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*WORKING GROUP "HOT LABORATORIES AND REMOTE HANDLING"
PLENARY MEETING 1985*

PURIFICATION OF NEUTRON-IRRADIATED HIGHLY-ENRICHED URANIUM
USED FOR PREPARING NUCLEAR ISOTOPES OF MEDICAL VALUE.

R. Boden, A. Daniëls, A.C. Demildt, P. De Regge, D. Huys, L. Sannen

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TEC/39.Z1904/X8800/24/LS/fq

May, 10th, 1985

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ABSTRACT

At the request of our colleagues of the "National Institute for Radioelements" (I.R.E.) at Fleurus, the hot cell laboratory (L.H.M.A.) of the Research Centre at Mol has stored during several years neutron irradiated uranium as $\text{Na}_2\text{U}_x\text{O}_{3x+1}$ precipitate.

As the stored quantity of the uranate was growing steadily (proportional to I.R.E.'s isotope production), it was proposed by I.R.E. that the nuclear centre should perform also chemical purification of this uranium. The prime condition however was that the purified uranium could be handled without shielding nor alpha containment (plutonium) precautions after the purification process.

This stored uranium has a ^{235}U enrichment of about 90 % and was irradiated during a maximum of 96 hours at a thermal flux of about $1.5 \times 10^{14} \text{ n.cm}^{-2}.\text{s}^{-1}$ (BR2 reactor and others), having a burn-up of about 20 Mwd.kg⁻¹.

Uranate batches of 500 g are dissolved in 9 M HNO_3 and diluted to 4 M HNO_3 . This solution is then contacted with a 30 % tributyl phosphate-dodecane solution in an 8 stage mixer-settler apparatus. The extracted uranium, still contaminated with small amounts of plutonium and some fission products, is then washed with 1.5 molar nitric acid in a second 8-stage mixer-settler mounted in series with the first one. Finally the back extraction is performed with a 0.01 M HNO_3 solution in a 12-stage mixer-settler.

After transfer of the uranyl nitrate solution from the hot cell to a glove-box, a last purification is performed by a supplementary solvent extraction with a solution of 0.5 M TTA (thenoyl - trifluoroacetone) in xylene using a separation funnel.

The final step consists of precipitating the uranium peroxide (yellow cake) by adding hydrogen peroxide after the acidity of the solution has been lowered with ammonium hydroxide (pH 2.8 to 3). The filtered yellow cake is then heated in a furnace to transform the peroxide to the black U_3O_8 powder, which is convenient to our customer (I.R.E.).

EXPERIMENTAL

The overall purification procedure is composed of three successive steps:

- the dissolution and preconditioning;
- the main extractive purification;
- the final purification and conversion.

The first two steps are performed in a hot cell equipped with master-slave manipulators, while the third step is conducted in a glove-box and a fume-hood.

1. Dissolution and preconditioning

To meet criticality safety, batches of maximum 550 g ^{235}U are handled at a time. So four inox containers are introduced in the hot cell and their contents are leached with boiling 9 molar nitric acid during 4 hours. The solution is filtered on a buchner (2.2 μm filter paper) and the remaining pulp is washed several times with 9 M HNO_3 .

To destroy the organic materials in the solution, hydrogen peroxide is added to the boiling filtrate. Then the solution is filtered a second time through a nucleopore filter (0.4 μm). This twofold filtration with the intermediate destruction of organic materials is necessary to obtain a clear uranyl solution (free from finally divided particles) which is suitable for feeding into the mixer-settler batteries without risk of suspension accumulations at the phase boundary.

The final uranium concentration and nitric acid molarity are adjusted to respectively \pm 0.9 M and 3.5 to 4 M by evaporation and addition of concentrated nitric acid. Typically a 2.5 liter solution with (530 g \pm 30 g)U and an acidity of 3.8 M HNO_3 is obtained.

2. Solvent extraction purification

The uranyl nitrate solution is decontaminated from the major part of the fission products by means of a liquid-liquid extraction with 30 % tributyl phosphate (TBP) in dodecane. This is performed in three serial mixer-settler batteries where the uranium is first separated, then purified and finally recovered as an aqueous uranyl nitrate solution. The flow sheet of this continuous solvent extraction process is given in [Fig.1].

The feed solution (HAF) is introduced at a rate of 50 ml/hour. The organic phase (30 % TBP/dodecane) at 200 ml/hour is scrubbed with 1.5 M HNO_3 at 25 ml/hour which is then combined with the main feed yielding a high level waste flowrate around 75 ml/hour. The high level waste is continuously evaporated to reduce the volume and is collected in the high active waste (HAW) storage tank. The distillate is collected in the low level waste (LLW) storage tank. The organic phase is stripped with 0.01 M HNO_3 at a flowrate of 285 ml/hour and collected in the organic waste storage tank (HCW). The stripping aqueous phase is fed into a continuous evaporator to concentrate the uranium. The distillate is discarded into a low level waste storage tank (LCW) and the uranium solution is collected into the transfer flask (HCP). This flask, typically containing 2.5 liter of solution, is transferred to a glove-box for further treatment.

In the first eight-stage mixer-settler battery (MSB1) the U is extracted in the organic phase. A feed solution with a high U concentration, leading to a high organic phase loading, and a high acidity is used to suppress crud formation and fission product co-extraction [1]. In the second eight-stage battery (MSB2) some fission products, still coextracted in the first mixer-settler battery (Zr-Nb), are scrubbed with a lower acidity solution. Since this scrub action is favoured at higher temperatures [2], the second battery is heated to 54° C. The low acidity feed solution of the third twelve-stage mixer-settler battery (MSB3) reextracts the U into the aqueous phase.

Foregoing solvent extraction process is performed continuously (three days + two nights) to reduce the residence time and hence degradation of the organic phase. During this period the hot cell is held under N_2 atmosphere to reduce fire risks.

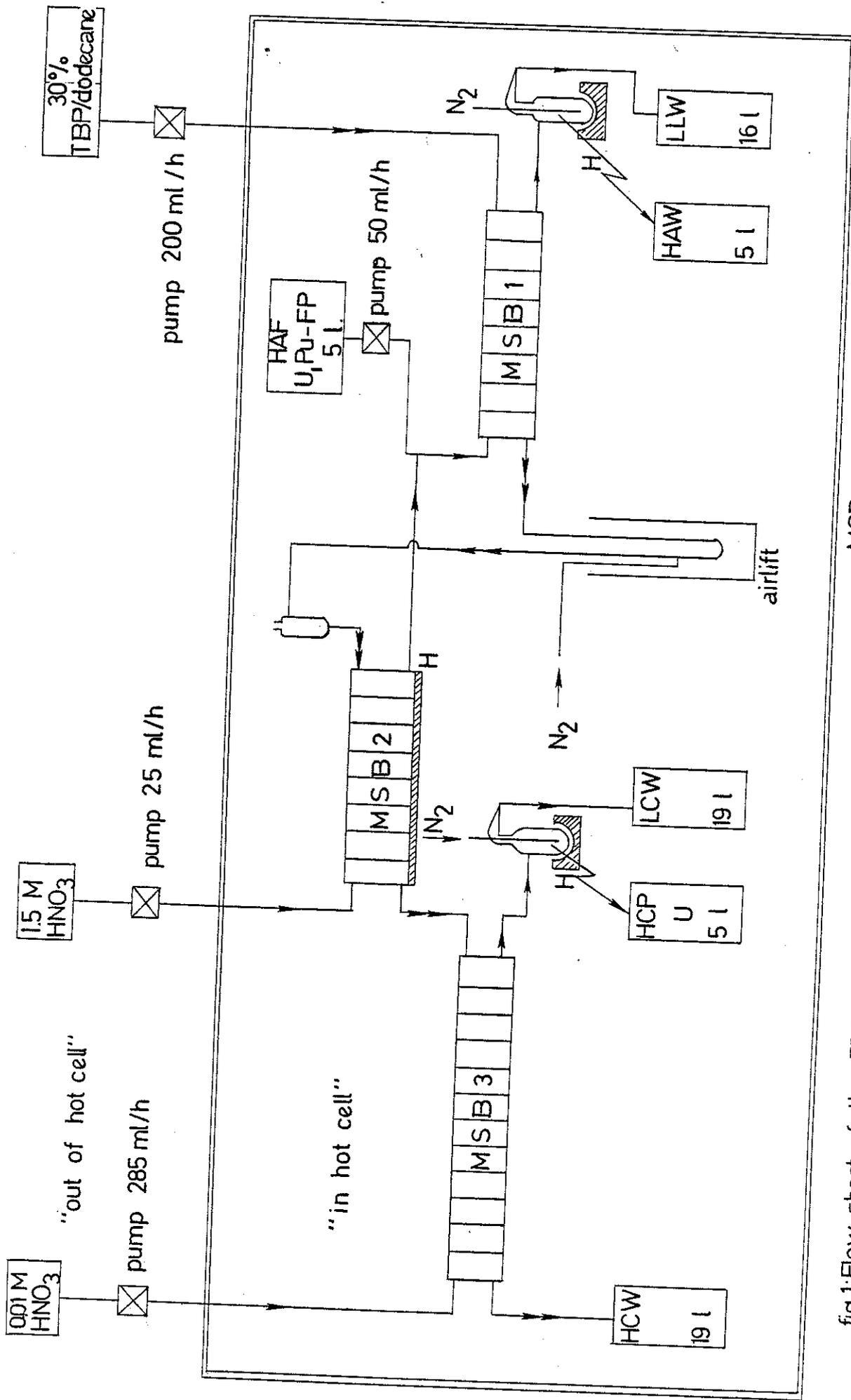


fig.1:Flow sheet of the TBP solvent extraction process

MSB = mixer settler battery
 H = heating jacket
 — = aqueous phase flow
 - - - = organic phase flow

The mixer-settler batteries used are of the pump-mix type (ERIES, France) with a set of well-defined stages each comprising a mixing chamber of 15 ml and a settling chamber of 49 ml. This allows an easy control of the distribution of a chemical compound throughout the set since no pollution occurs between adjoining stages. The general shape of the system is oblong. It consists essentially of a lower block containing the mixer volumes, the settler volumes, and connection piping, and an upper block containing the mixer drive gears and the volute-vaned impellers. This separate construction of a lower liquid enclosing part and a dismountable upper mechanical part is very useful when malfunction occurs. The horizontal arrangement of the stages permits interruption of steady-state operation and shut down for several hours without losing the concentration gradient in the battery, so that it can be restarted relatively easy. Besides these more specific benefits, also the general advantages of mixer-settlers have led to their use in this application, such as flexibility (only slow changes in performance with phase flow ratio and rates and hence easy adaptation to changing feed solution characteristics), high efficiency and reliability.

3. Final purification and conversion

The uranyl nitrate solution is transferred from the hot cell to a glove-box and is roughly divided into four equal parts containing approximately 130 g of uranium for further treatment.

First a batch extraction with a solution of thenoyltrifluoroacetone (TTA) in xylene is carried out to reduce the residual zirconium and plutonium contamination of the uranium [3,4]. Therefore 50 ml of a solution 0.5 M TTA/xylene is added and the mixture is stirred vigorously during 30 minutes. After the two phases have settled out, they are separated by use of a separation funnel. The organic phase is discarded and two more extractions with fresh TTA solutions are performed on the aqueous phase.

The uranyl nitrate solution is then buffered with ammonium acetate and adjusted to pH 2.8 as measured by means of a glass electrode. Hydrogen

peroxide (H_2O_2 35%, 1.2 ml/g U) is added to precipitate the uranium peroxide at a final pH of about 1.2. The precipitate is washed by decantation with buffered peroxide solutions composed of (per liter) 80 ml concentrated acetic acid, 50 ml H_2O_2 35%, 40 ml concentrated HNO_3 and neutralized to pH 1.2 with NH_4OH . Finally the precipitate is filtered on 7 μm filter paper. A final washing with water to remove the wash water salts is carried out and the precipitate is dried at moderate temperature by infrared radiation. The filter cake is then easily removed from the paper filter and transferred into a quartz beaker.

The uranium peroxide is decomposed into U_3O_8 by heating at 850°C in a furnace installed in a fume-hood during 16 hours. The black U_3O_8 is then transferred into tared plastic bottles and sealed for transport.

RESULTS

The purification of uranium is surveyed by analytical measurements to examine the chemical yields and decontamination factors in the different process stages. Uranium measurements by alphanetric methods in the dissolution phase were supported by mass spectrometric isotopic dilution analysis. Characterization of the final products was carried out by spark source mass spectrometry, gammaspectrometric analysis for total and radioactive impurities and high precision titration for the uranium assay.

The overall efficiency of the purification process is found to be better than 90% what is good considering the many process steps (dissolution, extractions, conversion) which are involved. The stoichiometry of the final U_3O_8 product is within 0.3% of the theoretical value.

A typical picture of the decontamination factors achieved for some radioactive contaminants in the different process stages is provided in table 2. The total β - γ activity of the purified uranium ranged from 90 to 180 nCi/g U, what is slightly higher than the specifications which are recommended by our customer (70 nCi/gU). The elements responsible for the residual contamination were not always the same but differed among the several batches which have been purified. Mainly, the following isotopes participate in the residual activity : ^{95}Zr (2 - 6 nCi/g U), ^{95}Nb (2 - 87 nCi/g U), ^{106}Ru (0 - 13 nCi/g U), ^{125}Sb (0 - 32 nCi/g U), ^{134}Cs (0 - 3 nCi/g U), ^{137}Cs (0 - 87 nCi/g U), ^{144}Ce (12 - 90 nCi/g U), ^{154}Eu (0 - 27 nCi/g U). No explanation can be found for the difference in residual contamination between the different batches which all have been treated identically. Also the Pu- and Th-contents of the final product was varying, from 8 to 53 $\mu g/gU$ for Pu and from 9 to 62 $\mu g/gU$ for Th. The low plutonium decontamination (see also table 2) is mainly due to the large quantities of zirconium (~ 8 mg Zr/g U) which are still present in the uranyl solution resulting from the TBP solvent extraction process. This zirconium is consuming most of the β -diketon in the thenoyltrifluoroacetone solvent extraction purification and consequently prevents the plutonium to be extracted from the uranyl solution.

Enhancement of the plutonium decontamination (down to 1 $\mu\text{g Pu/g U}$) will be obtained by improvement of the scrubbing action in the second mixer settler battery (optimum pH, larger flowrate and non recycling of the low acidity scrub solution) and of the thenoyltrifluoroacetone extraction (optimum pH, insertion of a reduction-oxidation cycle to convert all Pu to Pu (IV) and the use of more extractant).

The chemical purity of the U_3O_8 was very good since only a few elements were found to be present in quantities greater than 10 ppm :
P(8 - 80 ppm), S(2 - 150 ppm), Cl(3 - 70 ppm), K(2 - 70 ppm),
Zr(40 - 460 ppm). As a result, the total boron equivalency of all chemical contaminants does not exceed 1 ppm (the recommended limit equals 2.5 ppm).

From the above results it can be concluded that the purification of the highly enriched uranium was successfully both in view of the efficiency and the purity of the product obtained.

Table 2 : Decontamination factors achieved in the process steps

Operation	Pu	²⁴¹ Am	¹⁴⁴ Ce	¹³⁷ Cs	¹⁰⁶ Ru	¹²⁵ Sb	⁹⁵ Zr	¹⁵⁴ Eu
TBP extraction cycle	3.4	90	1.2x10 ⁶	1.04x10 ³	1.86x10 ⁴	4.2x10 ³	6.1	3.5x10 ²
TTA extraction	4.5	1.1	1	1.2	1.5	1.3	41.4	1
Peroxide precipitation	1	7	2	52	> 30	1	1	2.2
Total (measured)	11	6.8x10 ²	2.3x10 ⁶	6.26x10 ⁴	> 7.3x10 ⁵	5.8x10 ³	179	7.5x10 ²

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