliminated the corrosion of nickel based alloys which is a prominent feature of the older route to UF_4.

2.4 Conversion of Uranium Tetrafluoride to Uranium Hexafluoride

Uranium hexafluoride (UF_6), both natural and Magnox reactor depleted, has been produced at Springfields for more than 20 years by the reaction of UF_4 with F_2 in fluidised bed reactors. Two UF_6 production units are currently available: The first, commissioned in 1968, has a capacity of 3,000 t U per year and a second larger unit, commissioned in 1974 has a capacity of 6,500 t U per year. To date, more than 60,000 t U as UF_6 has been produced, most of which on behalf of overseas utilities. The provision of a third unit, for conversion of uranium arising from the reprocessing of irradiated oxide fuel is discussed in Part B of this paper.

2.4.1 Fluorine Production.

Descriptions of the Springfields facilities for fluorine production are given in a number of previous publications [Refs 1,2]. Fluorine is produced by the electrolysis of AHF in the fused salt KF2HF at 85-90°C in mild steel cells using amorphous carbon anodes and water cooled mild steel cathodes. The most recent increment of fluorine capacity was provided by the introduction of 12 KVa cells to augment the 5 KVa cells originally installed.

Because the economics of UF_6 production are largely determined by the costs of fluorine generation considerable development effort has been focussed on this area. Short term development work has been aimed at improving the reliability of cell components and has led to the introduction of fine grain structure porous carbon anodes with improved compatibility with molten fluoride systems. Longer term development work is concerned with optimisation of electrode properties and cell geometries to minimise inefficient current usage. The prime target is the reduction of anode over voltage which is uniquely high for commercial electrolytic systems.

2.4.2 UF_6 Production.

UF_4 is fed at a controlled rate into an inert fluidised bed of calcium fluoride which serves to dispense rapidly the highly exothermic reaction heat and so prevent the possibility of the sintering of feed UF_4 and the formation of undesirable intermediate reaction products. The bed is maintained at ∼450°C in a monel reactor fluidised with a mixture of nitrogen and fluorine and operating at a negative pressure. The fluorine reacts instantaneously with the UF_4 to form gaseous uranium hexafluoride, which is first filtered to remove entrained solids and then condensed. The incondensible gases containing nitrogen and unused fluorine are recycled, using a reciprocating compressor, to the base of the reactor where fresh fluorine is introduced at a rate equivalent to its usage. Control of reaction temperature within the desired range is achieved by a combination of electric muff heating or forced air cooling.

Hexafluoride is removed from the condenser by liquefaction and gravity run off into the appropriate transit cylinder from where a gassing back operation is performed to eliminate light gas contamination. A bank of four condensers is provided to operate as cooling or liquefying units in turn using a fluorocarbon liquid at -40°C when on primary or back up cooling duties and fluorocarbon vapour at 90°C for liquefaction of UF_6.

In recent years attention at the UF_6 production stage has been centred on issues concerning containment of HF or UF_6 releases. Modifications have been made at the UF_6 filling stations so that all filling and sampling operations can be carried out remotely and operators are located in a specially constructed control corridor physically isolated from the filling station. No other operations are permitted in the filling station area whilst cylinder filling is in progress.

In the event of a release of UF_6 within the confines of the filling station a hex release shutdown and alarm procedure would be activated either by an operator or automatically by a UF_6 leak detector. The automatic shutdown and alarm procedure shuts off the filling station ventilation system, closes the cylinder valve and the condenser liquid run off valve and sounds alarms at the Hex Plant Control Panel and the Works Emergency Control Centre which is quickly able to muster trained resources to deal with UF_6 leaks.

As a final measure, both the UF_6 Filling Station and HF Stock Room will be coupled to a spray tower which can be brought into use in an emergency.

2.5 Reduction of Uranium Tetrafluoride to Uranium Metal

The continuing requirement for uranium metal fuel for the UK Magnox reactor programme has meant that uranium metal has remained an important nuclear fuel intermediate at Springfields since the start of the site. Now that there is a revival of interest in uranium metal production as a consequence of the atomic vapour laser isotope separation programmes being pursued in the USA, France and elsewhere it is appropriate to include some comments on the development and current status of the uranium metal production stage at Springfields.

2.5.1 Development of the UF_4 Reduction Process.

In common with most other countries at the time, the UK first produced massive uranium metal billets by reduction of loose charges of mixtures of UF_4 and calcium chips or turnings

$$UF_4 + 2Ca \rightarrow 2CaF_2 + U + 134 \text{ Kcal.}$$

For economic reasons magnesium was then considered as a reducing agent despite the unfavourable heat of reaction

$$UF_4 + 2Mg \rightarrow MgF_2 + U + 82 \text{ Kcal.}$$

The loose charge method, suitable for the calcium reduction process, was unsuitable for magnesium reduction since the temperature immediately following reduction would be less than the slag melting point ($\sim$ 1450°C) at the operating scale proposed and slag metal separation would not be possible. It was therefore necessary to select a process and equipment which would allow for increasing the heat content of the charge before onset of reaction. A programme of development work in the early 1950s which addressed features such as the following:

i. charge density, which should be as high as possible to ensure maximum thermal conductivity, facilitating maximum preheating and minimum heat loss during the reaction

ii. charge geometry, which should be designed to avoid premature local ignition before adequate preheating of the whole charge

iii. excess magnesium requirements

iv. choice of reactor containment

led to the introduction of the first plant scale production process in 1954. This process forms the basis of the magnesium reduction plant in use today for production of both natural and tails depleted uranium billets. To date approximately 40,000 t U has been produced at Springfields.

2.5.2 Description of the UF_4 Reduction Process.

Pelleting of the UF_4/Mg Mixture

Pneumatically conveyed or drummed UF_4 and drummed magnesium raspings are charged to separate hoppers on the pelleting press. From these hoppers the reactants are fed directly to their respective weighing machines where approximately 3 kg UF_4 and 0.5 kg magnesium are automatically and precisely weighed out. In accordance with a predetermined programme, the contents of each weighing machine are dispensed into one of six rotating mixing buckets located around the periphery of a horizontal wheel which is keyed into a vertical shaft. The continuously rotating buckets are indexed 60° at a time until the completely mixed contents of each bucket are discharged into the die hopper of a 200 ton hydraulic press and the empty buckets return to the filling station to begin a new pellet mixing cycle.

From the die hopper the UF_4/magnesium mixture is fed to the hydraulic press which produces cylindrical pellets approximately 5" diameter x $3^1/_4$" high (125 mm x 85 mm) at a pressure of about 10 tons/cm^2 and at a rate of 4-5 pellets per minute. At the end of each pellet cycle the press die is sprayed with lubricant to ensure easy removal of the subsequent pellet.

Reduction of UF_4/Mg Pellets

Pellets containing pure magnesium swarf are blended with pellets containing Magnox (a magnesium alloy) swarf arisings from the Component Manufacturing Plant, in an appropriate ratio to give the desired reduction batch size, generally about 350 kg U.

The pellets are then loaded into the internal reactor assembly which consists essentially of a graphite lined stainless steel catchpot supporting a spigotted graphite liner. Pellets of UF_4/Mg are layered around the inside wall of the liner and the charge built up by the addition of liners and pellets until the complete charge has been assembled. The assembly is then sealed into a stainless steel reactor and pressure tested.

After pressure testing the reactor is charged to a preheated electric furnace and the lid is connected to the pressure relief and service lines. For approximately 75% of the pre-ignition heat soaking period the reactor is evacuated to remove moisture which would otherwise interfere with the effectiveness of the reduction. For the remainder of the heat soak period the reactor is padded with argon gas to a pressure of 0.7 to 1.0 bar above atmospheric [Refs 3,4]. After approximately 100 minutes heat soaking the charge fires with a noticeable pressure increase. The furnace is then switched off and the reactor assembly allowed to cool for one hour before disconnection and removal to the cooling bay. Twenty four hours later the reactor is broken down to yield a billet which proceeds to the uranium casting plant, a magnesium fluoride slag which is crushed and recycled for recovery of uranium values and reactor components such as liners and catch pots which are recycled within the reduction plant.

The combination of high quality UF_4 feed (<1% of both UO_2 and UO_2F_2) and pelleted reactants yields a high quality billet product with a metal recovery efficiency of 97% or greater.

While the main activities in the reduction plant are concerned with uranium billet production for the Magnox nuclear reactor programme recently introduced variations on the basic reduction process theme include:

i. uranium alloy production by co-reduction with the appropriate alloying compound

ii. adjustment to the change in feed material from fluidised bed UF_4 to rotary kiln UF_4.

2.6 Alternative Routes to UF_4

i. Although all the major Yellow Cake converters are still using traditional dry route conversion technology at the front end of the fuel cycle the expensive chemicals (HNO_3.AHF) and the high temperature energy intensive steps involved are sufficient incentive to revive interest in more direct wet routes to UF_4 incorporating electrolytic reduction.

Some recent development work at Springfields has concentrated attention on the electrolytic reduction of uranium (vi) to uranium (iv) in both sulphate and mixed fluoride/sulphate systems. Highly efficient reduction can be achieved in both systems although the flexibility of the sulphate system is limited by the well established low solubilities of uranium (iv) sulphate. The definition of the conditions required to achieve high solubility of uranium (iv) in the fluoride sulphate system offers prospects for efficient and economic wet route UF_4 processes. This development has potential for applications not only in conventional Yellow Cake conversion but also for the conversion of uranium arising from the reprocessing of irradiated oxide fuels.

ii. A renewal of interest in processes for reduction of tails depleted UF_6 to UF_4 to satisfy the increasing demand for depleted uranium for laser enrichment and for non-nuclear uses, has prompted a revival of development work on the fluidised bed route from UF_6 to UF_4. The early results from this work look very promising.

3. RADIOACTIVE DISCHARGES AND ENVIRONMENTAL MONITORING

3.1 Liquid Radioactive Effluent

Virtually all of the radioactivity in the liquid effluent discharged from the Springfields site stems from purification stage raffinate which is neutralised with lime slurry before discharge into the tidal estuary of the River Ribble some two miles from the site [Ref 5]. Control of this discharge is subject to the provisions of the Radioactive Substances Act (1960) and is in accordance with a Certificate of Authorisation granted jointly by the Department of Environment and the Ministry of Agriculture, Fisheries and Food. The Authorisation imposes limitations and conditions relating to the methods of disposal and quantities permitted to be discharged, the samples to be taken and analysed, and the records to be kept. In order to demonstrate compliance with the Authorisation the combined site effluent is continuously sampled and analysed for total alpha and total beta.

3.1.1 Liquid Radioactive Effluent Discharges.

In the most recent 12 months period reported [Ref 5] the alpha discharge was 0.8 TBq (21.6 Ci) and the beta discharge was 152 TBq (4,100 Ci). Both the alpha and beta activity discharges are from the non-uranium members of the decay chain and represented 6% and 34% of the respective authorised limits.

3.1.2 Environmental Impact.

In outline, BNFL's policy on radioactive effluent management is to operate well within statutory requirements and to keep any radiation exposure as low as reasonably achievable (ALARA). An important consequence of this policy is that discharges are limited so that the committed dose equivalent to a representative member of the critical group should be no greater than 0.5 mSv, related to each year of operation. In the Springfields case the critical group are people living in house boats moored in the Ribble estuary. For the most recent 12 month period for which a report is available analysis of silt samples showed that the annual dose to the critical group attributable to Springfields discharges was 0.003 mSv, predominantly from ^{234}Pa.

3.1.3 Raffinate Treatment Proposals.

The interest shown in recent years by potential licensees of the BNFL conversion process has prompted development of a raffinate treatment process for use in situations where the prevailing regulations or the plant location would call for removal of activity before discharge of raffinate.

Evaluation of the candidate processes, initially from a theoretical stand point and then by a programme of laboratory scale experiments led to the conclusion that a viable process for purification plant raffinate decontamination would comprise:

i. selective solvent extraction of thorium isotopes and immobilisation of the radioactive extract as an active solid residue for eventual disposal.

and ii. treatment of the radioactively decontaminated raffinate to immobilise the heavy metals as a non-radioactive solid residue for disposal at a municipal site.

For a notional 10,000 t U per year UF_6 conversion plant using a UOC feed model which reflects the whole range of impurities likely to be encountered in the future it can be predicted that a raffinate treatment plant on the lines of that outlined, would generate about 55 t per year of a radioactive sludge.

A pilot plant for progressing the next stage of the raffinate treatment development programme will be brought into operation in 1987.

3.2 Airborne Radioactive Effluent

Elimination of particulate uranium from the gaseous discharge of UOC conversion plants is effected by a combination of primary filters or cyclones backed up by absolute filters. All such discharges are via stacks of the appropriate height which are sampled on a continuous or regular programmed basis and which are regulated in accordance with a Certificate of Authorisation. The alpha activity discharges consists almost entirely of uranium and are accompanied by an effectively equal beta activity from uranium daughters.

3.2.1 Airborne Discharges.

The airborne discharge from the whole of the Springfields site for the most recently reported 12 month period was 0.001 TBq (0.03 Ci).

3.3 Solid Radioactive Effluent

Solid radioactive effluent from Springfields consists of inactive or lightly contaminated and mainly incombustible wastes such as incinerator ash, building rubble, glassware scrap metal and ore processing residues. This effluent is disposed of in accordance with a Certificate of Authorisation granted jointly by the Department of Environment and the Ministry of Agriculture Fisheries and Food.

In the most recently reported 12 month period the discharge amounted to 0.04 TBq in 11,650 t of solid effluent.

SUMMARY

Springfields Works, which was the first factory to operate in the UK atomic energy programme will, in a few months time, be celebrating the 40th anniversary of its start-up.

Since that time in addition to meeting approximately 15% of current world demand for UF_6 conversion;

i. Springfields has produced 3½ million Magnox fuel elements and $1^3/_4$ million AGR fuel pins; an energy equivalent roughly equal to 600 million tons of coal

ii. Springfields IDR technology either directly or under licence has produced a significant proportion of the ceramic grade uranium dioxide currently used in nuclear fuel fabrication throughout the world.

BNFL believes that the experience gained in the past coupled with the results of the ongoing in house research and development provides a good technology base for dealing with the problems and opportunities which have to be faced in the future.

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PART II

REFINING OF IRRADIATED URANIUM MATERIALS

CONVERSION OF URANIUM ORE CONCENTRATES AND REPROCESSED URANIUM TO NUCLEAR FUEL INTERMEDIATES AT BNFL SPRINGFIELDS

Part B: Reprocessed uranium

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Abstract

Some 25,000 t U as UO_3 have been recovered from irradiated uranium metal fuel (Magnox) since reprocessing began at the Sellafield Works of BNFL more than 30 years ago. More than 15,000 t U equivalent of this reactor depleted uranium have been converted to uranium hexafluoride at Springfields Works.

This paper summarises past experience of converting reprocessed uranium to UF_6 and the changes which will be encountered in the future.

1. INTRODUCTION

Some 25,000 t U as UO_3 have been recovered from irradiated uranium metal fuel (Magnox) since reprocessing began at the Sellafield Works of BNFL more than 30 years ago. More than 15,000 t U equivalent of this reactor depleted uranium, at ^{235}U levels of less than 0.711% have been converted to uranium hexafluoride at Springfields Works and subsequently enriched at the BNFL diffusion plants or Urenco Centrifuge plant at Capenhurst. This source of enriched uranium accounts for 75% of the AGR fuel made to date and its reactor performance has been equal to that of fuel derived from non-irradiated uranium.

In the early 1990s uranium originating from the reprocessing of irradiated oxide fuel (AGR and LWR) will emerge from the THORP reprocessing plant at Sellafield.

In order to return this uranium to the nuclear fuel cycle plants will be provided at Springfields Works which will:

a. convert the uranium to UF_6 suitable for feeding to diffusion or centrifuge plants

and b. convert the product of the enrichment plants into finished AGR or PWR fuel assemblies.

This paper summarises past experience of converting reprocessed uranium to UF_6 and the changes which will be encountered in the future.

2. CONVERSION OF URANIUM RECOVERED FROM THE REPROCESSING OF IRRADIATED MAGNOX FUEL

2.1 Process Description and Operating Experience

The process plant used for converting, to UF_6, pure uranyl nitrate generated by the reprocessing of irradiated Magnox fuel has traditionally been similar to that used for converting pure uranyl nitrate derived from uranium ore concentrates. This process plant has been fully described in previous papers [Refs 1,2] and consisted essentially of the following principal stages:

i. continuous evaporation of pure uranyl nitrate in multi-effect climbing film evaporators

ii. continuous denitration of molten uranyl nitrate hexahydrate in a single stage fluidised bed to produce uranium trioxide

iii. batchwise reduction and hydrofluorination in single stage fluidised beds to produce uranium tetrafluoride

iv. continuous fluorination of uranium tetrafluoride in a single stage fluidised bed to produce uranium hexafluoride.

In the early years of conversion of reprocessed Magnox depleted uranium (MDU) the feed to the Springfields conversion sequence consisted of MDU pure uranyl nitrate at approximately 250 g U/l and with ^{235}U concentrations of 0.4 to 0.6%. This liquor was transported from Sellafield to Springfields in stainless steel road tankers and then fed to one of the UN -> UF_4 processing lines in the Fluidised Bed Plant. However, shortly after the start up of the 2nd Uranium Plant at Springfields, evaporation and denitration units, identical to those developed at Springfields were installed at Sellafield. Since 1964 all MDU UO_3 has been produced at the reprocessing site and, after appropriate under cover storage in 50 gallon mild steel drums, is transported by road to Springfields for conversion to UF_6.

Following the successful introduction of the first Rotary Kiln UF_4 Plant at Springfields a second such plant is now under construction to replace the fluidised bed reduction and hydrofluorination stages which have recently been phased out for reasons of economy and safety. Future MDU processing campaigns will therefore incorporate rotary kiln technology instead of fluidised bed technology in the long established UO_3 to UF_6 conversion sequence.

Whilst the majority of the MDU UO_3 produced at Sellafield has been enriched at the Capenhurst diffusion plants for subsequent processing into AGR fuel, smaller quantities at lower enrichments were diverted to stock prior to the recent closure of the diffusion plants. This stock is currently being fed to the URENCO centrifuge plants as will arisings of UF_6 from future MDU conversion campaigns.

Although most of the BNFL experience of conversion of MDU relates to eventual use of the uranium in AGR fuel a small quantity of pseudo-natural uranium has been produced from blends of reprocessed MDU and uranium derived from the reprocessing of irradiated oxide fuel. Blending of the two components as uranyl nitrate was carried out at Springfields and the pseudo-natural liquor was then converted to uranium billets via the conventional UN to metal sequence described previously. No unforeseen problems were encountered in Magnox fuel manufacture nor in the subsequent second irradiation cycle of the pseudo-natural uranium metal.

2.2 Health Physics and Safety Considerations

2.2.1 Origins of the Radiological Hazards.

In the Springfields process sequence from UO_3 to UF_6 the main radiological hazard arises from the possibility of uranium dust inhalation, a hazard which can be exacerbated by the presence of trace quantities of transuranic elements when MDU is being converted. These elements, although present in an insignificant amount by mass, could by virtue of their high specific activity, constitute a significant proportion of the Derived Air Concentration (DAC) of the activity in air.

To ensure that the proportion of the DAC taken up by the transuranic elements is kept within levels which do not constitute a major problem, it is the practice to define a limiting transuranic specification which is related to the uranium.

The presence of residual fission products in the MDU can also lead to unacceptable external radiation levels unless controlled. Experience has shown that radiation levels of up to 15 millirem per hour at the surface of drums or reaction vessels can be tolerated without significant exposure of personnel. This level has been prescribed as the limiting radiation level acceptable in the Springfields conversion sequence.

The main radionuclides of interest to the plants in the UO_3 to UF_6 sequence when converting MDU are:

Transuranic elements	Plutonium. Neptunium
Residual fission products	^{106}Ruthenium

The concentration of ^{228}Th, the decay product of ^{232}U, in MDU derived from the reprocessing of the relatively low burn-up Magnox fuel is below the level at which Health Physics problems became significant.

2.2.2 Health Physics and Safety Experience.

UO_3 to UF_4 Stages

No significant air contamination or external exposure dose rate problems were encountered at the fluidised bed UO_3 to UF_4 stages where all powder transport and reacting systems were completely enclosed. For the same reasons no difficulties are anticipated at the rotary kiln UO_3 to UF_4 stages during future MDU conversion campaigns.

UF_4 to UF_6 Stage

Virtually all the trace plutonium and ruthenium present in the original feed UO_3 is retained on the calcium fluoride particulate solids which are from time to time removed from the fluidised bed system in the form of reactor residues or reactor filter residues. An important consequence of this feature is that the UF_4 to UF_6 reaction acts as a very effective decontamination stage for these nuclides.

During MDU conversion campaigns solid residues are removed from the fluidised bed reactor system in accordance with well developed techniques, operated under Health and Safety Department supervision, involving temporary containment, pressure suit respiratory and contamination protection, and control of radiation exposure. The residues are sealed in small mild steel drums and, after appropriate storage to allow for the equilibriation of the short lived ^{238}U daughters which are also removed at the UF_4 to UF_6 stage, the residues are transported to a Company disposal site.

General Comments

The concentrations of transuranic alpha emitters in uranium recovered from the reprocessing operation are sufficiently low as to have only limited radiological impact on the conversion stages at Springfields.

Much the same comment applies to the principal fission product contaminants, ^{99}Tc a long half-life soft beta emitter and ^{106}Ru a short half-life gamma emitter (via its daughters).

In the case of MDU feed material interim storage of the UO_3 product of the reprocessing plant and appropriate campaign scheduling effectively eliminated the radiological impact of ^{106}Ru on the UO_3 to UF_6 conversion stages.

2.3 Product Quality

More than 15,000 t of MDU has been processed through the conversion stages at Springfields. Of chief concern was the residual fission product concentration and the transuranic alpha activity.

A number of campaigns have been specially carried out at Springfields converting UO_3 with very high levels of transuranic alpha activity, essentially due to neptunium. It was found that most of the neptunium content could be removed and prevented from entering an enrichment plant. The primary mode of neptunium removal was again shown to be adsorption on calcium fluoride in the fluidised bed reactor system. Residual neptunium was removed in special traps and further decontamination took place during the vaporisation from the UF_6 transit cylinders when feeding the enrichment plant. These experiments have demonstrated the specification requirements for uranium products of reprocessing plants for conversion to UF_6 for supply to enrichment plants.

3. CONVERSION OF URANIUM RECOVERED FROM THE REPROCESSING OF IRRADIATED OXIDE FUEL (AGR.LWR)

3.1 Health Physics and Safety Considerations

In addition to the naturally occurring isotopes of uranium, ^{234}U, ^{235}U and ^{238}U, other uranium isotopes are produced in nuclear fuel during and after irradiation. These are principally ^{232}U, ^{233}U and ^{236}U of which ^{232}U has the greatest potential for impact on the Health Physics aspects of the conversion.

As previously mentioned the resultant low levels of ^{232}U in the relatively low burn-up Magnox fuel meant that the Health Physics implications of MDU conversion were associated principally with residual transuranic alpha emitters such as plutonium and neptunium and residual fission products such as ruthenium.

However BNFL are currently planning to construct at Springfields a new dedicated plant for the conversion of the oxide reprocessed uranium (ORP) which will be produced as UO_3 in the Thermal Oxide Reprocessing Plant (THORP) at Sellafield. It is intended that the Springfields conversion plant will be available coincident with the commissioning of THORP in the early 1990s. It is envisaged that shortly afterwards a comprehensive fuel manufacturing facility will be provided at Springfields to produce AGR and PWR fuel from ORP UF_6 enriched in URENCO centrifuge plants.

3.1.1 Characteristics of ORP Uranium.

Some of the implications for the proposed conversion plant for handling ORP uranium from the reprocessing of higher burn up AGR and LWR oxide fuel are discussed below by comparing the principal differences between ORP uranium and non-irradiated or natural uranium (NIU).

^{232} Uranium

This isotope which does not exist in natural uranium can be formed by a number of routes (Fig 1) and it can be seen that all the principal uranium isotopes are potential sources of ^{232}U following irradiation. The ^{232}U concentration in ORP uranium depends on several factors including:

i. The elapsed time between the hex vaporisation stage of fuel manufacture and the start of irradiation

ii. The fuel burn up

iii. The cooling time before reprocessing

iv. The concentrations of ^{232}U, ^{234}U, ^{235}U and ^{236}U before irradiation.

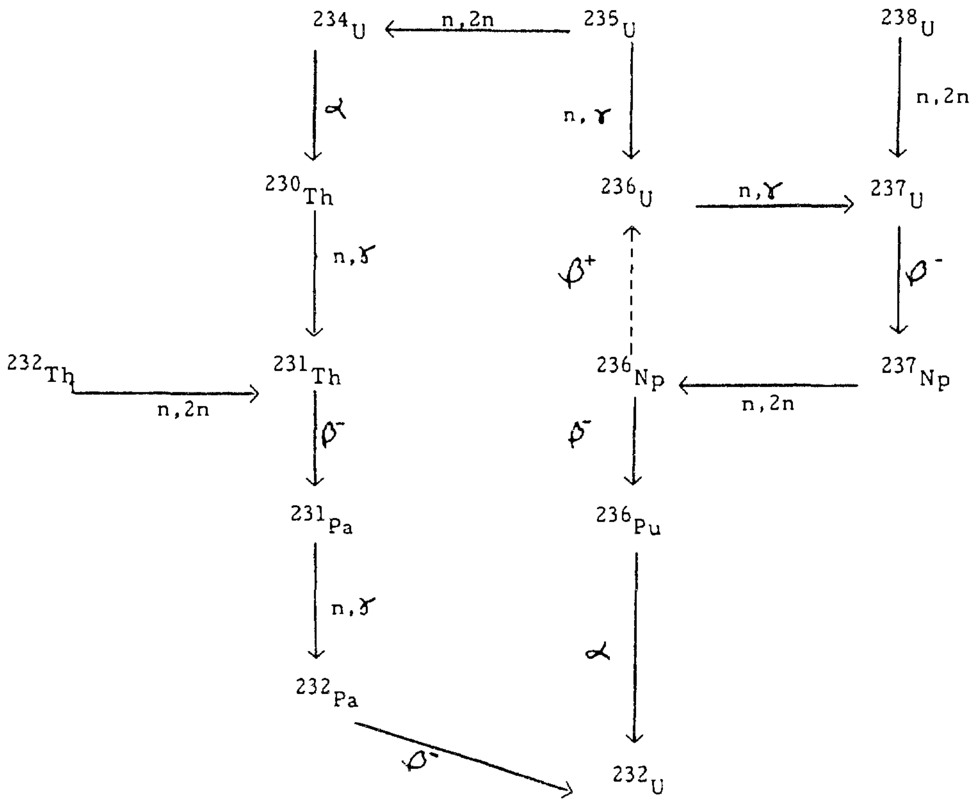

FIGURE 1 Production Routes for ^{232}U

Typical concentrations of ^{232}U in ORP uranium are a few parts per billion on a total uranium basis. ^{232}U has a 72 year half-life and is the parent of a complex decay chain (Fig 2). The immediate daughter ^{228}Th has a half-life of 1.9 years which is much greater than the half lives of subsequent daughters, these being of the order of minutes or days. ^{228}Th therefore controls the concentrations of all daughters as a function of time from the point when ^{228}Th is separated from its parent by chemical or vaporisation processes. The build up of ^{228}Th with time from separation from the parent ^{232}U is illustrated by the table:

Time since separation	% of Equilibrium
1 month	3
1 year	33
4 years	83
10 years	100

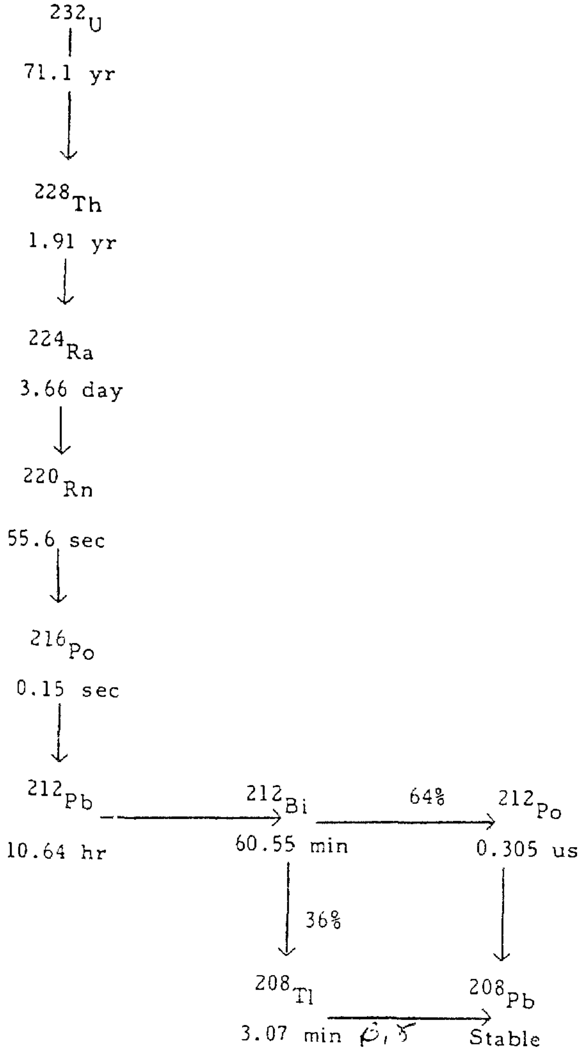

FIGURE 2 Decay of ^{232}U

At equilibrium the activity of ^{228}Th is equal to the activity of ^{232}U as are the activities of each of the subsequent daughters although as ^{220}Rn is a noble gas its concentration and that of subsequent daughters is affected by the containment of the material and its chemical form. The annual limit of intake of ^{232}U is therefore more restrictive than for ^{234}U, ^{235}U and ^{238}U due to the presence of the short lived daughters which are bone seekers with long body retention times.

One of the ^{232}U daughters, ^{208}Tl emits very penetrating 2.6 MeV gamma radiation which represents an additional, independent radiological hazard. For example, the ingrowth of this daughter reaches a maximum after a decade of storage, at which point the gamma dose rate from the ORP uranium can be two orders of magnitude greater than that of non-irradiated uranium. Since separation from the gamma emitting daughters can occur at a number of steps in the sequence UO_3 to finished fuel the increase in gamma dose rate is influenced by the time interval between these steps.

^{234}Uranium

This isotope constitutes 0.005% of non-irradiated uranium and is concentrated during each enrichment process. Typical concentrations in ORP are 0.02%, increasing to 0.13% after further enrichment. The main cause for concern is the 2-3 fold rise in specific alpha activity which is of particular significance because of the potential consequences with respect to airborne activity.

^{235}Uranium

The mean discharge ^{235}U concentration from oxide reactors is expected to be about 0.9% and the range about this mean is expected to be 0.6 - 1.2.

^{236}Uranium

This isotope does not occur naturally and is produced from ^{235}U by neutron capture. It functions mainly as a neutron poison, requiring extra enrichment and thus imposing an economic penalty on the ORP fuel cycle.

Transuranic Alpha Emitters

These are produced during irradiation and arise from neutron capture and decaychains. They comprise essentially the residual traces of neptunium and plutonium after the reprocessing operation and both isotopes are present in the ORP uranium at sufficiently low concentrations to have limited impact.

Fission Products

These are principally the traces of ruthenium and technetium remaining in the ORP uranium after reprocessing. ^{106}Ru is a short half life (1 Year) isotope which increases the gamma activity of the uranium (via its daughter). ^{99}Tc is a long half life soft beta emitter.

3.1.2 Health Physics Aspects of ORP Conversion Plant Design.

Detailed study of the Health Physics implications of introducing ORP uranium into the Springfields conversion process led to the conclusion that the consequences of the increased ^{232}U concentrations would be:

i. a more restrictive airborne contamination limit due to the alpha emitting daughters

and ii. an increased gamma dose rate due to the 2.6 MeV gamma emitting ^{208}Tl daughter.

To ensure that the external plus internal radiation dose uptake satisfied statutory requirements and was consistent with BNFL policy guidelines it would be necessary to make extensive use of shielding and remote handling equipment in the conversion process. Backfitting of existing equipment was ruled out and following a full scale plant trial, it was decided to provide a dedicated plant for the conversion of ORP UO_3 to UF_6.

The choice of the fluidised bed route for the production of ORP UF_6 means that the majority of the non-uranic impurities will be removed by adsorption on the calcium fluoride bed material. All of the residual plutonium and uranium decay products and most of the ruthenium and neptunium will be immobilised in the fluidised bed residues which will require special handling arrangements for their removal, storage and eventual disposal. Similar arrangements will be provided to deal with the residues generated in the transit cylinder washing facility and those arising from neptunium and plutonium traps.

3.2 ORP Uranium Conversion. BNFL's Intentions

3.2.1 Project Assessment.

BNFL had two principal objects in mind when evaluating the recycling of ORP uranium to finished AGR or PWR assemblies:

i. to ensure that the radiation dose uptake was consistent with BNFL policy guidelines and within statutory limits

and ii. to ensure that the economic case for recycle of ORP uranium was sufficiently attractive to persuade utilities to adopt recycling as soon as possible.

Consideration of the Health Physics implications of recycling indicated that, by comparison with non-irradiated uranium extra costs would be involved because of the additional plant complexity associated with the extra shielding, containment and handling constraints. Nevertheless, despite substantial processing cost premiums compared with non-irradiated uranium, there is a strong economic incentive to recycle.

Early in the project evaluation exercise consideration was given to the possibility of blending ORP uranium with non-irradiated uranium at some stage in the overall sequence, pure uranyl nitrate to finished fuel. However as this would require all the downstream plant to accommodate ORP derived feedstock the concept of blending was rejected in favour of the segregation concept. Segregation permits ORP uranium to be confined to the minimum volume of processing equipment, and is particularly well suited to the URENCO centrifuge enrichment technology which can accommodate modules designed specifically to handle reprocessed uranium.

It is now BNFL's intention to construct a new segregated conversion facility at Springfields which will come on stream coincident with the commissioning of THORP at Sellafield in the early 1990s. It is envisaged that shortly afterwards a fuel manufacturing facility designed to process ORP uranium from enriched UF_6 through to finished AGR and PWR fuel will be commissioned.

3.2.2 ORP Uranium Conversion Technology.

The reference design of the conversion facility at Springfields has the following characteristics:

i. The 650 t U per year unit will be broadly compatible with the average output of THORP and will be brought on line at the same time.

ii. The conversion unit will accept feed UO_3 containing a maximum ^{235}U content of 1.3%. This specification will embrace more than 95% of THORP product and was arrived at by balancing the cost of separative work lost by blending against the increased unit costs of the geometrically more restricted plants able to accommodate higher ^{235}U assays.

iii. The plant will be designed to limit the average annual effective dose equivalent (ie the summation of external and internal radiation doses) received by plant personnel to not more than 0.5 rem (5 mSv) per year.

Uranyl Nitrate Evaporation and Denitration

The evaporation and denitration of the pure uranyl nitrate produced in the uranium purification section of THORP will be carried out at Sellafield in plant incorporated into the THORP complex.

After any necessary ^{235}U assay adjustment the uranyl nitrate liquor will be fed into a geometrically safe single stage continuous evaporator. The concentrated uranyl nitrate evaporator product, at ~ 1000g U/l, will then be continuously denitrated at 300°C in a geometrically safe electrically heated fluidised bed reactor. The UO_3 product of the denitration stage, a free flowing powder, will be precooled during transport from the denitrator to storage hoppers and will then be drummed off for transport to Springfields.

Conversion of ORP UO_3 to UF_6

The ORP conversion plant will differ from the UF_6 plant described briefly in the previous paper in that:

i. all process equipment such as hoppers, reactors, condensers, cold traps, scrubbers etc will be of geometrically safe design

ii. there will be extensive use of shielding, containment and remote handling equipment appropriate to the increased radiological hazards previously discussed. A particular example of this increased hazard when processing high burn up ORP uranium will be the problem of handling calcium fluoride reactor residues in which will be concentrated the residual transuranic alpha emitters and fission products together with the decay daughters of the uranium isotopes notably ^{232}U

iii. An appropriately shielded dedicated facility will be provided for the periodic washing of UF_6 cylinders in the ORP transport cycle. The washing facility will also contain equipment for immobilising the gamma emitting solid residues, mainly ^{232}U daughters, removed from the cylinders during each washing cycle.

3.3 Uranium Recycle and Effluent Disposal

3.3.1 Enriched Uranium Residues Recovery Plant, EURRP.

Enriched uranium containing residues of many types arise from the diverse range of processing operations carried out at Springfields. These residues have hitherto been recovered in a mass controlled, batch operated plant. A new plant has recently been installed and commissioned based on safe by shape equipment. The new plant which will also be available for treatment of enriched ORP recycles is to be used to process residues in the 1 to 5% enrichment range and has improved in line storage facilities to meet current standards of uranium accounting. Where possible the recovery processes are continuous. Another key feature of the new recovery plant is that it has been designed to give very low air contamination levels in all operator areas, and this has been achieved by putting virtually all the equipment into cubicles.

The processes used are essentially similar to those used in the existing plant, standard wet processes being used for dirty residues and dry processes for clean residues. The principal end product is pure uranium dioxide.

The essential steps in the recovery process are pre-treatment of impure residues followed by dissolution in nitric acid. The impure uranyl nitrate is purified by solvent extraction using pulsed sieve plate columns, one for extraction and strip, and a second for back-wash.

Ammonium diuranate (ADU) is precipitated from the pure UN solution and filtered off. The ADU is then calcined to produce U_30_8 which can then be reduced to UO_2. Uncontaminated clean residues can also be integrated into the overall recovery process by means of oxidation or oxidation/reduction processes involving belt furnaces.

This residue recovery plant is a major addition to the facilities at Springfields. The plant overall has dimensions of 60 metres by 53 metres. It is capable of dealing with 40-70 tU of enriched residues per year depending on the purity and enrichment of the feed streams.

3.3.2 Enriched ORP Residues Recycle.

Solid residues from the ORP fuel fabrication processes, such as reject pellets, grinding sludges, etc will be scheduled for recovery in EURRP at the optimum time with respect to ingrowth of ^{232}U daughters and the subsequent return of the recovered ORP uranium to an ORP fuel manufacturing campaign.

3.3.3 ORP Liquid Effluent.

It is intended that the EURRP raffinate stream arising from treatment of ORP residues will be decontaminated on a campaign basis in a dedicated facility on the lines of those proposed for the UOC purification plant raffinate described in the previous paper. After such treatment the liquid effluent will be suitable for discharge to the local estuary.

3.3.4 ORP Solid Effluent.

The ORP solid effluent, at the forecast scale of operations will amount to less than 50 t bulk per year of Intermediate Level Waste. These arisings will be disposed of at one of the controlled NIREX sites.

4. SUMMARY

BNFL has considerable experience of recycling reprocessed uranium into new fuel. Shortly after the THORP reprocessing plant comes into operation in the early 1990s BNFL intends to be able to offer a comprehensive recycle service comprising conversion, enrichment and fuel fabrication or ORP uranium.

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NITROX PROCESS: A PROCESS DEVELOPED BY COMURHEX OF CONTINUOUS DENITRATION

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Abstract

COMURHEX(subsidiary of PECHINEY) has developped since 1982 a process to obtain sinterable oxydes by direct denitration of uranyl nitrate.

This process can be used to produce mixed sinterable powder of UO2/PuO2.

Some experiments were made and proved the feasibility of the Nitrox process.

The paper resumes the advantages of the Nitrox process and gives some experimental details.

Recycling to the energy line of the plutonium originating from spent fuels reprocessing requires the development of processes for the preparation of composite UO_2/PuO_2 powders of characteristics appropriate to the manufacture of sintered pellets.

Additionally, and as always where plutonium is being handled, the various powder preparation operations have to be designed to curtail as far as possible the formation of gaseous effluents or contaminated liquids, the decontamination of which is seen as expensive.

Again, plutonium is one of the "sensitive" materials, the use, possession and shipment of which are subject to extremely severe regulations intended to ensure complete control over utilisation.

Based on these considerations, the Comurhex company (a member of the Pechiney Group) has developed the Nitrox process, a new method of manufacture of composite UO2/PuO2 powders by direct thermal denitration of a uranyl and plutonium nitrates solution.

I - MIXED U / Pu FUELS IN THE "LIGHT WATER" REACTOR FUEL CYCLE

Reprocessing the spent fuels from light water reactors will make it possible to recycle weakly enriched uranium (ca. 0.9% U 235) and plutonium.

The plutonium produced, if recycled in its entirety, could be used to produce some 10 to 15% of fuel requirements.

It may be estimated that in 1995 and beyond some 2 000 metric tons per annum (tpa) of "light water" spent fuels could be reprocessed worldwide. Under these conditions, reprocessing would yield the plutonium potentially sufficient for the manufacture of 200 to 300 tpa of composite fuels.

The recycling stakes are therefore substantial and have attracted the interest of the firms in the fuel cycle industry.

II - MANUFACTURE OF COMPOSITE FUEL

On leaving the reprocessing stage, the recyclable uranium and plutonium are in the form of nitric acid solutions.

Two principal types of process have therefore been developed with a view to the production from nitrate solutions of the mixed UO2/PuO2 powder suitable for the manufacture of the sintered pellets.

The first route corresponds to the separate preparation of the two UO2 and PuO2 powders, of characteristics such that on mixing they will yield the mixed UO2/PuO2 powder ready for pelleting and sintering.

Mixing is very frequently a two-stage process ; an initial "master" powder is prepared at high PuO2 concentration and the UO2/PuO2 mix then adjusted by addition of UO2 powder.

In the second route, the mixed powder is prepared directly by coprecipitation of the uranium and plutonium salts from the mixed nitrates solution.

These two process series exhibit certain shortcomings :

The production of mixed powders by mixing PuO2 and UO2 demands very precise adjustment of the particle sizes of the two powdered oxides. This type of process involves grinding operations which generate polluting aerosols. Account also has to be taken, when these aerosols deposit on walls, of what happens to the americium 241, which exhibits very substantial alpha-activity.

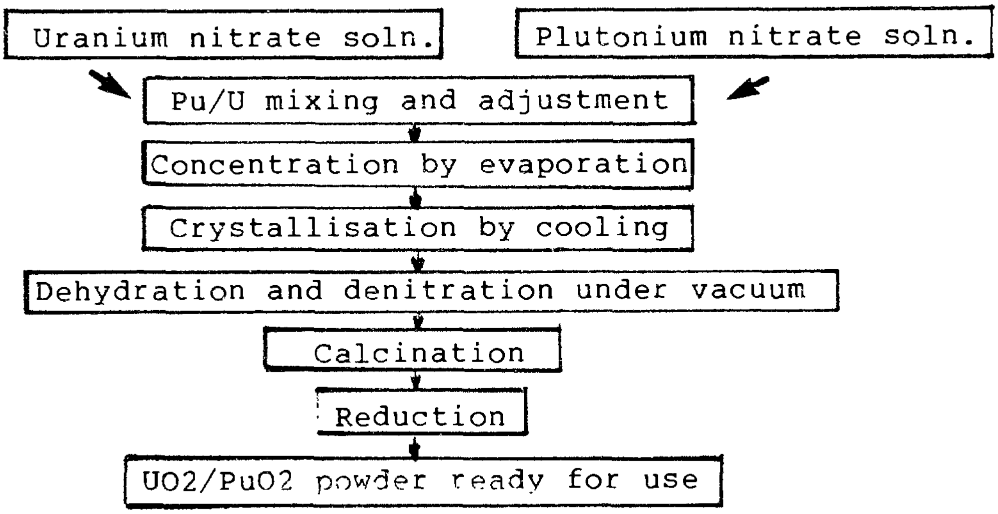
Processes employing coprecipitation more often than not entail aqueous effluents which require to be decontaminated.

After production of the powder by one or other process, the operations of pelleting, sintering and loading of rods can be carried out in an environment technologically suited to the handling of plutonium.

III - THE NITROX PROCESS

This continuous process, developed between 1982 and 1985 by the Comurhex company, basically consists of preparing the mixed UO2/PuO2 powder by direct thermal denitration of a suitably adjusted solution of uranyl and plutonium nitrates.

The main process stages are represented below :



After mixing the nitrate solutions in the chosen ratio of Pu/(U + Pu), they are taken down to a concentration of some 1 200 grams U + Pu metal/litre.

The concentrated solution is then crystallised by cooling.

The nitrate powder so obtained is dehydrated and then denitrated at reduced pressure.

The mixture of oxides obtained can then be calcined and reduced.

The characteristics of the UO2/PuO2 powder obtained depend on temperature and pressure values in the course of the dehydration, denitration and calcination operations and on the duration of the heating steps.

Main features of the process are described here after :

The main step in the process is that of denitration and dehydration. This operation is conducted using a combination of pressure and temperature calculated to obviate melting of the nitrates at the denitration stage (cf. Fig. 1).

Operating conditions must at all times be below the equilibrium curve.

An example is given of a pilot operation under which dehydration/denitration operations were carried out in three stages. Main experimental data are tabulated below :

A - Dehydration and denitration

Temp. steps (°C)	Duration (hrs)	UO3	UO3 + 6% Pu (PuO2)
20	1.5		
260	1.5		
400	1.5		
Specific surface of oxides		32 ml/g	40 ml/g
O/M ratio		3.079	2.955

B - Calcination and reduction

	UO2	UO2 - PuO2
Calcination	1 hr - 600°C	1 hr - 525°C
Reduction	1 hr - 600°C	2 hr - 700°C
O/M	2.102	2.073
BET surface	6.2 ml/g	6.5 ml/g
Density	1.7 g/cc	2.4 g/cc

C - Sintering

	UO2	UO2 - PuO2
Pelletising pressure	3.5	3.5
Crude density	49%	52%
Sintered density	96%	94%

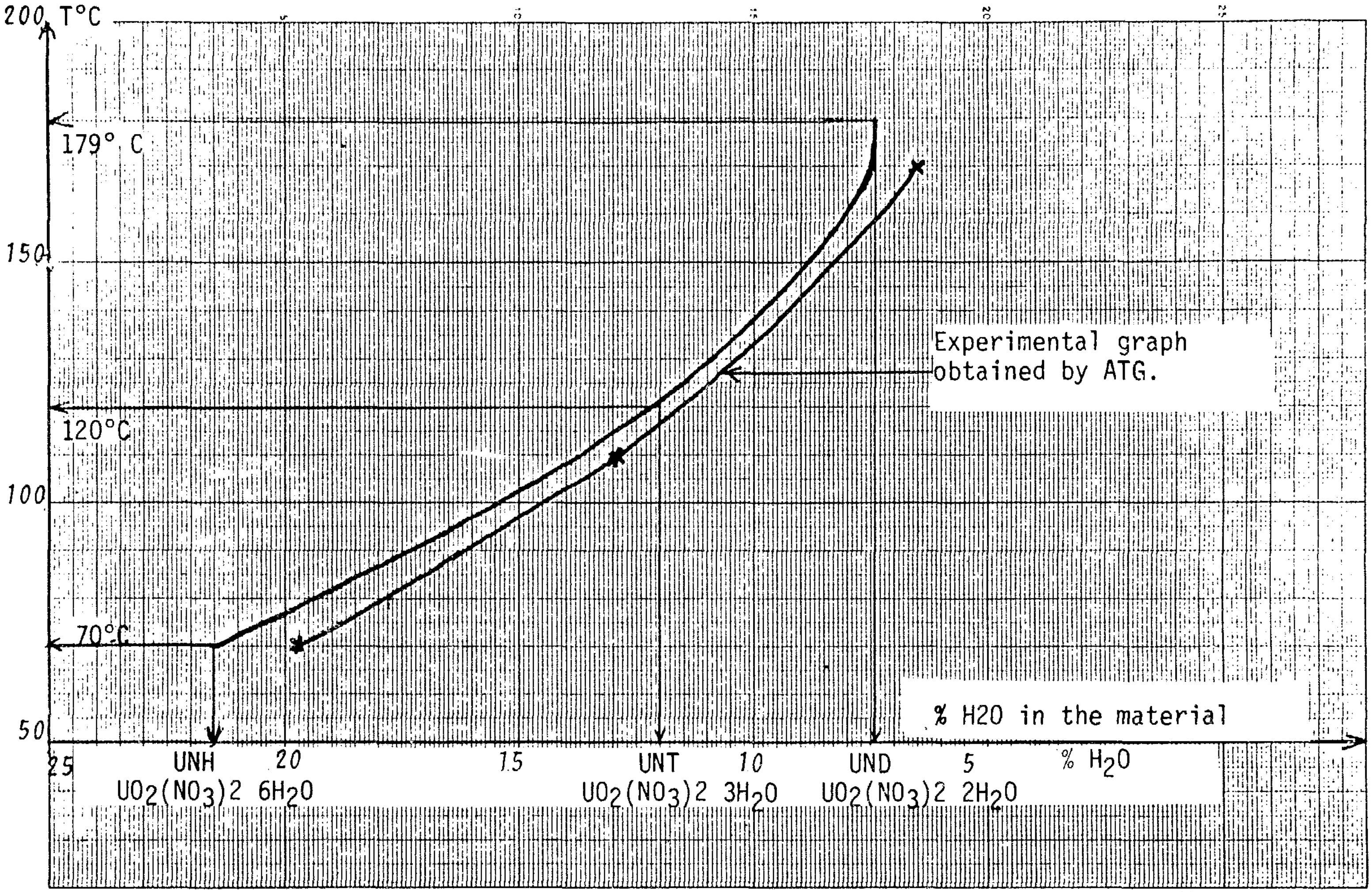

200 T°C
179° C
150
120°C
100
70°C
50
Experimental graph
obtained by ATG.
% H2O in the material
25
UNH
UO2(NO3)2 6H2O
20
15
UNT
UO2(NO3)2 3H2O
10
UND
UO2(NO3)2 2H2O
5
% H2O

Fig. 1.

IV - PRINCIPAL ADVANTAGES OF THE PROCESS

The process presents several substantial advantages, viz :

Competitive operating costs

Good control of environmental factors

Operating safety

Ease of operation

Flexibility and adaptability to the various feedstocks employed and finished products sought.

Good final product quality and reproducibility.

Competitive operating and capital costs

The process flowsheet down to the powder for sintering is straightforward and involves few essential equipment.

All the plant and equipment employed is normally available in industry and necessitates small special adaptation. The process eliminates or reduces the impact of a number of costly operations existing with competing processes, such as : adjustment of U/Pu concentrations ; particle size reduction ; Pu inventory questions ; the problems of treating liquid effluents and of aerosol contamination.

Additionally, the process comprises a single step of production of sinterable powder, leading directly to the mixed UO2/PuO2 powder ; it therefore eliminates the independent stages of production of UO2 and PuO2 powders which are generally indispensable in processes employing the UO2/PuO2 powder mix.

Good control of environmental factors

The process generates no aqueous effluents since it necessitates neither filtration nor washing.

Nor does it generate any plutonium- or uranium-bearing aerosols since it entails no grinding or micronising, in contrast to a number of other processes.

The oxides of nitrogen and water vapour produced by the denitration operation are recombined as concentrated nitric acid and can therefore be recycled.

Operating safety

a) As regards problems of criticality, all the initial part of the process (evaporation and crystallisation) can be carried out under conditions of favourable geometry.

The dehydration/denitration furnace can be controlled by mass or geometry, the remainder of the process being carried out in the absence of water.

Also worth noting is that the process does not involve transit via a "master" mix of high Pu content and that as from the nitrate solution stage the uranium and plutonium can be mixed in the concentrations required in the finished fuel.

b) The Pu inventory is easy to establish, being by control of concentration in nitrate solution.

c) The problems of shipment of the Pu feedstock can be very much simplified since the Nitrox process can take the uranium and plutonium in separate or premixed nitrate solutions. Mixing can take place as from the reprocessing plant, thereby avoiding the problems associated with the shipment of Pu on its own.

d) Also deserving of mention is that in this process the plutonium can remain in solution and be converted to oxide only at the stage of production of the mixed powder. In this way, its chemical purification to remove americium can be carried out just prior to use.

Ease of operation

a) Adjustment of U/Pu concentrations can be carried out in a single step at the nitrate solution stage.

b) The process can be employed to obtain sinterable powders of substantial Pu content, up to 25% and even beyond.

c) Trials carried out have shown that the parameters yielding the sinterable composite powder are easy to control.

What is involved is maintaining a heating programme by adjustment of temperature and pressure, these being easier to control than chemical parameters (pH etc.) or physical parameters (particle size distributions obtained by grinding operations) which it is essential to set under certain rival processes.

d) The powder obtained before pelleting and sintering exhibits good fluidity and, moreover, high density (of the order of 2.5 to 2.8 kg/dm3), thus facilitating the pelleting operation.

e) Compacting is carried out at relatively low pressures (of the order of 3 t/cm2).

f) Sintering is effected at the usual temperatures.

g) The pellets obtained have a good mechanical strength.

Flexibility and adaptability to various feedstocks employed and finished products sought

As regards feedstocks, it is possible in this process to employ uranium and plutonium nitrates either mixed or separate.

As for the sinterable powder, this can be prepared so as to meet various sintering procedures.

The solubility in concentrated nitric acid of the sintered pellets obtained is excellent ; solution efficiencies of better than 99.95% have been obtained on non-irradiated pellets.

Also, the composite material, at every stage of the production process, is soluble in nitric acid, thus guaranteeing easy recycling of production rejects and further enhancing the advantages of initial mixing of the two liquid nitrates.

Reproducibility

It should be noted that the reproducibility of the characteristics of the pellets is excellent, by virtue of the simplicity of the process of production of the sinterable powder and the ease with which the parameters determining these characteristics can be controlled.

V - CONCLUSION

The Nitrox process constitues an important and original step forward in the preparation of composite powders.

Economically well placed, it resolves the delicate problems of plutonium-bearing aerosols or effluents.

Its flexibility makes it possible to envisage its use just as easily at the reprocesssing plant stages as at any other site.

The Nitrox process thus plays a part in completing the fuel cycle and in ensuring safety in handling the plutoniferous materials arising from reprocessing.

RECENT DEVELOPMENTS IN THE PURIFICATION OF URANIUM RECOVERED FROM IRRADIATED MATERIALS

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Abstract

Experience is reported on the recovery of highly enriched uranium from targets irradiated for the production of isotopes for medical use. The raw material consists of uranates on filter textures, paper tissues and plastic bags. The uranium is leached out by nitric acid ; organic material is destroyed by hydrogen peroxide and the filtered solution is fed into a Purex-type extraction cycle. Uranium is extracted with tributylphosphate dissolved in dodecane. The extraction cycle using mixer-settlers consists of eight decontamination stages, eight scrubbing stages and twelve stripping stages.

The decontaminated uranium is further handled outside the shielded facility in a glove-box. Using tenoyltrifluoroacetone as an extractant the zirconium, niobium and plutonium quantities still present with the uranium are removed until the final product specifications are reached. The uranium is finally precipitated from a buffered ammonium acetate solution in the form of uranium peroxide, which is filtered off and calcined at 850 °C to U_3O_8. The final product meets the specifications for recycling into the targets with respect to its residual radioactivity (less than 2600 Bq/g), to its plutonium content (less than 1 ppm) and to its total impurities with a boron equivalent of less than 1 ppm.

Presently about 2440 g of uranium have been treated in five campaigns. The chemical yield of the wet chemical operations is around 96 percent including sampling for product characterisations and analyses.

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1. INTRODUCTION

For the production of ^{99}Mo, ^{131}I and ^{133}Xe radioisotopes, highly enriched uranium targets are irradiated in different reactors by the Belgian National Institute for Radioelements (IRE). The targets typically consist of 4.2 g uranium metal with an ^{235}U enrichment of 89 to 93 % clad into about 30 g of aluminium in a tubular form. The targets are reprocessed shortly after their irradiation at IRE by dissolution in a mixture of sodium hydroxide and sodium nitrate. This operation provokes the liberation of xenon in the gaseous form and the dissolution of iodine and molybdenum as I^- and MoO_4^{2-} respectively [1]. The uranium and most of the other fission products are left as a precipitate of hydroxides or uranates of undefined composition. The precipitate is filtered and washed on a glass-fiber filter. The filters are then collected into a polyethylene bag and some paper tissues used for cleaning the dissolution and filtration equipment are added. After treatment of about 140 g of uranium the material is stored in a stainless steel container and transported to SCK/CEN Mol. Over a few years of operation about 4.5 kg of highly enriched uranium has been accumulated and its recovery and recycling into the process were considered. This decision was based on economical reasons as well as on inventory and supply considerations. The procedures used to recycle and purify this material and the experience thereby obtained are reported in this paper.

2. CHARACTERISTICS OF RAW AND FINISHED PRODUCTS

The raw material obtained from IRE in a stainless steel container typically consists of about 160 g of sodium uranate with an ^{235}U content of 130 g, packed together with 35 g of glass fiber filters, about 80 g of paper tissues and 20 g of polyethylene Decay heat and radiolysis during storage usually transform the whole content into a brown-coloured adherent residue whose transfer from the container is only possible with spoons and scrapers. The characteristics of the end product, U_3O_8, are well-defined :

- combined total impurities should not exceed 2500 ppm with a limit of 500 ppm for any element and specific lower limits for elements with high boron equivalence ;
- the beta and gamma emitting impurities should not exceed 2600 Bq per gram of uranium ;
- the plutonium content should be less than 1 ppm and spontaneous fissions due to transplutonium elements should not exceed 1500 min^{-1}.

3. PROCESS FLOW SHEET

Taking into account the characteristics of the feed material and the associated radioactivity levels a first extraction cycle based on the Purex process and carried out in a shielded cell was considered. Because of the high enrichment of the uranium and the restricted quantities of material involved, small mixer-settler batteries of critically safe geometry were chosen to form the heart of the extraction system.

The capacity of the mixer-settler batteries being 500 ml hour^{-1} and the aqueous to organic phase flow ratio in the stripping (HC) section being set at 1.43, an organic phase flow rate (HCP) of 200 ml h^{-1} is obtained [2]. This flow ratio is the determining factor because a single organic phase passes all three of the batteries. The decontamination battery is operated at a high loading factor using 30 % TBP in dodecane and tolerates a concentration of 80 g l^{-1} in the organic phase and an aqueous phase acidity of 3.5 to 4 N. This leads to an active feed flow rate (HAF) of 50 ml h^{-1}. In practice the feed concentration (HAF) is lower at about 230 g l^{-1} uranium and the organic phase is loaded to 58 g l^{-1}. The resulting throughput of the installation is then 12 to 13 g h^{-1}. The scrubbing flow rate (HAS) was calculated from the condition that the organic to total aqueous flow rate should exceed 1.85 (for 2.5 l/kg U in HAS). This results in a scrubbing flow rate of 40 ml h^{-1}. Actually 50 ml h^{-1} are used at an acidity of 1.5 N to remove zirconium and niobium fission products. A split scrubbing phase with two different acidities has been considered but has not been implemented. The characteristics of this flow sheet are presented in table I.

TABLE I : Flow sheet characteristics for the decontamination cycle

Stream	1	2	3	4	5	6	7	8
Code	HAF	HAS	HAX	HAW	HAP	HCX	HCP	HCW
Flow (mlh^{-1})	50	40 (50)	200	90	200	285	285	200
U conc. (M)	1.35	-	-	-	0.34	-	0.237	-
U conc. (gl^{-1})	320	-	-	-	80	-	56	-
H^{+}(M)	4	3(1.5)	-	3.6(2.7)	0.05	0.01	0.01	-
TBP (vol.%)	-	-	30	-	30	-	-	30

Operation of this process requires additionnal equipment such as dosing pumps and storage tanks of the appropriate capacities. They are shown on figure 1. The combined aqueous stream leaving the decontamination battery (HAW) is continuously evaporated, the distillate being low-level aqueous waste. Similarly the uranium product solution is continuously concentrated to reach a final volume of about 2.5 liter. This solution containing the decontaminated uranium is transferred from the shielded facility into a

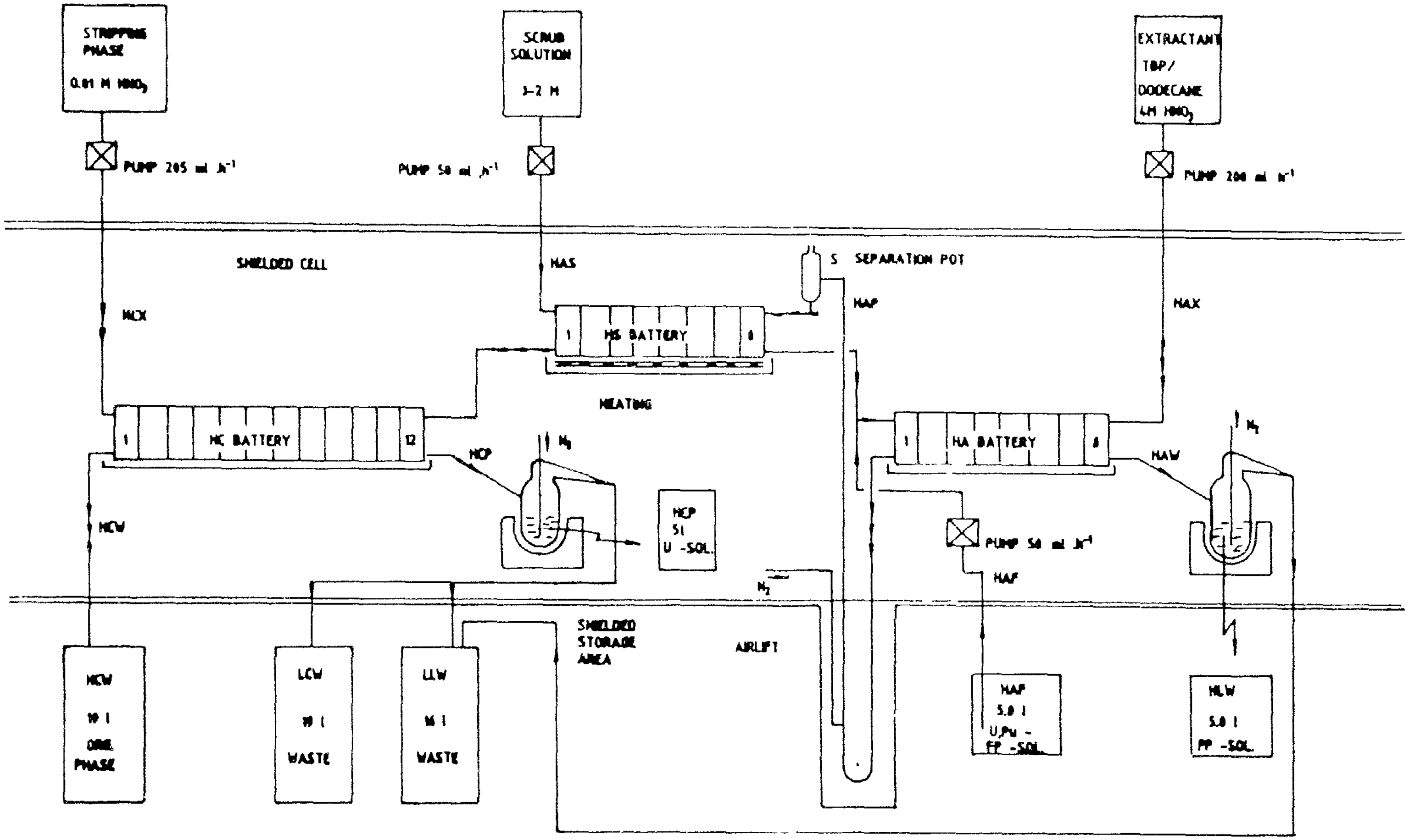

Fig. 1. Extraction flow sheet and auxiliary equipment

glove box for further purification, particularly from zirconium and plutonium. Therefore batch extractions with small volumes of xylene containing 0.5 M tenoyltrifluoroacetone are carried out.

For this operation and also in view of the final precipitation, packing and shipment of the uranium the solution is subdivided in quantities containing about 130 g U. After the phase separation and when satisfactory decontamination is achieved, the uranium is precipitated as uranium peroxide in a buffered ammonium acetate solution. The precipitate is washed, filtered and calcined to U_3O_8.

4. EQUIPMENT

4.1. Hot cell equipment

All equipment for the dissolution, the clarification and the first extraction cycle is mounted on a working surface of 200 x 65 cm in a cell shielded with 15 cm of lead. The manipulations are carried out with three pairs of masterslave manipulators on 3 working positions. An overhead crane of 250 kg load capacity and a service area behind the working table are also provided.
The dissolver equipment consists of a dissolution vessel and off-gas treatment limited to a condensor and sodium hydroxide washing bottles connected to a vacuum pump.
The extraction equipment consists of three sets of mixer settlers with 8 stages for the extraction and scrubbing operations and 12 stages for the stripping operation. Storage tanks are provided for feed solutions, reagents and effluents of the extraction operation. Two continuous evaporators are provided for the concentration of high level liquid waste and for the uranium product solution. Liquid transport from and to the storage tanks is done by vacuum or air lifts. Only one pump is installed into the shielded cell for supplying the high active feed solution to the first mixer settler battery.

4.2. Glove box equipment

The glove box equipment consists of ordinary laboratory scale instrumentation for the mixing, batch extraction, precipitation and filtration operations. Final conversion to U_3O_8 is carried out in a furnace using silica crucibles.

5. SEQUENCE OF OPERATIONS

The sequence of operations for the recovery of the uranium is given in the following paragraphs.

5.1. High active feed preparation

The raw materials obtained from IRE are stored in stainless steel containers and have the composition given in section 2. Figure 2 shows a block diagram of the feed preparation procedure. Most of the uranium is recovered by leaching the raw material with 9 M nitric acid. Insoluble material, glass fibers and plastic are retained in a basket, transferred onto a 2.2 μ filter paper and thoroughly washed. After drying this residue is transferred back to the initial stainless steel container. Tests on a few containers have shown that the residue contains less than 2 % of the uranium ; systematic gammaspectrometric measurements of the residues are being carried out to verify their uranium content using ^{144}Ce-Pr as an indicator of fissile material.

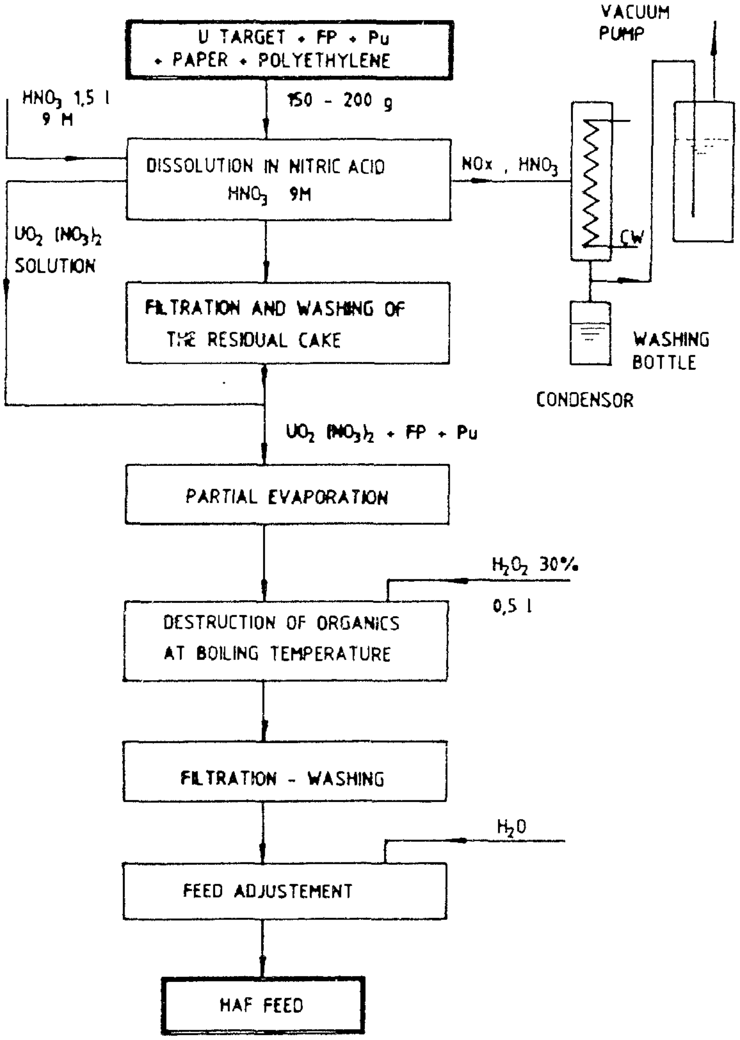

Fig. 2. Block diagram of the HAF preparation from the uranium target

To destroy the organic material in solution, hydrogen peroxide is added and the mixture is boiled. The solution is then filtered a second time through a 0.4 μm nucleopore filter. For criticality reasons the quantities that can be treated in a single operation are limited to 550 g ^{235}U which corresponds to the combined solution obtained from four to five raw material containers. The final uranium concentrations and nitric acid molarity are then adjusted respectively to 0.9 M and 3.5 to 4 M by evaporation or addition of concentrated nitric acid. Typically 2.5 liter of feed solution is then obtained and stored in the high active feed tank. This feed preparation phase is the critical step in the whole of the procedure and particularly the leaching and filtration phases are relatively slow. The characteristics of the feed solution are given in table II.

TABLE II : **Characteristics of the Process Solutions**
Typical values of current runs

	HAF Feed Solution	HCP Decontaminated Product Solution	Final Uranium Solution
Volume (ml)	2100	2475	2475
U g l^{-1}	259	214	214
Pu mg l^{-1}	25	14	< 1
^{144}Ce Bq l^{-1}	1.19 10^{12}	n.d.	n.d.
^{144}Pr Bq l^{-1}	1.19 10^{12}	n.d.	n.d.
^{137}Cs Bq l^{-1}	1.94 10^{10}	n.d.	n.d.
^{106}Ru Bq l^{-1}	5.62 10^{10}	3.36 10^{6}	~ 2.00 10^{6}
^{125}Sb Bq l^{-1}	4.07 10^{9}	n.d.	n.d.
^{95}Zr Bq l^{-1}	n.d.	2.71 10^{6}	~ 3.00 10^{4}
^{95}Nb Bq l^{-1}	n.d.	1.15 10^{6}	1.15 10^{6}
^{154}Eu Bq l^{-1}	n.d.	2.53 10^{5}	2.53 10^{5}

n.d. not determined.

5.2. Solvent extraction purification

The solvent extraction operation is carried out on a continuous basis usually lasting 50 hours for the actual production, preceded and followed by 8 hours for respectively battery equilibration and clean-out. The reagents are fed through dosing pumps from the supplies outside the shielded cell and the process is operated according to the flow sheet described in section 3 and shown in figure 3. The high active waste solution is evaporated at about 100 ml h^{-1}. Radiolysis products and organic remnants are gradually destroyed when they are fed into the boiling acid and no foaming or violent reactions have been observed. The volume reduction factor is limited because of the presence of significant

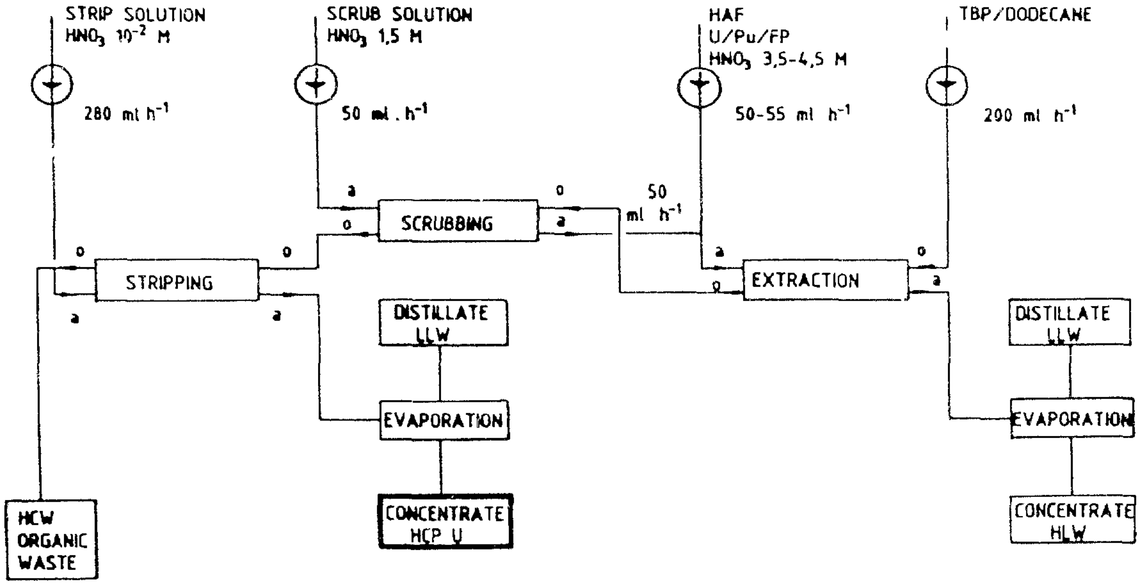

Fig. 3. Flow sheet of the liquid-liquid extraction process for the gross purification of uranium

quantities of sodium in the feed solution which eventually cristallises as sodium nitrate. Therefore regular transfers to the HAW storage are carried out to avoid clogging of the system. Radiolysis and formation of gas locks has been observed in the feed lines and an outgassing device has been installed between the HAF feed tank and the pump.

The high organic phase loading avoids crud formation at the phase boundaries and suppresses fission product coextraction [3]. No particular problems have been observed in this section. To favour the decontamination from zirconium-niobium in the scrubbing battery, it is operated at 54 °C.

The uranium product solution is continuously evaporated and concentrated to reach a concentration of about 1 M of uranium. Initially considerable foaming was observed in this evaporator as radiolysis products accumulate and acidity increases. The evaporator is now initially loaded with a small quantity of concentrated nitric acid and organic material is now destroyed immediately in the boiling acid. Thereby foaming has been completely avoided.

To reduce the fire risks during the extraction campaigns the shielded cell is maintained under nitrogen atmosphere. The characteristics of the product uranium solution are given in table II. Since no particular attention has been paid to plutonium until this stage, it is codecontaminated and coextracted with the uranium to a large extent.

5.3. Zirconium and plutonium removal

The solution as obtained from the evaporator does not meet yet the radiochemical and chemical purity specifications but is sufficiently decontaminated to be handled without shielding in a glove-box. Considerable purification is still obtained at the precipitation stage but zirconium and plutonium will coprecipitate quantitatively. Therefore a batch extraction procedure is applied to reach the desired specifications for those elements prior to the precipitation. The flowsheet of this operation is shown in figure 4.

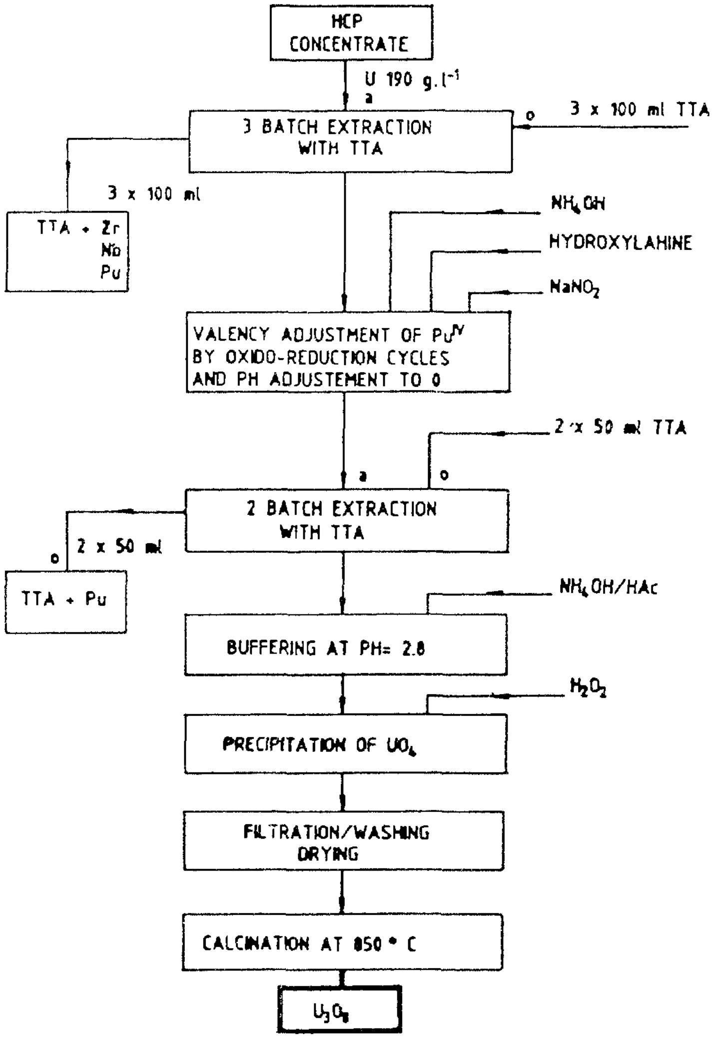

Fig. 4. Block diagram of the final purification of U

The extraction is carried out with 0.5 M tenoyltrifluoroacetone (TTA) dissolved in xylene. Three extractions are carried out at a volume ratio aqueous/organic of about 10 in a batch extraction installation to remove essentially all of the zirconium. The plutonium valency is then carefully adjusted to Pu^{4+} using hydroxyl-

amine-nitrate and sodium nitrite ; the acidity is reduced to less than 1 N and plutonium is quantitatively extracted with 2 batch extractions (TTA/xylene) in a volume ratio of 20 to 1.
The characteristics of the solution after this extraction stage are also presented in table II.

5.4. Uranium precipitation as peroxide

Precipitation of the uranium as peroxide has been selected because of the excellent removal from soluble and hydrolysable cations that can be achieved in this procedure. Different operational modes have been reported in the literature [4][5].
Taking into account the characteristics of the solution and the settling and filtration of the precipitate, the following procedure has been developed. The uranyl nitrate solution is buffered with ammonium acetate until a pH of 2.8 is reached.
Usually a few grams of an orange-red precipitate are formed at this stage containing a small quantity of uranium (30 to 35 weight %). The solution is filtered and uranium is now precipitated by the slow addition of hydrogen peroxide until about 1.2 ml/g U are reached. During this operation the pH decreases again and reaches a final value around 1.2. The bright yellow precipitate is allowed to settle and washed several times by decantation using a washing liquor containing ammonium nitrate, ammonium acetate buffer and excess hydrogen peroxide. The precipitate is then easily filtered on a 7 µm filter paper. A final washing with water removes the washing liquor salts. The precipitate is dried at moderate temperature and transferred into a silica beaker. It is then converted to U_3O_8 by heating in air at 850 °C during 16 hours.

5.5. Chemical yield and material balance

The quantities of uranium in a single stainless steel container are not well defined in spite of its high enrichment and the associated value. On the average, the total quantity in a number of containers corresponds roughly to the declared values by IRE. The first measurement concerning the chemical yield of the process is made in the clarified HAF solution. Sampling for concentration and free acid determinations before and after the decontamination cycle consume 4 to 6 g of uranium. The high active waste solution typically contains less than 3 g of uranium and the other waste streams contain negligeable quantities as shown in table III.
The chemical yield of the decontamination cycle in the shielded cell is thus around 98.5 %. About 2 g of uranium is lost to the TTA/xylene solution and 3 to 4 g into the orange-red precipitate.

TABLE III : Waste Stream Characteristics

Stream	Distillate HAF	Distillate U product	Organic Phase HCP	HAW
Volume (ml)	6850	14 500	11 050	2800
U mg l^{-1}	2.7	10.4	97	< 1300
Pu mg l^{-1}	0.0021	0.0006	0.035	< 1
^{144}Ce Bq l^{-1}	$1.50\ 10^{7}$	$8.4\ 10^{6}$	$2.6\ 10^{6}$	$1.33\ 10^{12}$
^{144}Pr Bq l^{-1}	$1.50\ 10^{7}$	$8.4\ 10^{6}$	$2.6\ 10^{6}$	$1.38\ 10^{12}$
^{137}Cs Bq l^{-1}	$6.5\ 10^{5}$	$5.4\ 10^{5}$	n.d.	$3.9\ 10^{10}$
^{106}Ru Bq l^{-1}	$2.44\ 10^{6}$	$3.9\ 10^{5}$	$9.2\ 10^{6}$	$7.0\ 10^{10}$
^{125}Sb Bq l^{-1}	$7.6\ 10^{5}$	$8.9\ 10^{4}$	$1.18\ 10^{5}$	n.d.
^{95}Zr Bq l^{-1}	n.d.	n.d.	$6.7\ 10^{5}$	n.d.
^{95}Nb Bq l^{-1}	n.d.	n.d.	$6.3\ 10^{5}$	n.d.

n.d. not determined.

Filtrates and washing liquors contain typically less than 0.2 g of uranium. Sampling of the final product further consumes 3 to 4 g so that the net chemical yield of the operation is around 96 %. The overall material balance is hampered by the uncertainty on the raw materials and the inaccuracy of the volume measurements in some storage thanks in the shielded cell.

6. CHARACTERISTICS OF THE END PRODUCT

The characteristics of the end products in the different campaigns are not identical due to small proces adjustments carried out as a result of earlier experience. Particularly the conditions for the scrubbing stage, the plutonium removal and the peroxide precipitation have been modified with respect to their initial values and yielded considerable improvement of the end product purity. The characteristics as they are now achieved are summarised below.

6.1. Product stoechiometry and enrichment

The uranium content of the converted oxide is typically within 0.3 % of the theoretical value of 0.8466 for a product with this isotopic composition. The ^{235}U content is around 92 weight percent. The ^{234}U content of 0.70 weight percent is extremely useful for the process analyses before decontamination because they can be based on alphaspectrometric measurements of ^{234}U.

6.2. Radiochemical purity

Presently a radiochemical purity better than the specified 2600 Bq/g U is achieved. The earlier batches however showed residual activities of ^{95}Nb (up to 3200 Bq/g), ^{106}Ru (up to 500 Bq/g), ^{125}Sb (up to 1200 Bq/g), ^{137}Cs and ^{144}Ce (both up to 3900 Bq/g) and ^{154}Eu (up to 1100 Bq/g). Plutonium concentrations up to 60 ppm in the earlier batches have now been lowered to less than 1 ppm. Transplutonium elements are undetectable in the final product. The thorium content is variable and ranges from 10 to 60 ppm.

6.3. Chemical purity

The chemical purity fulfills all specifications and only a few elements exceeding 10 ppm are detected by spark source mass spectrometry. Most important in the earlier batches was zirconium at 400 to 500 ppm but current batches range below 10 ppm. Similarly the residual phosphate content has been lowered from 80 ppm to about 5 ppm. Chlorine ranges from 5 to 70 ppm and, rather unexpectedly, sulfur is systematically present in quantities around from 50 to 150 ppm. The origin of this sulfur contamination is not clear at this moment but could come from radiolysis of TTA.

The total boron equivalency of all chemical contaminants does not exceed 1 ppm boron equivalent whereas the recommended specification is set at 2.5 ppm.
An example of a specification sheet accompanying each product batch is given in table IV.

TABLE IV : Typical End Product Specifications

Uranium batch UT4-020

	Atom percent
$^{234}U/U$	0.706
$^{235}U/U$	92.199
$^{236}U/U$	0.690
$^{238}U/U$	6.405

Atomic Weight : 235.237

Weight U_3O_8 : 151.46 g
Weight % U : 84.54 g
Uranium : 128.044 g

Impurities

Radioactive

	Bq/g U
^{95}Zr	< 185
^{95}Nb	< 1110
^{106}Ru	< 315
^{137}Cs	< 85
$^{144}Ce-Pr$	< 370
^{154}Eu	< 1130

Actinides

	µg/g U
Pu	< 1
Th	1.1

Chemical

	µg/g U (1 σ = ± 50 %)
Li	< 0.002
B	0.083
Na	0.61
Al	2.0
Si	0.22
P	1.6
Ca	1.1
Ti	0.030
V	< 0.001
Cr	0.079
Mn	0.013
Fe	0.89
Co	0.072
Ni	0.56
Cu	0.006
Zn	0.096
Ag	0.047
Sn	2.4
Ba	< 0.010
Pb	< 0.10
S	53
Cl	5.8
K	18
Zr	2.6

7. CONCLUSION

The experience has shown that highly enriched uranium can be recycled and converted from irradiated targets into nuclear grade base material with relatively simple means. By one single Purex-based extraction cycle, followed by specific chemical separation techniques for the removal of plutonium and some residual fission products, decontamination factors in the range of 10^5 to 10^6 are obtained. Further purification is achieved by the precipitation of uranium with hydrogen peroxide in well-specified conditions whereby an easily filterable precipitate is obtained. Up to now about 2.5 kg of this material have been processed without particular difficulties and with a chemical yield of about 96 %. About half of the losses are due to sampling and analytical waste. Unrecoverable quantities discarded to the process waste are below 0.5 percent.

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THE REPROCESSED URANIUM CONVERSION: TEN YEARS OF OPERATION OF COMURHEX

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Abstract

This facility was in the middle of the 1960 a pilot plant to convert UF6 to sinterable UO2.

In the 1970 this plant after some modification was redesigned and provided for the conversion of UNH coming from LWR to UF6. At the end of 1985, 1300 t/U has been converted and delivered to enrichment plants.

The conversion of reprocessed uranium from light water reactors is :

- slightly enriched 0,9 % to 2,25 %
- contains impurities

During the conversion process COMURHEX has to eliminate not only chemical but radiochemical impurities otherwise the material would never meet the specification for re-enrichment.

In this paper we are looking the main impurities and decontamination effect of the COMURHEX process.

I - HISTORICAL

1. Slightly depleted uranyl nitrate to UF6(see Fig 1).

Since 1970, COMURHEX has converted about 10.000 t/U of reprocessed uranyl nitrate coming from the French graphite-gas reactors. This is slightly depleted uranium and, provided some precautions are taken, it can be converted in a normal conversion plant.

1.1. Hightly enriched uranium hexafluoride to UO2.

In 1967 this facility has been built for the "deconversion" of hightly enriched UF6 to produce sinterable UO2.

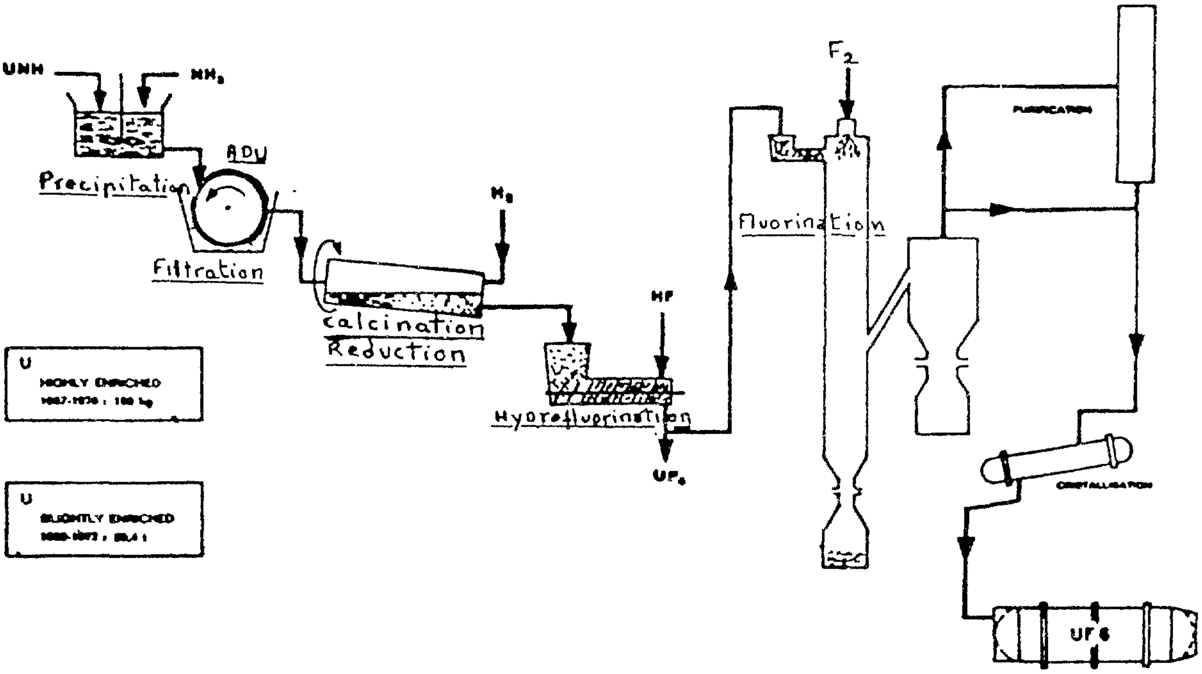

Fig.1. Uranium from reprocessing.

Capacity : few kg U/h

Total production : 1967-1970   200 kg U

Process : wet process (see Fig 1)

1.2. Slightly enriched uranium hexafluoride to UO2

1969-1970 deconversion by wet process of UF6 slightly enriched   3,5 % 235

Capacity : 8 kg U/h

Total production   60 t/U

1.3. Slightly enriched uranyl nitrate to UO2 (see Fig 2.3.)

In the 1970 the facility is modified for the conversion of reprocessed uranyl nitrate in UF4 and erection of a fluorination plant to convert UF4 to UF6.

Capacity:originally the capacity was 200 t U/Y (30 kg U/h) in 1986 the capacity is around 400 t/U/Y (60 kg U/h).

2 - PROCESS DESCRIPTION

UNH UF4   After acceptance of uranyl nitrate by controlling,

. Chemical elements (U contained, and impurities)

. Radiochemical activity (α β γ)

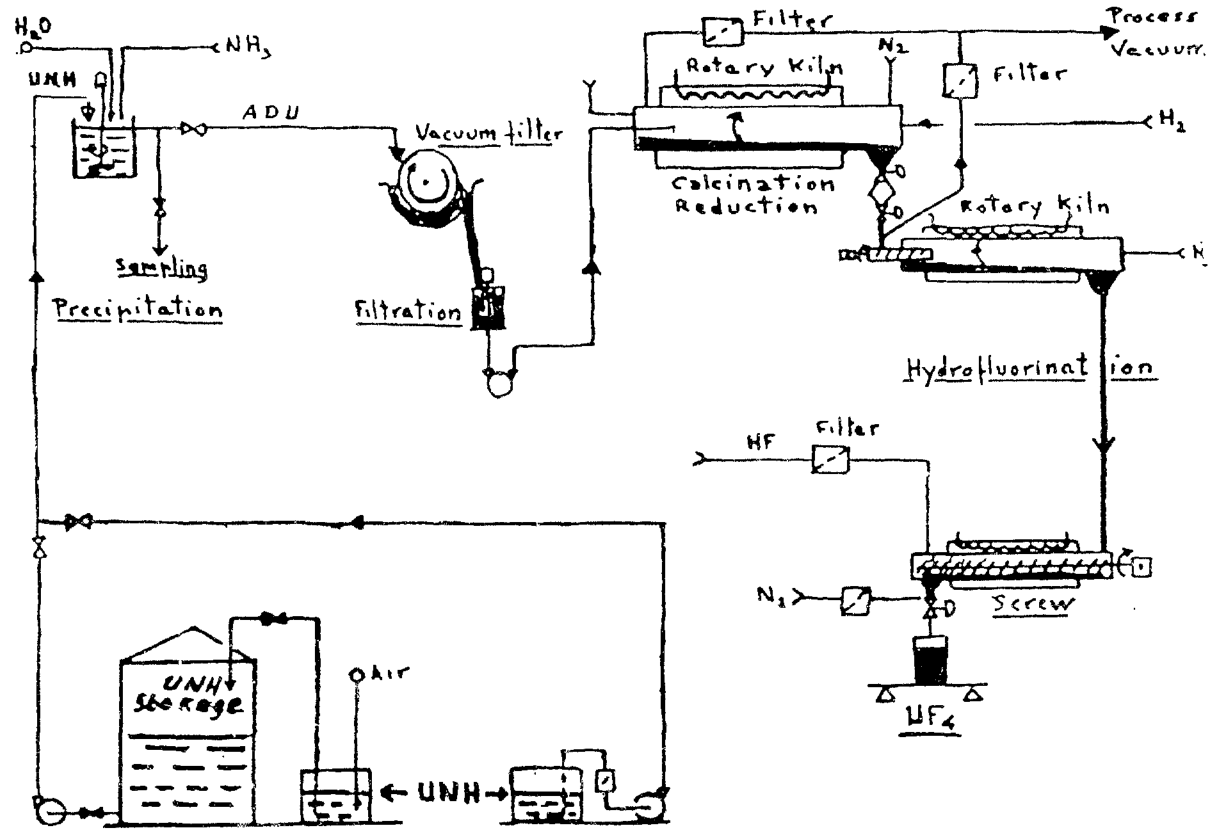

Fig.2. Conversion of UNH to UF_4.

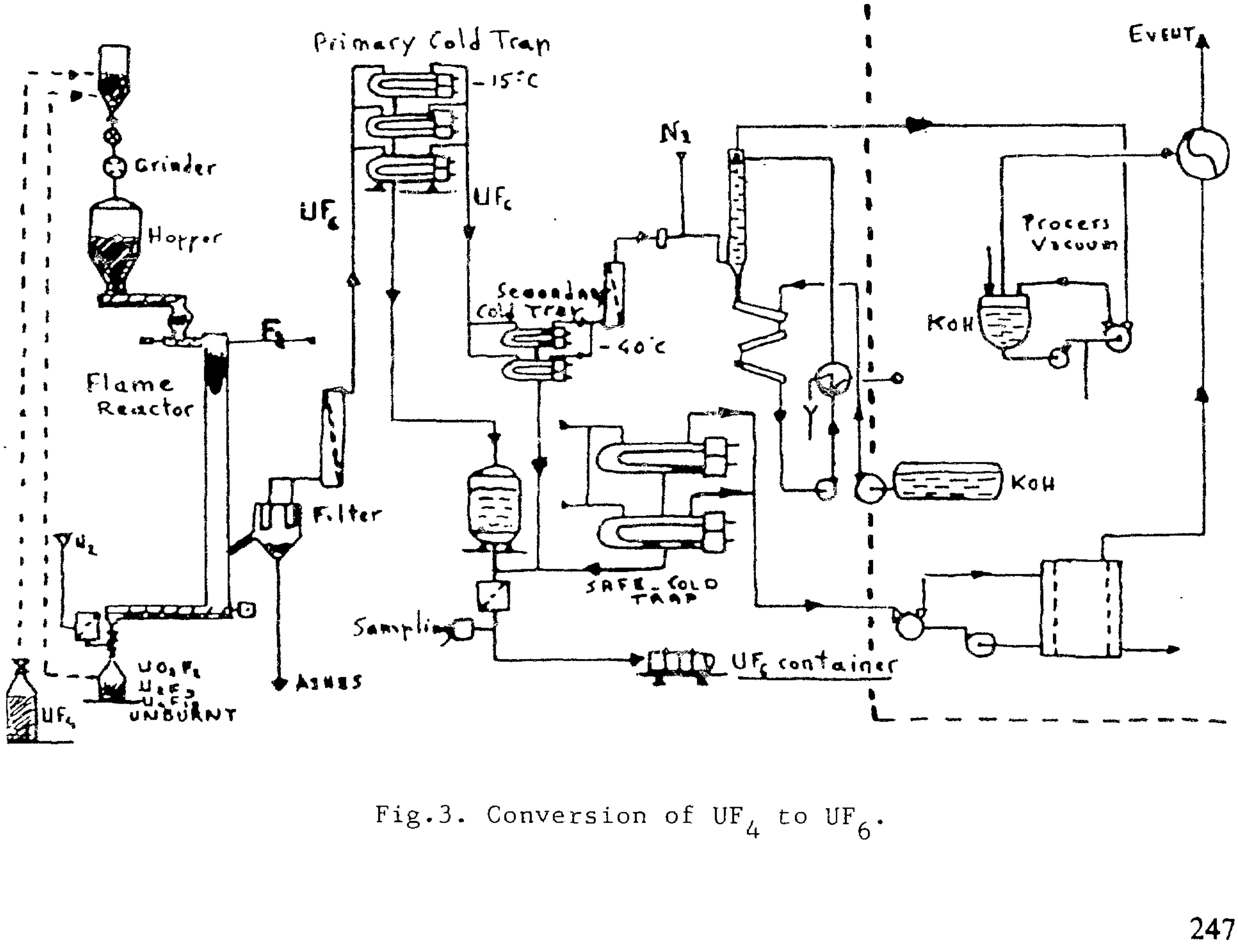

Fig.3. Conversion of UF_4 to UF_6.

2.1. UNH is pumped into a precipitation tank where it reacts with ammonia solution to give ADU ammonia diuranate.

This reaction is controlled by temperature and pH measurements.

2.2. The second step is a filtration with a vacum filter where the excess liquid is drained and ADU is fed into a mixer. Because the thixotropic property of ADU it is possible to pump the ADU sludge by means a metering pump into the following step.

2.3. Calcination Reduction ADU → UO_2

This drying, calcination and reduction is made in a rotary kiln heated by electrical furnace, in a first part of the rotary kiln ADU is dried, the second step consists in a transformation into UO_3 and UO_3 is reduced into UO_2 by a countercurrent of hydrogen obtained from the cracking of ammonia temperature along this rotary kiln is from 130° C to 650° C at the exit.

2.4. Hydrofluorination

From the first rotary kiln UO_2 is introduced to a second rotary kiln through an intermediate air tight valve, after the rotary kiln,hydrofluorination is completed into a screw. HF is introduced at the end of the screw.

Through an air tight valve UF_4 is collected into drums before the fluorination step.

2.5. Fluorination UF_4 → UF_6

After grinding UF_4 is fed into a flame reactor by means of a dosing screw to control the ratio between UF_4 and fluorine, in order to obtain a maximum efficiency a fluorine excess is necessary but the efficiency of fluorination is not 100 % and small quantitie of unburnt product is collected into a drum as UO_2F_2, U_2F_9, U_4F_{17} UF_5. UF_6 is filtered by means of sintered "monel filters" (10 µ porosity) unburnt materials are recycled at the top of the flame reactor until the accumulated dust reaches a radiation level of 500 µ Rem.

After filtering the purified UF_6 passes through two cold traps assembled in line and will be solidified at -40°C.

As soon as the capacity of a cold trap is reached the coolant is switched off and a heating liquid secures the melting of UF6 which is drained into an appropriate transportation container.

3 COMURHEX Experience in Reprocessed Uranium

3.1 COMURHEX, in its Pierrelatte plant, has been converting reprocessed uranium from light water fuel elements since 1972. Since then, more than 40 batches have been converted representing a total of 1300 T.

These batches comprised fuel elements from various burn-ups from 15 000 to 33 000 MW/d/t. Before reprocessing these fuel elements have been stored in cooling pools during 3 to 6 years.

The initial enrichment level (U 235) of these fuels was from 2 to 4 %. Consequently we have different types of reprocessed uranium :

- U 235 content between 0,7 and 2 %
- U 232 content between 0,03 and 0,15 ppm compared to U 235
- U 236 content between 0,135 and 0,435 % compared to U235

Through these various batches, COMURHEX has acquired a large experience in this field and we have recently made a general study about the characteristics of the different batches.

This study has proved that the U 232 content is a function of both burn-up and cooling time before retreatment ; but the measurements seem to be always under the theoretical values.

Example : The isotopic composition of a LWR fuel element after a 3 years cooling for a 33 000 MW/d/T burn-up.

Isotope	% in weight
U 232	10^{-7} (100 ppb/U 235)
U 233	10^{-6} (1 ppm/U 235)
U 234	0,02
U 235	0,09
U 236	0,4

3.2 Moreover, reprocessed U. has α, β, γ activities.

The α activity comes in general from the transuranian elements, Np, Pu, Am, Cm, but essentially plutonium and neptunium 237.

The β activity comes essentially from ruthenium 106 which gives volatil fluorides and oxyfluorides with a complex behaviour during the fuel cycle.

The γ activity comes essentially from thallium 206, daughter product of the U 232 with a short life.

3.3. Influence of the various isotopic composition of uranium.

- U 232 is a filiation product of Pu 236 and has daughter products with α β γ activities.

  Up to now, the DOE specifications U 232 gives a limit of 0,110 ppm (U 232/U 235). This value will change in the future due to increasing cooling periods and higher burn-ups. Therefore, it is necessary to adapt the level of U 232 in enricher's specification. We think this value could be 3 times higher than the current level today this specification is studied by ASTM Nuclear Comittee. We'll have to take into account in the fuel cycle (conversion, enrichment, fuel fabrication) of the changing in the U 232 filiation products. The first of them, thorium 228 (period 1,91/year) produces a non volatil fluoride that can be filtered from UF6.

- U 233 in reprocessed uranium remains at an extremely low concentration and far below the enrichment specifications.

- U 236 follows the increasing burn-ups. As soon as the burn-up reaches 33 000 MW/d/T, concentration of ex reprocessing U. reaches and even overpasses 50 % of U 235.

  This isotope has a high cross section and helps to generate within the reactor artificial isotopes such as neptunium 237 and U 232.

  Moreover, it is a neutronic poison that needs in LWR an overenrichment in U 235.

  This overenrichment is around 0,5 % of supplementary U 235 by 1 % of U 236.

- Finally, U 234 interferes in radiochemical activity of reprocessed uranium and is also, but at a lower degree, a neutronic poison.

4 - DECONTAMINATION EFFECT OF THE PROCESS

4.1. First it is obvious that the conversion of the uranyl nitrate solution into UF6 does not carry out any variation of the isotopic assay of uranium. It is the reason why the specifications concerning the minor isotopes of uranium are the same in the uranyl nitrate solution and UF6.

4.2. The decontamination effect of the process can concern only the metallic impurities or the radiochemical impurities (No comments about metallic impurities).

In the first step of conversion, from uranyl nitrate solution into UF4, no purification effect can be noticed. All the impurities are co-precipitated with the uranium. All the chemical compounds have approximately the same behaviour as uranium.

In the second step, that means during the fluorination of the UF4 into UF6, we can notice a considerable effect of decontamination.

4.3. α activity

The ratio elements must be divided into two groups :

The transuranian elements as Np, Pu which give alpha radiations can be removed from the UF6. These compounds form hexafluorides at the highest valency with physical properties close to UF6, but the kinetic of fluorination is very low specially for Pu and they are not stable in absence of a fluorine atmosphere. They are inclined to convert into a lower valency, as a solid product. So, the main part of them are found in the ash or dust which are collected at the bottom of the flame reactor or filter.

In any case, if a small amount of them can be found in the liquid UF6, they can be separated by filtering the liquid UF6 through a 2 microns filter of sintered monel alloy, before filling the container.

4.4. β and γ activities

The fission products as Ru, Tc (Zr, Nb, Cs) or the filiation products as Th (Pa ...) give beta and gamma radiations. Their behaviour is quite different, according to the vapor pressure.

The fluorides of ruthenium and technecium have approximately the same vapor pressure as UF6. For them, no significant deco-factor is noticed.

For the other elements, the fluorides are not volatile and they are are collected with the dust.

4.5. Starting with an alpha activity of 15.000 dpm at the entry of the process, the output material is close to

150 dpm, that means a factor of decontamination of about 100. The beta and gamma activities are reduced in a lower proportion (factor 2 to 4).

The process, as developed by COMURHEX, is able to convert and purify up to 400 t per year of reprocessed uranium, at a maximum U5 content of 2.25 % and produces an output material fullfilling today's requirements of the enrichment plants.

Though the yield of the process for a more 10 tons amount can be fixed at around 99,5 % with respect of the uranium balance, about 1 % of the uranium is bound to the dust output. This output of 1 % uranium in the dust is the tribute, we have to pay to improve the quality of the UF6 during the conversion.

In short, according to the amount, this means an immediate uranium recovering of 98 to 98,5 % UF6 and a 1 % dust production.

Concerning the dusts, it seems now that the best solution consists of a specific and appropriate treatment of the wastes in order to store them definitively in good conditions.

5 - URANYL NITRATE SOLUTION ACCEPTABLE BY COMURHEX

5.1. Usually the reference specifications are ASTM, but some of them must be defined accurately. COMURHEX's propositions can give some informations about the sentence "values agreed between purchaser and manufacturer" after an experience of more 1000 tons, and concerning only the alpha, beta and gamma activities.

5.2. α activity

As starting point, we are considering that the contamination of the air in the workshops must be, in any case, lower than 75-76 p Ci/m3 of air. For natural uranium the limit is 120 pCi/m3 of air.

To get this value, the alpha activity must be limited and calculated from three groups of elements.

The α activity of the transuranium elements as Pu 238, Pu 239-242 and Np 237 must not exceed 11.000 dpm. The activity of U 232 must be less than 46.300 dpm and the α activity for Am 241 - Cm 241 - 242 and all the daughter products of U 232 underneath 25.000 dpm (Th 228, Ra 224, Rn 220, Po 216, Bi 212, Tl 208).

In the calculation of the greatest admissible concentration, the weights of each group represent :

60 % for U element
25 % for transuranian
7 % for U 232
8 % for daughter products of U 232 and Am plus Cm.

5.3.β and γ activity

In order to protect more efficiently the workers against the radiations, we want to limit the total activity, due to the fission products to 30 µ Ci/kg U.
(13µ Ci/kg U for gamma activity and 17 µ Ci/kg U for activity).

The uranyl nitrate solutions delivered until now by La Hague are respecting these specifications.

In these conditions, we are able to assure the announced yield of conversion with an acceptable conversion cost.

6 - CONCLUSION

COMURHEX intention is to build up a new production facility at Pierrelatte plant with a nominal capacity of 1000/1200 tons U per year : UREX 2000.

COMURHEX has already established a detailed engineering study for this new facility and has been able to realise a pre-feasibility study.

PROBLEMS DUE TO IMPURITIES IN URANIUM RECOVERED FROM THE REPROCESSING OF USED LWR FUEL, FROM THE POINT OF VIEW OF RECYCLING

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Abstract

Specific impurities contained in uranium recovered from reprocessing of used LWR fuel create problems at the diverse stages of the fuel cycle when it is recycled via reenrichment. These impurities are mainly fission products and actinides.
They cause either handling problems (radiologic protection of personnel) or technical problems (such as neutron absorption by U_{236}).

A brief review of the impurities is given together with the problems they create.

Product specifications are briefly discussed, and suggestions as to desirable further purification (if it is possible) are made, among them proposed changes of specifications presently being discussed within ASTM.

It is most important, if further purification is considered necessary, to find the stage of the cycle where this can be done under the best economical conditions.

1. Introduction

Reprocessing of used LWR fuel yields two products: plutonium and recovered uranium. The amount of this uranium is about $95^{w}/o$ of the original fuel uranium fed into the reactor. Depending upon initial enrichment and burnup, its contents of U_{235} can be substantially higher than that of natural uranium (o.8 to 0.9 $^{w}/o$ U_{235} approximately). In this case, it contains valuable separative work and can be recycled to an advantage via reenrichment.

However, this recovered uranium contains impurities which are not - or only in extremely small traces - contained in natural uranium. These are mainly fission products and actinides, as well as impurities remaining from the dissolution of the fuel during reprocessing (elements contained in fuel cladding or provenient from process chemicals).

These impurities may cause two types of problems:

- handling problems, due mainly to radiological protection of the handling personnel, but also environmental problems
- problems caused to reactor operation due chiefly to neutron absorbing effects.

The present paper gives a brief review of the relevant impurities which cannot be further separated by reprocessing, the main problems they cause, and suggestions as to desirable further purification which may chiefly intervene during conversion to UF_6.

Current product specifications and proposals to change them are also discussed in short.

2. Specific impurities in recovered uranium and the problems they create.

2.2.1 Activity of fission products

Current specifications compare fission product β and γ activity with the activity of aged natural uranium. The latter is natural uranium which has been purified so as to remove decay products and which has been stored for 1 month at least in order to reach an equilibrium of short lived decay products Th_{234}, Pa_{234} and Th_{231}.

The activities of such aged natural uranium are (related to 1 gram of heavy metal):

α : 0.68 μ Ci/gHM ($2.52 \cdot 10^4$ Bq/gHM)
β : 0.68 μ Ci/gHM ($2.52 \cdot 10^4$ Bq/gHM)
γ : 0.16 μ Ci/gHM ($5.92 \cdot 10^3$ Bq/gHM)

The ratio of fission product activities in used LWR fuel to that of aged natural uranium gives an indication of decontamination factors required from a reprocessing plant for fission products. The following table shows some typical decontamination factors (DF) for three current LWR burnups and cooling times of 1 and 2 years before reprocessing:

Burnup (MWd/kgHM)	Cooling time 1 year		Cooling time 2years	
	DF (β)	DF (γ)	DF (β)	DF (γ)
30	2.0 + 6	5.1 + 6	1.0 + 6	3.0 + 6
36	2.1 + 6	6.8 + 6	1.1 + 6	4.0 + 6
40	2.3 + 6	8.0 + 6	1.17 + 6	4.8 + 6

Decontamination factors thus vary between 1.10^6 and 8.10^6.
In general, modern reprocessing plants have a DF of about 10^7 for fission products (this is not specific for each nuclide).Thus for fuel with burnups of 40000 MWd/kg and only one year cooling time, reprocessed uranium is within specifications concerning fission product activity.
Following isotopes are worthwhile to be mentioned separately:

- Zr_{95} ($\tau_{1/2}$ = 64 d)
  This isotope contributes to both the β and γ activity of the UNH and is difficult to separate within the Purex process. As it forms a non volatile fluoride, it will mainly cause a problem in the conversion plant. However with long cooling time before reprocessing (the German WAW-plant is planned to reprocess fuel with a cooling time of 7 years), the problem vanishes.

- Tc_{99} ($\tau_{1/2} = 2.1 . 10^5$ a)
  This long lived β-emitter shows a tendency to follow the uranium product. Due to the volatility of TcF_6 (Re.fig.1), it is carried through the conversion process and may create emission problems in the enrichment plant.

- Ru 106 ($\tau_{1/2}$ = 368 d)
  This isotope contributes largely to the β and γ activity of UNH. However, long cooling periods strongly reduce the problem. The volatility of RuF_6 is lower than that of UF_6 by a factor of about 10^3 (Re.fig.1). This means that a further strong decontamination takes place during conversion. Here it may contribute to waste problems.

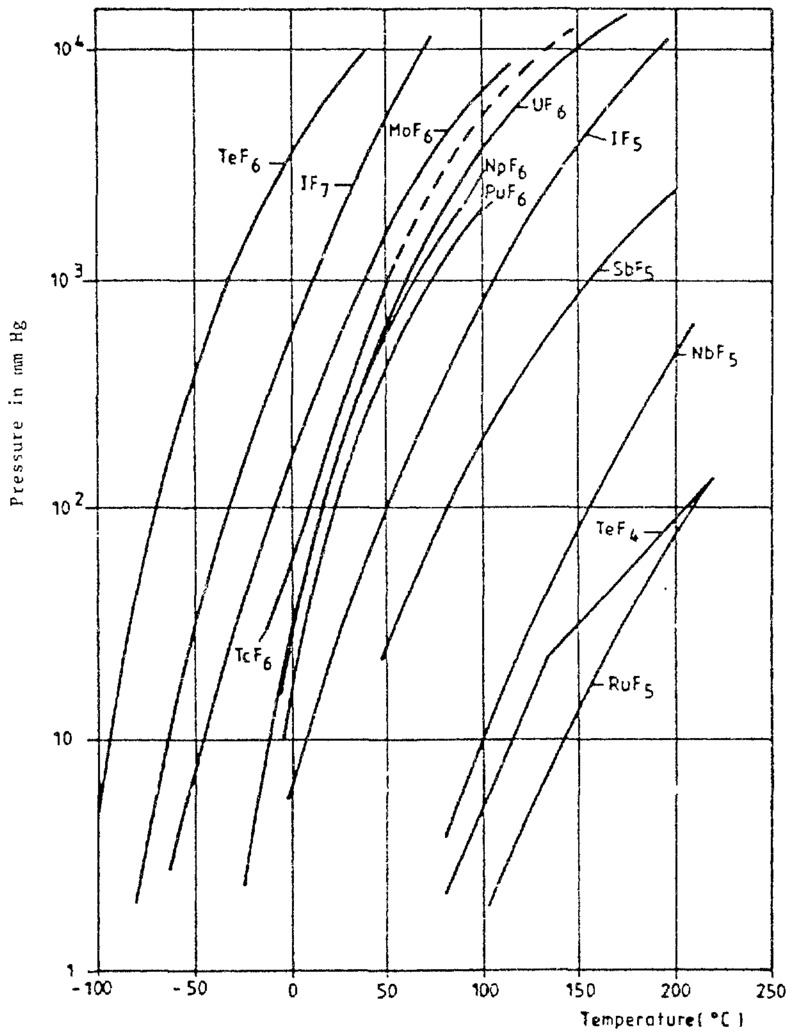

Fig. 1: Vapour pressures of volatile fluorides

2.2.2 Transuranic α activity

Transuranic isotopes are limited in UNH by a total admissible α activity of 15000 dpm/gU (disintegrations per minute per gram of uranium).

In UF_6 at present a limit of 1500 dpm/gU is admitted. However, this value is considered to be too high at present. The reason is that especially NpF_6 and PuF_6 have a similar degree of volatility to that of UF_6 (Re. fig. 1). In contact with metallic surfaces they decay easily to the non volatile tetrafluorides and thus create problems to the enrichment plant. There it seems that they are deposited mainly within the feed system, but presumably also within the centrifuges. This would cause an accumulation problem in the long run [1].

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[1] According to a private information from Uranit.

Following transuranic isotopes should be mentioned separately:

- $Np_{237}(\tau_{1/2} = 2.10^6$ a)

  As this isotope is chemically very similar to uranium, it is difficult to separate it by the Purex process. It mainly contributes to transuranic α activity in UNH and causes problems in the enrichment plant (see above).

- Plutonium

  ($\tau_{1/2}$: Pu_{238} = 87.7 a/Pu_{239} = 2.4 .10^4a/Pu_{240}=6.6 .10^3a)

  These 3 Pu isotopes also contribute to a large extent to the α activity of UNH and cause problems in the enrichment plant (see above).

- Americium and Curium

  ($\tau_{1/2}$: Am_{241} = 433 a /Am_{243} = 7.4 . 10^3 a/Cm_{242} = 163 d/ Cm_{244} = 18.1 a)

  These isotopes contribute to some extent to the α activity of UNH. Furthermore, Am_{241} concentration increases with cooling time (due to β-decay of Pu_{241}). The Cm isotopes decay relatively fast.
  In order to fulfill the specification of 1500 dpm/gU for total transuranic α activity, the reprocessing plant must have a common decontamination factor of about 10^6 for Pu, Am and Cm.

  Experience at the Karlsruhe pilot reprocessing plant (WAK) has shown the following distribution of transuranic α activity in UNH:

  Np: 60 %
  Pu: 34 %
  Am and Cm: 6 %.

  Thus efforts should concentrate mainly on the removal of Np.

2.2.3 Uranium isotopes

As uranium isotopes cannot be separated by chemical means, the problems they may cause can only be mastered by a judicious choice of recycling strategy. This may change in future with the availability of laser enrichment, which has the capacity to remove isotopes specifically.

Following uranium isotopes should be mentioned:

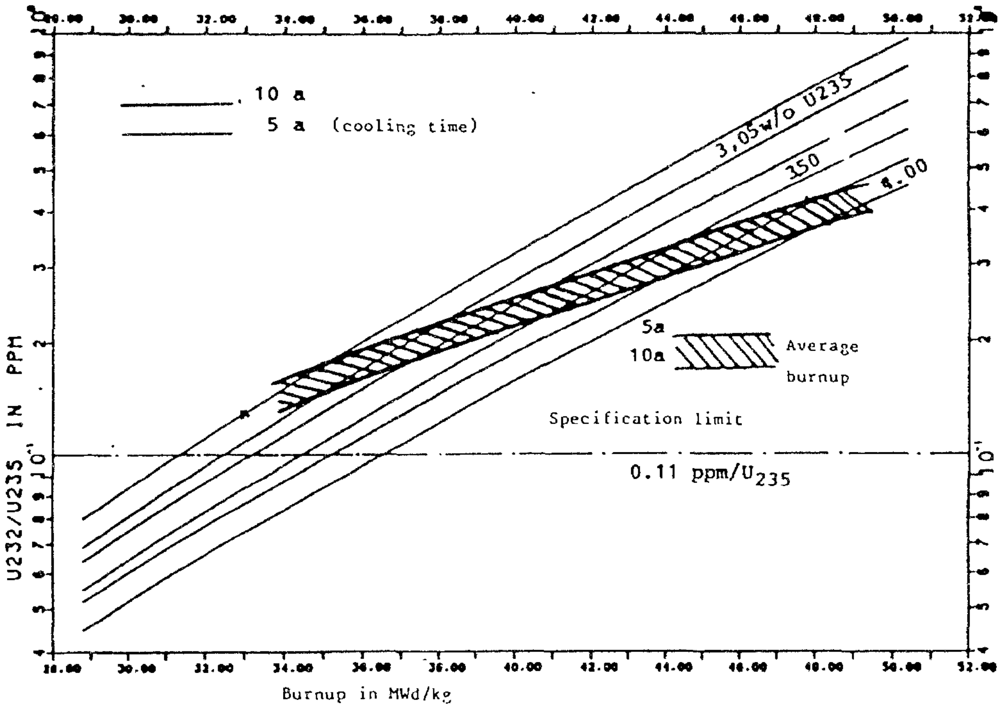
- U_{232} ($\tau_{1/2} = 70$ a)

  U_{232} has a strong radiological effect due especially to strong γ emission of decay product Tl_{208}. This may affect all stages of recycling and particularly enrichment, the first decay product Th_{228} being deposited as a solid fluoride.

This is evident from the decay series of U_{232}:

$$\underset{\text{72 yr}}{{}^{232}\mathrm{U}} \xrightarrow{\alpha} \underset{\text{1.91 yr}}{{}^{228}\mathrm{Th}} \xrightarrow{\alpha} \underset{\text{3.64 d}}{{}^{224}\mathrm{Ra}} \xrightarrow{\alpha} \underset{\text{55 sec}}{{}^{220}\mathrm{Rn}} \xrightarrow{\alpha} \underset{\text{0.145 sec}}{{}^{215}\mathrm{Po}} \xrightarrow{\alpha} \underset{\text{10.6 h}}{{}^{212}\mathrm{Pb}} \xrightarrow{\beta} \underset{\text{60 min}}{{}^{212}\mathrm{Bi}} \xrightarrow[\alpha]{(36\ \%)} \underset{\text{3.1 min}}{{}^{208}\mathrm{Tl}} \longrightarrow \underset{\text{stable}}{{}^{208}\mathrm{Pb}}$$

The current specification limit for U_{232} is 0.11 ppm /U_{235}, which is very stringent and would be reached by used fuel according to present burnup and initial enrichment standards after 7 years of cooling time (Re. fig. 2).



Amount of U_{232} particles as a function of burnup and initial U_{235} enrichment
Basis Origen P = 36 MW/kg cooling times 5 to 10 years

Fig. 2

- U_{233} ($\tau_{1/2} = 1.6 \;.\; 10^5$ a)

  This isotope is mentioned in specifications. However, due to its low concentration, it has practically no influence on the cycle.

- U_{234} ($\tau_{1/2} = 2.4 \;.\; 10^5$ a)

  In natural uranium this isotope has a concentration of about 0.0055 %. After burnup, it is about 0.013 %. U_{234} mainly is a problem in fuel manufacturing, as it contributes about 80 % of the uranium α activity.

- U_{236} ($\tau_{1/2} = 2.3 \;.\; 10^7$ a)

  U_{236} is mainly created in the reactor through neutron absorption of U_{235}. Fig. 3 shows the U_{236} concentration as function of burnup and residual U_{235} contents. It causes no problems during processing steps, but is a neutron absorber and thus must be compensated for by a higher U_{235} enrichment if the material is to be recycled. For every % U_{236} in the recovered uranium, the U_{235} enrichment must be 0.15 % higher than for equivalent natural uranium fuel.

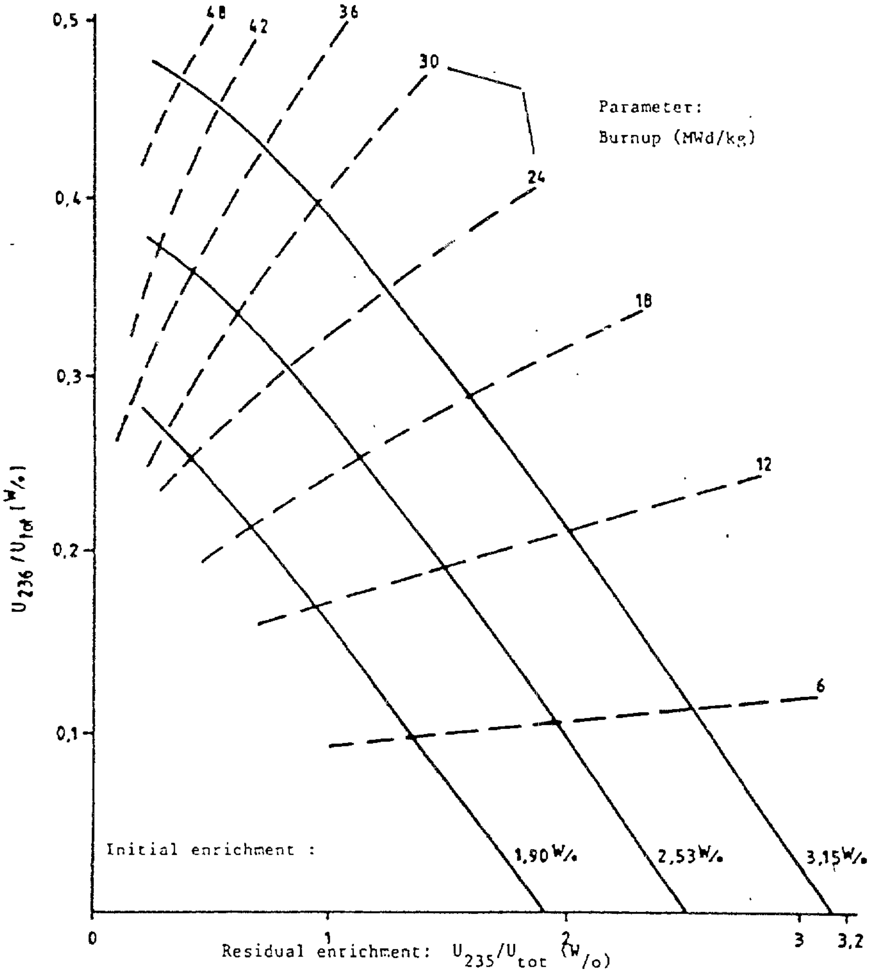


Fig. 3: U_{236} contents as a function of residual U_{235} enrichment for PWR fuel

3. Specifications and suggestions for their modification and for further purification of reprocessed uranium.

Problems concerning specifications of recovered LWR uranium have been a matter of concern for several years. In some cases they are so stringent as to make U recycling nearly impossible in future (e. g. U_{232}), in other cases they are too "generous" and should thus be lowered (e. g. α activity, Tc_{99}).
In general, the current standard of modern LWR reprocessing plants is such, that further purification of the product uranium could only be achieved at very high costs. It is thus important to see whether such further purification cannot - where required - be carried out more economically at other stages of the fuel cycle.

3.1 Elements and isotopes forming volatile fluorides

These elements are carried on into the UF_6. The problem will thus be with the enricher and the fuel manufacturer. Nuclides forming volatile fluorides are divided into two groups:

a) Nuclides specified in relation to U_{235}: Cr, Mo, Va, W, U_{233}, U_{232}:

	US-DOE UNH specs	US-DOE UF_6 specs	ASTM proposals for UF_6 specs
Cr	3000 ppm/U_{235}	1500 ppm/U_{235}	no change
Mo	500 "	200 "	"
W	500 "	200 "	"
Va	500 "	200 "	"
U_{233}	500 "	500 "	"
U_{232}	0.11 "	0.11 "	0.3 - 0.5 ppm/U_{235}

Current experience with WAK reprocessing plant shows that for all nuclides (except U_{232}), values in UNH can be kept to the values specified for UF_6, which are roughly half the values specified for UNH.

Concerning U_{232}, it has been proposed within ASTM to go from 0.11 ppm/U_{235} to o.3 ppm/U_{235}, lately even to 0.5 ppm/U_{235}. The latter value would allow to recycle uranium with original enrichments of 4 % and burnup up to 50.000 MWd/tHM (Re. fig. 2). This high concentration of U_{232} could cause problems due to decay products. However, sublimating UF_6 from one container to the other, or feeding into a plant (enrichment, fuel manufacturing), will segregate most of the decay products which form non volatile fluorides (Re. 2.2.3). They would then create a radwaste problem with the rinsing solution for the UF_6 cylinders.

b) Nuclides specified in relation to total uranium: Sb; Br; (C, P, Si); total halogenides; Nb, Ru, S, Ta, Ti.
No problems have been encountered so far with these elements, and there is no suggestion to change the current specifications.

3.2 Elements forming non volatile fluorides (As, Al, Ba, Be, Bi, Cd, Ca, Cm, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sn, Sr, Th, Zn, Zr).
No problems are known with these elements except for Zr (Re. 2.2.1).

3.3 Boron equivalent (B, Cd, Co, Eu, Gd, Li, Sm).
The total Boron equivalent of 8 ppm/U_{tot} presents no difficulties.

3.4 Transuranic α activity.
The generally admitted TRU α activity is of 15000 dpm/gU_{tot} in UNH and 1500 dpm/gU_{tot} in UF_6 (before enrichment).
However, enrichers find the value for UF_6 too high, and US-DOE proposed to go down to 25 dpm/gU_{tot} in UF_6. This seems unrealistic, as it is practically on the analytical threshold.
On the other hand, conversion has a DF for TRU-isotopes which is larger than 10, and effective filters are known to reduce them further (for example Ni wool). Discussions are going on within ASTM, and it seems that a value around 200 dpm/gU_{tot} in UF_6 could be agreed upon.
Reductions of α activity in UNH would be uneconomical, as they would make necessary very costly supplementary purification systems in the reprocessing plant.

3.5 β and γ activities of fission products

	US-DOE UNH specs.		US-DOE UF_6 specs	
	γ (μCi/kgU)	β (μCi/kgU)	γ (μCi/kgU)	β (μCi/kgU)
a) if not less than 75 % of total f.p. activity is due to Ru isotopes	320	1360	32	68
b) if less than 75 % of total f.p. activity is due to Ru isotopes	160	680		

The only problem encountered here is Tc_{99} (Re. 2.2.1), which had not been specified separately in the old US-DOE specifications. In 1978 a recommendation was issued by US-DOE to limit Tc in UF_6 (Before enrichment) to 0.4 ppm/U. It seems that conversion can remove a large part of Tc, as the volatile TcF_6 (which is carried through into the UF_6, Re fig. 1) is rather unstable and forms to an important extent non volatile compounds. Reprocessing could admit a limit of 8 ppm/u in UNH. Reduction of Tc in UF_6 would relieve the enrichment plant. This problem is still being discussed within ASTM.

3.6 Specifications for reenriched UF_6 2)

It is of interest within the cycle to consider the specifications set up by the fuel manufacturer for reenriched UF_6 concerning recovered LWR uranium. These specifications are meant for uranium reenriched to a maximum of 5 % U_{235}.

3.6.1 Elements forming volatile fluorids:

a) Nuclides specified in relation to U_{235}:

	RBU specs (ppm/U_{235})
Cr	1000
Mo	1000
W	1000
Va	1000

No problem is expected with these values as compared to UF_6 specifications before enrichment, as the absolute concentration of the impurities would remain unchanged in the worst case (that is, they would all be carried into the enriched product), whereas the U_{235} concentration will raise by a factor of 3 to 5 in average. In reality, at least part of the impurities will go into the tails stream.

b) Nuclides specified in relation to total uranium.

In sum, they should not excede 300 ppm/U.

No problems should arise here, as a great part of the impurities will go into the tails stream.

---

2) According to a communication from RBU.

3.6.2 Uranium isotopes

-U_{232}: 20 ng/gU

This means that uranium with a U_{232} content of about 0.5 ppm/U_{235} before enrichment could be used.

-U_{234}: 0.13 ^{w}/o of total uranium.

This is based upon current experience and will cause no problems.

3.6.3 Nuclides forming non volatile fluorides

In sum they should not excede 300 ppm of total uranium. This causes no problems.

3.6.4 Transuranic isotopes

The α activity of these should not excede 25 Bq/gU. This is the same as 1500 dpm/gU and is equivalent to current UF_6 specifications before enrichment.

3.6.5 Fission products

β activity shall not excede 1000 Bq/gU (leading nuclides are: Tc_{99}, Cs_{137}, Ce_{144}, Ru_{106}, Rh_{102}).

This is equivalent to 27 μCi/kgU, or a factor of about 2.5 times less than current UF_6 specifications before enrichment. An equivalent decontamination must thus occur during enrichment.

3.6.6 Th_{228}

This isotope is specified to $8.4 \cdot 10^{-5}$ $\mu g/_{gU}$:

As it is the first decay product of U_{232} and is deposited as a solid fluoride mainly in the enrichment plant, this means that recovered uranium should not be stored for more than a few months after enrichment before going on to fuel manufacturing.

4. Experience with uranium recycling in FRG

So far about 200 kg of uranium recovered from reprocessing have been reenriched and recycled in FRG. They were contained in 108 pins of a fuel assembly loaded into the reactor of the Obrigheim power station in 1983. No major problems occurred during the processing. It must however be stated that the uranium used for this project (it came from the reactor of Gundremmingen A power station, which was shut down in 1977) had only reached burnups of about 18000 MWd/tU. Fuel manufacturing was also uncritical, however handling of recovered uranium with higher contents of U_{232} decay products may make it necessary to shield parts of the process.

It also was seen that part of the impurities (mainly U_{232} decay products and possibly to some extent fission products) went into the AUC filtering solutions, which may cause a radwaste problem to some extent.

In order to demonstrate the recycling of uranium at an industrial scale, a programme has been initiated to recycle 8 complete fuel assemblies in the reactor of Neckarwestheim power plant. To this effect, some 13 tons of uranium recovered by reprocessing used fuel of the Neckarwestheim plant at La Hague were converted to UF_6 at the COMURHEX plant in Pierrelatte and reenriched at the URENCO plant in Almelo. Currently 4 fuel assemblies are being manufactured by RBU in Hanau; they are scheduled to be loaded into the reactor in July this year. About 7 tons of uranium will be recovered from the current reprocessing of Neckarwestheim fuel at the WAK reprocessing facility near Karlsruhe. They are scheduled to be converted by COMURHEX in spring of this year, reenriched by URENCO in summer and autumn and then shipped to RBU for fuel manufacturing. A second batch of 4 fuel assemblies will be loaded into Neckarwestheim reactor in 1987.

The original fuel from which the uranium was recovered had reached burnups of about 30 to 33 GWd/tU, with cooling times of 2 to 3 years before reprocessing.

5. Conclusions

Uranium recovered from reprocessing of used LWR fuel can be recycled via reenrichment. However, some of the impurities it contains create problems, so it will be necessary to reduce them.
The standards reached by modern reprocessing plants would make a further purification of UNH solutions so costly as to seriously compromise the economic advantages of recycling. However, further purification can be performed quite effectively and at relatively low costs at other stages of the fuel cycle, chiefly at the conversion stage. Transfer of products (mainly UF_6) from one container to another or feeding into facilities also achieves effective purification for certain isotopes.

These matters will have to be investigated carefully by countries wishing to choose the reprocessing and recycling alternative for their used fuel.

CONVERSION OF REPROCESSED URANIUM IN JAPAN

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Abstract

In 1981 Power Reactor and Nuclear Fuel Development Corporation (PNC) constructed the Conversion Test Facility-Ⅱ (CTF-Ⅱ) in order to develop the conversion process of reprocessed uranium and to obtain the scale-up data and technical know-hows which will be practically applied the plan of a pilot or a commercial conversion plant in Japan.

The facility which converts the reprocessed UO_3 to UF_6 has the capacity to convert 4 tons of U per year. The UO_3 produced by the fluidized-bed denitrator in the reprocessing plant in Tokai Works, PNC, is used as a starting material. The process of the CTF-Ⅱ consists of mainly UO_3 hydration, dehydration and reduction, hydrofluorination and F_2 fluorination sections.

The main items researched by the facility are as follows:

(1) Investigating the behaviors of the fission products such as Ru and Zr and the transuranic elements such as Pu and Np contained very small amounts in the reprocessed uranium, and separating those elements from uranium.

(2) Improving the chemical reactivity of reprocessed uranium prepared by the fluidized-bed denitrator.

The facility has converted approximately 5 tons U; besides the followings have become clear:

(1) The chemical reactivities in reduction, hydrofluorination, and F_2 fluorination are improved by hydration of UO_3.

(2) Both amounts of F.P and TRU containing in product UF_6 are less than these in the specification of the uranium enrichment pilot plant in PNC.

1. INTRODUCTION

The establishment of the nuclear fuel cycle using reprocessed uranium and purified plutonium can use efficiently uranium resources and considerably be decreased the quantity of yellowcake imported into Japan. In Japan it has a pressing need to develop and accomplish the recycle utlization of reprocessed uranium into LWR, because many LWRs are smoothly operating in Japan.

The reprocessed uranium would be utlized in the near future as the LWR fuel after fabrication following conversion and enrichment, and also as the ATR fuel mixed with plutonium.

PNC is developing to utlize both the fuels described above at CTF-Ⅱ in the Ningyo-Toge Works and the Tokai Works. The main researchs being carried out at CTF-Ⅱ are as follows:

(1) Improvement of the chemical reactivity of UO_3.

The low reaction rates, particuralIy a lower hydrofluorination rate, are given as the main characteristics of the UO_3 produced by the fluidized bed denitrator. Therefore, we need to improve the chemical reactivity of reprocessed UO_3.

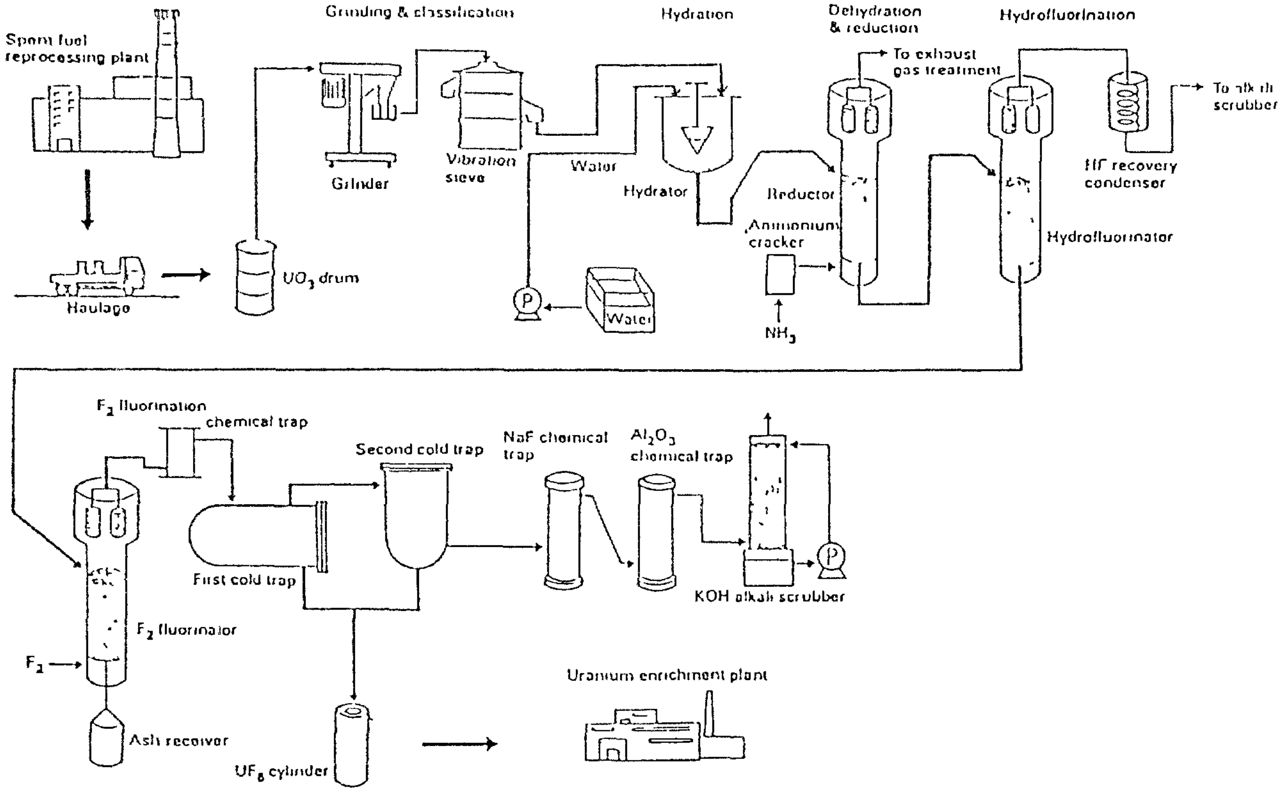
(2) Investigations of the behaviors and the elimination of the radioactive impurities.

The reprocessed uranium is purified enough and its radioactivity is nearly the same as nutural uranium. However, the reprocessed uranium contains the very small quantities of radioactive impulities, such as F.P and TRU. It is known that these impurities accompany with uranium or remain in the facilities in conversion process. The confirming the behaviors of the impurities and the eliminating the impurities from the reprocessed UO_3 are very important to establish the UF_6 conversion process and to operate the following uranium enrichment facilities.

In 1981, the CTF-Ⅱ was constracted in order to solve those problems, to obtain a scale-up data and technical know-hows, and the many data regarding those described above are being obtained at present. The data will considerably contribute to the plan of a pilot or a commercial conversion plant in Japan.

2 . OUTLINE OF THE CTF-Ⅱ

The CTF-Ⅱ converts the reprocessed UO_3 which is produced by the fluidized-bed denitrator in the reprocessing plant in Tokai Works, PNC. The CTF-Ⅱ has the capacity to convert 10 mols U/hr(4 tons U/y) and has converted approximately 5 tons U since the hot running. The process of the CTF-Ⅱ is dry process, which consists of mainly hydration, dehydration and reduction, hydrofluorination and F_2 fluorination sections. Figure 1 shows the flow sheet of tne conversion process, and in the outline of the conversion process every section as follows will be descrived.



FLOW SHEET OF REPROCESSED URANIUM CONVERSION PROCESS

FIG. 1

(1) Grinding and classification

The feed UO_3 is charged into the feed tank from a UO_3 container by a pneumatic conveyor. Then the UO_3 is charged into the grinder and the next vibration sieve from the feed tank through the screw feeder. The produced UO_3 is put into a product hopper which is also used as a feed hopper of the hydration process. The powder sizes of the UO_3 is approximately 100μm to 200μm. On the other hand, the over-sized powder is returned to the feed tank from the recycle hopper by a pneumatic conveyor.

(2) Hydration

The feed UO_3 powder is charged into the hydrator from the feed hopper through a rotary valve. As the UO_3 is stirred with water at a constant feed rate, the UO_3 changes into the UO_3 hydrate. The product UO_3 hydrate is put into the product hopper which is also used as a feed hopper of the dehydration and reduction process. The reaction equation is as follows:

$$UO_3 + nH_2O \xrightarrow{\text{at room temperature}} UO_3 \cdot nH_2O$$

(3) Dehydration and Reduction

The feed $UO_3 \cdot nH_2O$ is charged into the fluidized-bed reductor from a feed hopper. The temperature in the reductor is maintained at approximately 550℃ with external electric hearters. The fluidizing and reacting gas is cracked ammonia, a mixture of H_2 and N_2. The product UO_2 is taken out of the reductor through a screw feeder and put into a product hopper which is also used as a feed hopper of the hydrofluorination process. This reductor, 2.2m in length with approximately 10cm in diameter, is constructed of type 316 stainless steel. The off-gas from the reductor, H_2-H_2O-N_2 gaseous mixture, is burn out with excess air by the H_2 gas burner. The equation of dehydration and reduction is as follows:

$$UO_3 \cdot nH_2O(S) + H_2(g) \xrightarrow{\sim 550^\circ C} UO_2(S) + (n+1)H_2O(g)$$

(4) Hydrofluorination

The product UO_2 from the reductor is charged into the fluidized-bed hydrofluorinator which is operated at about 400℃ with external electric hearters. The UO_2 is fluidized with HF diluted with N_2. The product UF_4 is taken out and put into a product hopper which is also used as a feed hopper of the F_2 fluorination process. The reactor, 2.0m in length with approximately 8cm in diameter, is constructed of Monel alloy. The off-gas from the hydrofluorinator, HF-H_2O-N_2 gaseous mixture, is chilled to about 0℃ to condence HF gas and is drawn through the alkali scrubber. The equation of hydro-fluorination is as follows:

$$UO_2(S) + 4HF(g) \xrightarrow{\sim 400^\circ C} UF_4(S) + 2H_2O(g)$$

(5) F_2 Fluorination

The product UF_4 from the hydrofluorinator is charged into the fluidized-bed fluorinator. Sintered Al_2O_3 which does not react with fluorine is charged into the fluorinator as the bed material, and the charged UF_4 is mixed and diluted with this Al_2O_3. UF_4 is converted to UF_6 gas by reaction with fluorine gas diluted with N_2 gas. The equation of the F_2 fluorination is as follows:

$$UF_4(S) + F_2(g) \xrightarrow{\sim 420^\circ C} UF_6(g)$$

The chemical trap in which MgF_2 and CoF_2 are packed is set subsequently to the fluorinator to remove a small amount of radioactive impurities such as F.P and TRU.

The fluorinator, 2.0m in length with approximately 8cm in diameter, is constructed of Nikle metal.

After reaction, UF_6 gas is cooled and trapped in two cold traps in series. The first cold trap is cooled at about 0℃ and the second at about -30℃. The off gases from the cold traps contain a small quantity of UF_6 and F_2. Those gases, therefore, are treated by the NaF chemical trap, the Al_2O_3 chemical trap, and the alkali scrubber to remove UF_6 gas, F_2 gas, and the residual gas in a small amount, respectively.

The solid UF_6 trapped in the cold traps is warmed with hot water up to about 80℃ to liquefy and the liquefied UF_6 is put into a 12B cylinder.

Some non-volatile fluorides remain in the fluidized-bed together with Al_2O_3 and removed into the ash receiver at regular intervals.

3 . THE RESULTS OF EXPERIMENTS

3.1 Improving the chemical reactivities

(1) Hydration

It occured at times in the operation that the fine powder in the hydrator aggregates to grow up to the large particles as same as several centi meters in diameter. To solve the problem, the operating factors, water feed speed, the ratio of UO_3 to water and stirring speed, were changed, and the optimal condition were determined. The hydrator is operating smoothly under the optimal condition at present.

It was identified by means of x-ray diffraction that the UO_3 hydrate produced at room temperature had the crystal forms of $UO_3 \cdot 2H_2O$ and/or $UO_3 \cdot 0.8H_2O$. When the UO_3 which had a surface area of approximately $0.5m^2/g$ was hydrated, the surface area of the UO_3 hydrate increased to approximately $3m^2/g$ greater than that of the UO_3. Figure 2 shows the increase of the surface area caused by the change from UO_3 to UO_3 hydrate.

(2) Dehydration and Reduction

The fluidized-bed reductor was operated smoothly for a long period. The production rate was approximately 2.5kg-U/hr in the continuous operation. The reaction reactivity was almost perfect and the O/U ratio of product UO_2 was about 2.05. The hydrogen gas utilization efficiency was as low as approximately 45%, because the amount of hydrogen gas supplied was twice of the stoichiometry. The experimental conditions in the fluidized-bed reductor, the fluidizing properties and powder properties are summarized in Table I .

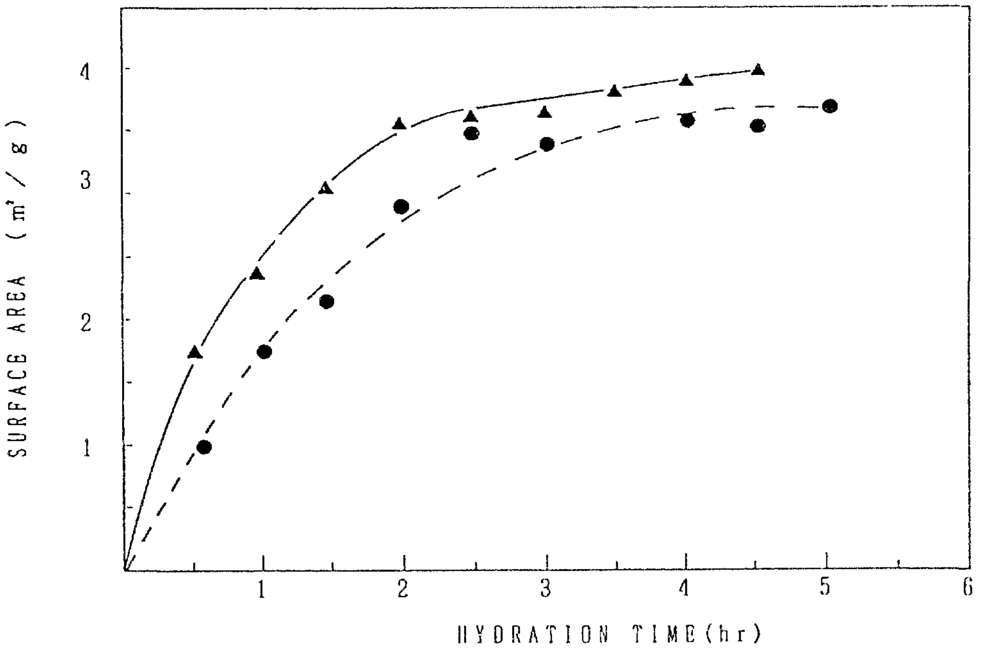


FIG. 2 TIME DEPENDENCE OF SURFACE AREA

TABLE. I EXPERIMENTAL CONDITIONS

	REACTION TEMP (℃)	FLUIDIZING VELOCITY (cm/sec)	INLET GAS VOLUME (Vol/o)	HOLD-UP TIME IN REACTOR (hr)	POWDER PROPERTIES		
					SURFACE AREA (m²/g)	AVERAGE POWDER SIZE (μm)	BULK DENSITY (g/cc)
DEHYDRATION & REDUCTION	550	15.0	45 (H_2)	4	2.90	200.8	2.52
					UO_3nH_2O		
HYDROFLUORINATION	400	23.0	50 (HF)	3	4.49	180.0	3.51
					UO_2		
F_2 FLUORINATION	420	10.0	30 (F_2)	0.3	0.98	197.4	3.01
					UF_4		

The kinetic curves measured the relation between the reduction time and the reduction ratios of the UO_3 and the UO_3 hydrates by differential thermal analysis (DTA) are shown in Fig. 3. As shown in Fig. 3, the reaction ratios of the UO_3 hydrates are higher than that of the UO_3.

(3) Hydrofluorination

The fluidized-bed hydrofluorinator has been operated with no troubles. The production rate was approximately 2.3kg-U/hr in the continuous treatment. The hydrofluorination reactivity was as high as approximately 95%. The hydrofluorine gas utilization efficiency was approximately 90%. The experimental conditions are summarized in Table I.

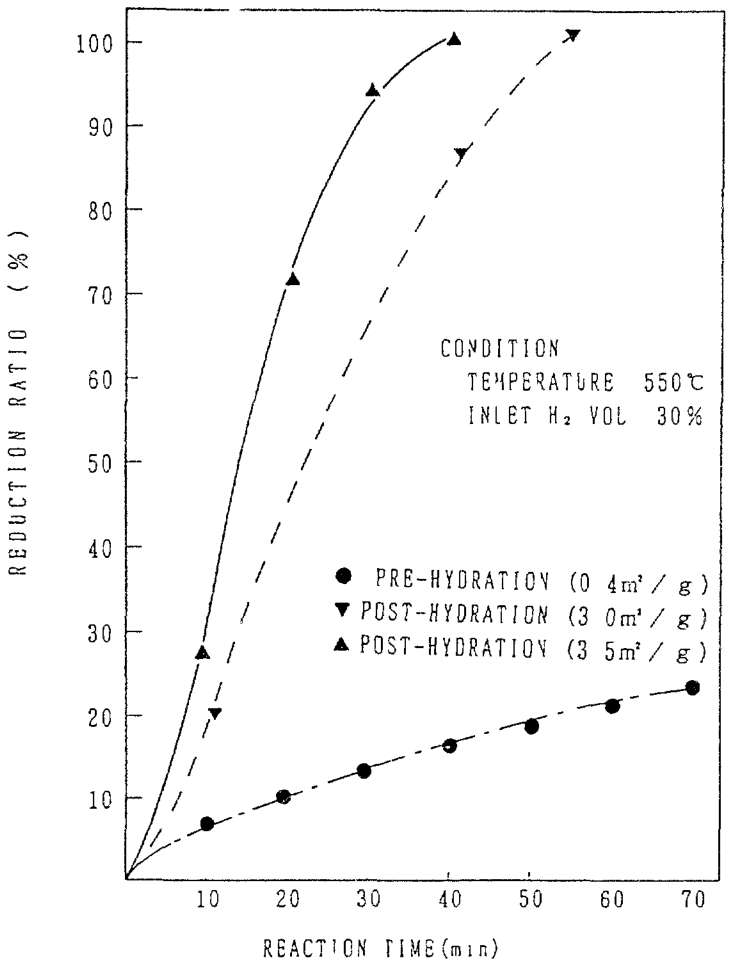


FIG 3 TIME DEPENDENCE OF REDUCTION RATIO BY MEANS OF D T A

The kinetic curves measured the relation between the reaction time and the reaction ratios by DTA are shown in Fig. 4. The reaction of the UO_2 derived from the UO_3 hydrates is rapid and complete compared with that of the UO_2 prepared by the direct reduction of fluidized-bed UO_3.

(4) F_2 fluorination

The production rate of the F_2 fluorination using the UF_4 which was produced with over 90% of the hydrofluorination ratio was approximately 2.1kg-U/hr. In the case, the fluorine utilization efficiency was as high as approximately 99% at 420℃. However, the production rate of the F_2 fluorination using the UF_4 which was produced with under 90% of the hydrofluorination ratio was under 80%. The experimental conditions are summarized in Table I.

The reaction rate and fluorination utilization efficiency at 370℃ of the UF_4 produced by PNC-process are higher than those of the UF_4 produced by CTF-Ⅱ, at 420℃. This fact may mainly be due to the smaller quantity of UO_2 in the UF_4 produced by PNC-process than that in UF_4 produced by CTF-Ⅱ.

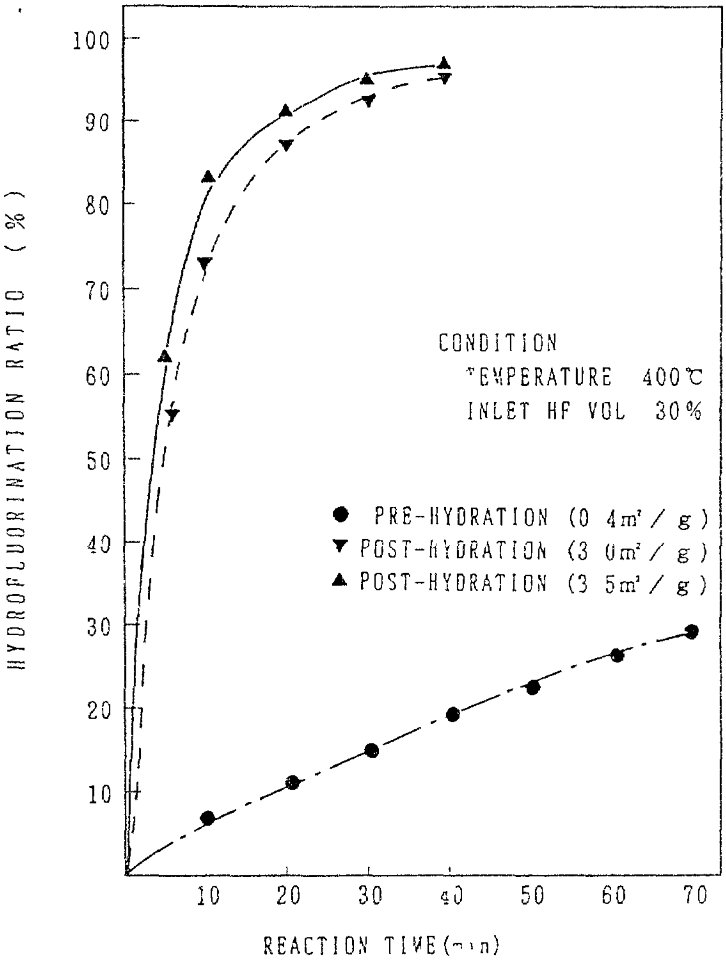


FIG 4 TIME DEPENDENCE OF HYDROFLUORINATION RATIO BY MEANS OF D T A

The kinetic curves measured the relation between the reaction time and the reaction ratios by DTA are shown in Fig. 5.

Main results of the above experiments, dehydration and reduction, hydrofluorination and F_2 fluorination, are shown in Table II.

3.2 Investigating the behaviors and the eliminating of the radioactive impurities.

A small amount of radioactive impurities contained in reprocessed UO_3 such as F.P and TRU behave with uranium to the UF_4 form in spite of the changes of the uranium forms in dry process. Most of these impurities change to these fluorides in the fluidized-bed fluorinator. Some of these fluorides having the lower boiling point temperature than that of F_2 fluorination temperature would behave with UF_6. However, in practical operation, the whole quantity of these fluorides in a fluidized-bed fluorinator, such as RuF_5, SbF_5, NpF_6 and PuF_6, does not always behave with UF_6. It is inferred that these fluorides

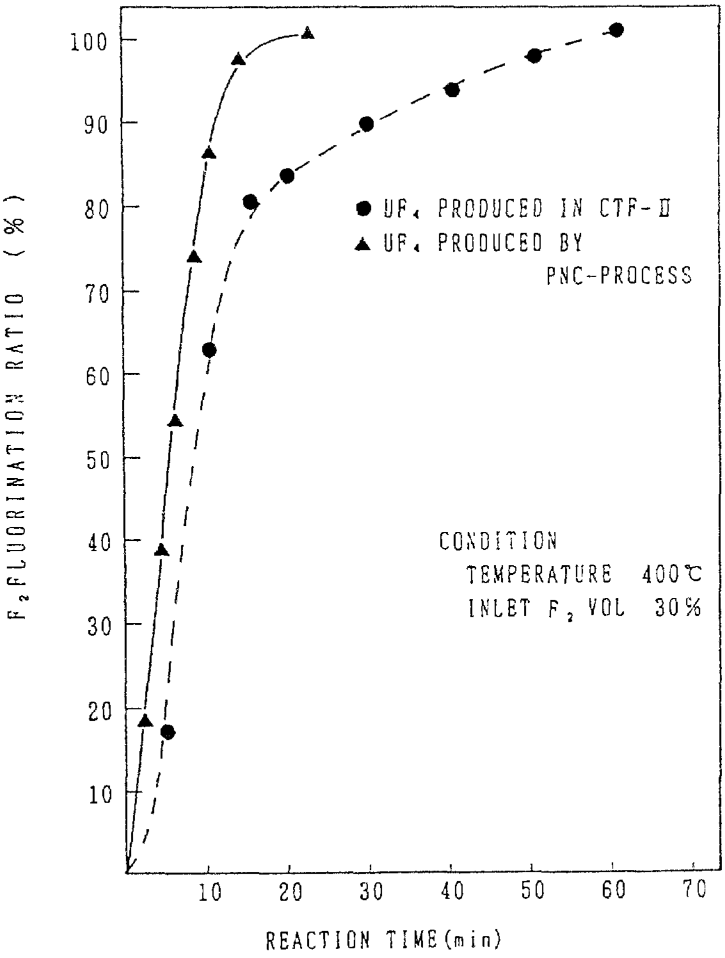


FIG.5 TIME DEPENDENCE OF F_2FLUORINATION RATIO BY MEANS OF D.T.A

TABLE. Ⅱ RESULTS OF CONTINUOUS TREATMENT

	CHEMICAL REACTIVITY (%)	OPERATING RATE (kg-u/hr)	GAS UTILIZATION EFFICIENCY (%)
DEHYDRATION & REDUCTION	100	2.5	44 (H_2)
HYDROFLUORINATION	95	2.3	90 (HF)
F_2 FLUORINATION	100	2.1	99 (F_2)

would remain in a fluorinator as a solid due to be reducted to these lower valency states. The behavior of PuF_6, as an example, is as follows:

$$PuF_6(g) + UF_4(S) \longrightarrow PuF_4(S) + UF_6(g) \quad [1]$$

The fluorides gas released from the fluorinator is trapped by the subsequent chemical trap packed with MgF_2 and CoF_2.

The non volatile fluorides, such as, SrF_2, CeF_4, AmF_3 and CmF_3, almost remain in the fluidized-bed fluorinator, and is removed together with the bed material, Al_2O_3, as a waste at regular intervals.

We have investigated mainly the behaviors of Pu and Np in F_2 fluorination. The results are as follows:

(1) In spite of the very small quantity of Pu in UO_3, Pu in UO_3 is sufficiently separated from UF_6 by the fluidized-bed fluorinator and the chemical trap. The amount of Pu containing in UF_6 is under 50 dpm/g-U. The value is less than the limited value of the lowest detection of alpha counting analysis.

(2) The behavior of Np is somewhat uncertain, because of the large error of analysis. However, in spite of the large error, it would be certain that the removal ratio of Np by the chemical trap is a little lower than the value in the literature [2].

(3) Because the amounts of F.P and TRU containing in UO_3 are very small quantities, these behaviors are uncertain. These contents in UF_6 are less than these values in the specification of the uranium enrichment pilot plant in PNC. The chemical data of representative sample and the specification are shown in Table Ⅲ.

TABLE Ⅲ ANALYSIS RESULTS AND SPECIFICATIONS OF F.P AND TRU

ITEM	ANALYSIS RESULTS	SPECIFICATIONS
F.P	Zr 95 < 10^{-3} Nb 95 < 10^{-3} Ru103 < 10^{-3} Ru106 < 10^{-2} Cs137 < 10^{-3} Ce144 < 10^{-3} TOTAL < 0.015 μCi/g-U	The total activity of the maximum gamma rays emitted from ^{95}Zr, ^{95}Nb, ^{103}Ru, ^{106}Ru, ^{137}Cs, and ^{144}Ce is 0.05 μCi/g-U
TRU	Np < 150 Pu < 50 Am < 100 Cm < 50 TOTAL < 350dpm/g-U	The total activity of the maximum alpha rays emitted from Np, Pu, Am, and Cm is 1500dpm/g-U

4 . CONCLUSION

The fundamental data and technical know-hows are being obtained by the CTF-Ⅱ operation, and the initial object is being nearly reached.

The facility would be scaled up in the near future, and after the operation of the expanded facility during a certain period, the plan of a commercial conversion plant would be started.

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PANEL DISCUSSION

(Summarized by H. Page, U.K.)

In his opening statement to the Technical Committee Meeting on Advances in Uranium Refining and Conversion, Mr. J.L. Zhu, Director of the Division of Nuclear Fuel Cycle, remarked that the contents of the papers scheduled for presentation indicated that, there had been considerable innovation at the front end of the nuclear fuel cycle in an increasing number of Member States since the previous conference in Paris in June 1979, despite the recent slowing down of nuclear power plant construction. By the end of the conference it had become quite evident to all participants that this was indeed the case.

While it can be seen that the major uranium supply/processing countries continue to refine and modify their traditional conversion processes in response to changes in market demand, feed and product specification, environmental constraints, regulatory practices etc., several other interesting developments have recently emerged.

Self sufficiency in fuel production is evidently one of the recent trends in the nuclear fuel cycle policy of an increasing number of Member States. This accounts for the launching of the many new laboratory and pilot scale projects described at the conference and explains the extensive research and development effort aimed at production of uranium fuel cycle intermediates, such as fluorides, metal and oxides, suitable for processing to nuclear fuel by Member States for their home based nuclear reactors. In a growing number of cases Member States are moving into nuclear fuel cycles which do not involve uranium enrichment.

An important issue, not only to the front end of the nuclear fuel cycle but to the cycle as a whole, concerns the fate of the uranium and plutonium recovered from the reprocessing of irradiated fuel. Member States without indigenous uranium and concerned about the economics of future fuel cycles based on "natural" uranium are showing a great deal of interest in recycling reprocessed irradiated uranium (REPU) back into the fuel cycle either in routes involving enrichment or as mixed uranium/plutonium oxide fuels (MOX).

A further development with potential for significant impact on traditional uranium conversion technology by the middle of the next decade is atomic vapour laser isotope separation (AVLIS) and existing convertors accustomed to providing uranium hexafluoride as the feed to enrichment facilities will need to keep in close touch with the progress of this technology which requires a feed of uranium metal.

However, while the technical options for uranium refining and conversion differ from country to country depending on criteria such as for example:

i) the types of nuclear reactor systems involved;
ii) the availability of natural uranium or other nuclear fuel resources

there remain, nevertheless, certain common features of the refining and conversion processes which are relevant to the industry as a whole and which merit inclusion in the agendas of future meetings of the Technical Committee.

In addition to future developments in the principal conversion process technologies, examples of issues of common interest identified as appropriate for future consideraton include:

1. Technology for refinery raffinate treatment and reagent recycle aimed at process economy and reduction of environmental impact;

2. The influence of factors such as equipment design and operating parameters on scale-up from laboratory to pilot plant to industrial scale;

3. The production, characterisation and quality control of nuclear fuel precursors such as uranium dioxide, in relation to the subsequent performance of the nuclear fuel;

4. Provision of opportunity for coordinated discussion, involving both regulators and operators on the methodology of the authorisation and control of radioactive and toxic effluent from uranium refining and conversion facilities;

5. The recycling of uranium recovered from the reprocessing of irradiated oxide fuels.

Already a number of utilities have contracted for the reprocessing of oxide fuels and significant quantities of recovered uranium will become available for reuse at the beginning of the 1990's. Factors influencing decisions regarding recycling or storage of this material of interest to existing convertors will include:

i. The evaluation of existing experience involving reprocessed uranium in:

    a. conversion to uranium hexafluoride (UF_6)

    b. enrichment of UF_6

    c. reconversion of UF_6 and fuel fabrication

    d. irradiation of fuel containing recycled uranium

ii. The prediction of the total quantities of and specification for the uranium which will arise from reprocessing operations. The levels of transuranic elements, fission products, ^{232}U and its daughters will be important in this context.

iii. The definition of feed and product specification for each stage in the sequence, reprocessed uranium to finished fuel.

iv. An assessment of the consequences of the foregoing on existing plants, processes and practices.

v. An evaluation of the comparative costs of fuel prepared from natural and recycled uranium.

In summary, there was general agreement amongst all participants that the Technical Committee Meeting had been a valuable forum for cooperation and information exchange between the Member States on the rapidly changing technologies at the front end of the nuclear fuel cycle.

However, in contrast to the historical situation where the major uranium convertors interfaced only with uranium suppliers and uranium enrichers the emergence of reprocessed uranium as a new factor in the fuel cycle had highlighted the need for a forum involving reprocessor, convertor, enricher, fuel fabricator and reactor operator to give effective consideration to the features of the closed fuel cycle which now have potential for impacting on each participant. The existing Technical Committee on uranium refining and conversion was not an appropriate forum for this purpose and the Division of Nuclear Fuel Cycle was invited to consider establishing such a forum.

The 1986 Technical Committee Meeting closed with a recommendation that the rapid rate of innovation in the fields of refining, conversion and nuclear fuel intermediate production technology would justify the convening of the next meeting in 3 years time in the Autumn of 1989.

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