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Advanced Course on Fuel Elements for Water Cooled Power Reactors

organized by the Netherlands'-Norwegian Reactor School
at Institutt for Atomenergi, Kjeller, Norway
22nd August-3rd September, 1960

Volume III

Lecture notes by

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C O N T E N T S

ADVANCED SUMMER INSTITUTE AT KJELLER

INTRODUCTION TO
AQUEOUS REPROCESSING OF URANIUM

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TABLE OF CONTENTS

INTRODUCTION TO AQUEOUS REPROCESSING OF URANIUM

by

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1. INTRODUCTION

In nuclear fuel cycles, the reprocessing step is of great importance for the economy of nuclear power. The processing of irradiated uranium fuel elements is concerned with separation and recovery of uranium and plutonium with efficient decontamination from fission products in order to facilitate refabrication into new fuel elements.

The removal of fission products involves the separation of a considerable number of elements with widely different chemical properties. Most of them are highly radioactive, which complicates the operation of the reprocessing plant, i.e. shielding of equipment, remote operation, removal of decay heat, radiation damage of solvents and materials of construction and disposal problems. In addition, critical masses of fissionable isotopes must be avoided, which may limit the batches being processed, equipment size or concentrations of the fissile isotopes.

The requirements for recovery and decontamination of plutonium and uranium (enriched fuel) are also very strict. Therefore, the processing of spent reactor fuels introduces many problems which become even more complex as the number of fuel element types increase, employing new materials and alloys in the core or the canning. In the years to come, the economic and safe reprocessing of nuclear fuels will present a real challenge to the chemist and chemical engineer.

In these introductory lectures, a short survey of the aqueous reprocessing methods will be given. Much emphasis will be laid upon the solvent extraction method, since this method is the most widely used. More comprehensive treatments of the various reprocessing methods are given in references (1), (2), (3), (4), (5), (6), (7) and (8).

2. NECESSITY OF THE REPROCESSING STEP

It might be appropriate first to discuss why it is necessary to reprocess the nuclear fuel. The main three reasons are:

1. Reactivity of the fuel becomes too low because of an accumulation of neutron absorbing fission products.
2. Reactivity of the fuel becomes too low because of consumption of fissionable materials, i.e. U-235, Pu-239, or U-233.
3. Physical damage either by corrosion or physical distortion under the heat, irradiation and strains produced by the fission process.

In standard power reactors, physical damage has generally been the most important factor in limiting the fuel life time. Of course, in special breeder or convertor-reactors other factors may be decisive, e.g. build-up of Pu-240 in Pu-239 or fission of converted fissile fuel.

The object of reprocessing is then to remove the fission products from the fuel elements and recover fissionable and fertile materials in a form which is suitable for further fabrication into fuel elements. If the spent fuel is to be refabricated by direct handling, i.e. without radiation shielding, it is necessary to reduce the concentration of fission products by a factor of 10^5 - 10^9 depending upon the burn-up ratio. Thus, for natural uranium which has been irradiated for 300 days, cooled for 100 days and with 0.1% burn-up, the required decontamination factor (D.F.) is 4×10^5. Because of the high value of fissile materials, the requirement to their recovery is usually as high as 99.9%. The necessary degree of separation of uranium and plutonium will depend on the fuel type and the fuel cycle to be employed.

3. COMPOSITION OF IRRADIATED URANIUM FUELS

Irradiated uranium fuels (unalloyed) contain, besides uranium isotopes and their radioactive decay products, plutonium and fission products. Plutonium is formed by the absorption of neutrons in U-238 according to the following equation:

$$(3.1)\quad {}_{92}U^{238}(n,\gamma){}_{92}U^{239} \xrightarrow[23m]{\beta} {}_{93}Np^{239} \xrightarrow[2.3d]{\beta} {}_{94}Pu^{239} \xrightarrow[24400y]{\alpha}$$

By absorption of neutrons in Pu^{239} small amounts of higher isotopes of plutonium are formed, Pu^{240}, Pu^{241}, Pu^{242}, and Pu^{243}. All of these are considered as reactor poisons, except Pu^{241}, which has a high fission cross section.

The fission products consist of all elements from zinc (atomic number 30) to gadolinium (atomic number 64), representing noble gases (Kr^{85}, Xe^{133}), alkalies (Cs^{137}), alkaline earths (Sr^{89}, Sr^{90}), halides (I^{131}), rare earths (La^{140}) and metals from groups 4, 5, 6, and 8 in the peridic system.

The composition of irradiated fuels will depend on type of fuel, neutron energy, irradiation time, neutron flux and cooling time. In Table 1 is listed the composition of natural uranium after 1000 MWD/tonne irradiation (for 300 days) and 100 days cooling time. It should be noted that the amount of plutonium formed is about equal to the total amount of fission products formed.

Some 200 isotopes have been detected in irradiated uranium fuels, as most of the primary fission-product pairs undergo several stages of β -decay. However, from a separation standpoint, it is the number of elements which counts. A considerable amount of the fission products are short-lived and decay rapidly. The fuel is usually cooled for 100 days or more in order to reduce the radioactivity of the fuel and the amount of unwanted isotopes, e.g. U^{237}, Np^{239}, I^{131}. With respect to plutonium recovery, this has also the advantage that all Np^{239} will decay to Pu^{239}.

The fission-product isotopes which cause the greatest separation difficulties in aqueous reprocessing methods are Zr^{95} (half-life 65 days), Nb^{95} (35 days), Ru^{103} (40 days) and Ru^{106} (1 year). Zirconium and niobium are amphoteric and exhibit complex hydrolytic properties, and they can form stable organic complexes which are soluble in organic solvents. Ruthenium is also amphoteric and may exist in all oxidation states from III to VIII. Like zirconium, ruthenium hydrolizes easily forming colloids which cause difficulties in the separation processes. The aqueous chemistry of ruthenium is very complex, and it forms complexes which are soluble in extractants used in reprocessing (see ref. 25 for a comprehensive review). In addition, ruthenium forms the volatile oxide RuO_4 under strongly

oxidizing conditions, and it may distill off during dissolving of the fuel. In view of the facts mentioned above, ruthenium is considered to be the most difficult fission-product element to remove by solvent extraction.

Gaseous or volatile fission products like Kr^{85}, Xe^{133} and I^{131} will normally be expelled with the off-gases from the fuel element dissolver. I^{131} (half-life 8.14 days) is only present in low concentrations, when the spent fuel has been cooled for 100 days. Iodine is usually removed from the off-gases by preheating the gas to 200°C and passing the gas through a contactor containing packing coated with silver nitrate.

4. METHODS OF SEPARATION

The methods are conveniently divided into two groups: aqueous and non-aqueous processes. The latter group includes: fractional distillation of fluorides, extraction with liquid metals or fused salts, vacuum volatilization of molten metals, oxidative slagging and electrorefining. All these methods are performed at high temperatures in non-aqueous media. They will be treated in detail in later lectures.

The aqueous methods comprise: precipitation, ion exchange and solvent extraction. The precipitation method is not used at present on a larger scale. But it is of historical interest since it was the first method which succeeded in separating plutonium from uranium on a larger scale, see ref. (9) for a historical description of the bismuth phosphate process. This process utilizes $BiPO_4$ and LaF_3 as alternate coprecipitation agents. Fission products and Pu(IV) are coprecipitated with these agents, but not Pu(VI) and UO_2^{2+} (complexed with SO_4^{--}). After a series of coprecipitations and dissolutions (in nitric acid) changing the valence state of plutonium every second time, 95% of plutonium could be recovered with an over-all decontamination factor of 10^8. However, no uranium was recovered.

Ion exchange has been used as a complete separation process for spent fuel at Chalk River in Canada (10). In this process a strong nitric solution (7,5M HNO_3) of the irradiated fuel is passed through an anion exchange column where Pu(IV) is adsorbed as nitrato anionic complex ($Pu(NO_3)_4^{--}$). The fission products and most of the uranium

pass through the column. The decontamination from uranium and fission products is further increased by washing the resin with 7,5 M nitric acid. Finally, plutonium is eluted from the column with a weak solution of hydroxylamine, reducing Pu(IV) to Pu(III), which is not retained by the resin. A less effective eluant is weak nitric acid (< 1 M).

After concentrating the eluate by evaporation, plutonium is re-oxidized by boiling 7.5 M nitric acid, and the cycle repeated. With this method decontamination factors of 2×10^5 for uranium and 5×10^4 for fission products (γ) have been obtained.

Ion exchange has found more widespread use in the purification and concentration of plutonium in the effluents from solvent extraction separation processes, and in the treatment of low-active wastes. This is partly due to the fact that organic ion-exchange resins are subject to radiation damage in fission-product solutions. The situation might change if more radiation-resistant resins could be developed. There is also much interest in the use of inorganic exchangers, e.g. silica gel, see ref. 11.

Solvent extraction is by far the method which has found most widespread use for processing irradiated fuels, and it is the only method which is being used in large-scale reprocessing plants in the Western World. At present, the following reprocessing plants are using solvent extraction methods: Savannah River, Hanford, Idaho Falls and Oak Ridge in the U.S., Windscale and Dounreay in Great Britain and Marcoule in France. Solvent extraction will be treated in more detail in the following chapters.

5. PRINCIPLES OF SOLVENT EXTRACTION OF METALS

5.1. General Principles

Solvent extraction, or liquid-liquid extraction, is based on the fact that the components to be separated have different distribution coefficients between two liquid phases. Normally, one phase is aqueous, and the other is an organic liquid, which is nearly immiscible with the aqueous phase. The distribution coefficient D is generally defined as:

$$(5.1)\quad D = \frac{\text{Conc. of component in organic phase}}{\text{Conc. of component in aqueous phase}}$$

For sake of brevity, the following symbols are often used for a particular component K_i:

$$(5.2)\quad D = \frac{[K_i]_o}{[K_i]_a} = \frac{C_{K_{i,o)}}}{C_{K_{i(a)}}}$$

When the solute exists as the same molecular species in the two phases, the distribution or partition coefficient is a constant when the solutions are ideal (Nernst's distribution law). This is not the case in aqueous processing, where the distribution coefficient will depend upon the concentration of solute, concentration of hydrogen-ion, and concentration of complexing and salting agents (if such agents are used).

Metals dissolved in aqueous solutions exist in the form of charged ions which, normally, are not extractable into an organic solvent. To render the metal extractable, it seems to be necessary that the metal ions are capable of forming an electrically neutral coordination (or solvation) compound with the solvent or with an added complexing agent. Anions in the aqueous phase may also take part in the complexing reaction. As an example, one can take the extraction of Pu(IV) with tributyl phosphate (TBP) from nitric acid solutions. The solubilization reaction can be written as:

$$(5.3)\quad Pu^{4+}_{(a)} + 4NO_3^-{}_{(a)} + 2TBP_{(o)} = Pu(NO_3)_4 \cdot 2TBP_{(o)}$$

with the following equilibrium constant (brackets indicating concentrations):

$$(5.4)\quad K_{Pu} = \frac{[Pu(NO_3)_4 \cdot 2TBP]_{(o)}}{[Pu^{4+}]_{(a)}\,[NO_3^-]^4_{(a)}\,[TBP]^2_{(o)}}$$

The distribution coefficient is:

$$(5.5)\quad D_{Pu} = \frac{[Pu(NO_3)_4 \cdot 2TBP]_o}{[Pu^{4+}]_{(a)}}$$

By combining equations (5.4) and (5.5) one obtains:

$$(5.6)\quad D_{Pu} = K_{Pu} \cdot [NO_3^-]^4_{(a)} \cdot [TBP]^2_{(o)}$$

Thus, the distribution coefficient should increase with increasing concentration of nitric ions (mechanism of salting agent) and concentration of uncombined TBP.

It should be noted that the TBP-solvent acts as a complexing agent forming a "saturated" compound in which all coordinate and ionic valences are internally satisfied through bonding with the metal, see fig. 3. Such a molecule exerts only a weak van der Waals type of attraction for other molecules, and for this reason would be expected to be soluble in solvents of low polarity, such as kerosene.

To form such coordination compounds as shown in fig. 3, there must be available empty electron orbitals of comparatively low energy, such as in elements of the transition groups, rare earths and the actinides. The alkalies and alkaline earths have no such empty orbitals, and these elements are, therefore, very little extracted by nonpolar organic solvents.

Solvent extraction is an attractive method for recovering and purifying a wide variety of reactor fuel materials. Because no solid phases are involved, it is readily adapted to continuous and counter-current contacting with remote control of the flows. It is a well-known chemical engineering operation, and hence will not be discussed to any great extent in these lectures. For a more complete treatment, it is referred to (1, chapter 6) and engineering textbooks, such as (12).

The principles of counter-current solvent extraction are shown in fig. 2A. The heavier, aqueous phase (e.g. a dissolver solution) is introduced in the middle of the column, and the lighter organic solvent at the bottom. In the column the organic solvent is intimately contacted with the aqueous feed, whereby the components in the feed (e.g. Pu, U, F.P.) will distribute themselves between the phases according to their relative solubilities or distribution coefficients. The components with high distribution coefficients will concentrate in the organic phase (e.g. U and Pu), whereas the components with low distribution coefficients will concentrate in the aqueous phase (e.g. fission products). Thus, a separation of the components in the feed solution has been achieved. The organic

extract, containing the solvent-extractable compounds (e.g. U, Pu) is removed at the top, whilst the depleted aqueous raffinate, containing the less-extractable compounds (e.g. fission products) is removed at the bottom. To further increase the separation, the organic phase is scrubbed with a suitable aqueous solution, in order to back-extract less-extractable compounds.

The extraction column is usually packed with Raschig rings, or equipped with perforated plates, and very often one of the phases is pulsed, in order to increase the contact area and break up droplets of the dispersed phase.

The principle of a mixer-settler, fig. 2B, is the same as for an extraction column. The contacting of the two phases is brought about by mechanical agitation in a separate mixer. The two phases are led from the mixer into the settler where the phases are separated. By connecting the mixer-settler units in series, as shown in fig. 2B, the extraction can be performed as a multistage countercurrent operation.

For calculation of extraction columns, the scrub and extraction sections are divided (hypothically) in stages, as in a mixer-settler, and it is assumed that extraction equilibrium is reached within one stage (theoretical stage). In the extraction section, the following material balance can be made for any one of the components below an arbitrary state n:

$$(5.7) \quad (S + F)\, x_n = E y_{n-1} + (S + F)\, x_R$$

$$(5.8) \quad y_{n-1} = \frac{S + F}{E} \, (x_n - x_R)$$

where F, S and E are the flows in litres per hour of feed solution F, scrub solution S and organic solvent or extract E; x and y are the molar concentrations of the more extractable compound in respectively aqueous and organic phase. It is assumed that the phases are completely immiscible and constant volume flow rates.

For each stage we have the following equilibrium relation:

$$(5.9) \quad y_n = D_n \cdot x_n$$

where D_n is the distribution coefficient at the conditions of n'th stage.

(5.8) is the equation of the operating line relating the concentration of aqueous phase (x_n) leaving and organic phase (y_n -1) entering stage n, whereas (5.9) relates the concentrations of aqueous phase (x_n) and organic phase (y_n) leaving stage n.

By employing equations (5.8) and (5.9) it is possible to correlate the concentrations throughout the column (or mixer-settler bank) and calculate the necessary number of stages for a certain separation. This may be performed graphically by the McCabe-Thiele method, as illustrated in fig. 2C. This calculation can also be performed by a stepwise algebraic procedure. If the concentration of the aqueous raffinate, $x_R = x_1$, is known or assumed, the composition of the organic phase y, leaving stage 1 can be calculated by equation (5.9), $y_1 = D_1/x_1$. The concentration of aqueous phase leaving stage 2, x_2, can now be calculated by equation (5.8):

$$x_2 = \frac{E}{S + F} \quad y_1 + x_1$$

The concentration of organic phase leaving stage 2, y_2, can again be calculated from equation (5.9) and, thus, the procedure can be repeated up to the top stage in the extraction section, the feed stage. If no scrub section is used, the composition of the aqueous phase entering the feed stage is $x_F = x_{n+1}$. In this way, the number of stages which are required to reduce the concentration from x_F in the feed to x_R in the raffinate can be calculated.

If the distribution coefficient is constant, the following equation can easily be derived for calculation of the number of stages n:

$$(5.10) \qquad \frac{x_F}{x_R} = \frac{x_{n+1}}{x_1} = \frac{R^{n+1} - 1}{R - 1}$$

where R, called the extraction factor, is defined by

$$(5.11) \qquad R = D \cdot \frac{E}{S + F}$$

5.2. Selection of Solvent

According to Benedict and Pigford (Ref. 1, page 219) a solvent suitable for solvent extraction of metals should meet the following requirements:

1. It should be selective; i.e. the ratio of distribution coefficients should be high.
2. It should have good capacity for extraction; i.e., distribution coefficients in the extraction section should be of the order of unity or higher.
3. It should be readily stripped for metals; i.e. distribution coefficients in the stripping section should be no greater than unity.
4. It should be relatively immiscible with water, to reduce solubility losses.
5. Its density should be appreciably different from water, and it should have low viscosity and fairly high interfacial tension, in order to obtain good phase separation and easy flows of the two phases.
6. For safety reasons it should be relatively nonvolatile, non-inflammable and nontoxic.
7. It should be readily purified, preferably by fractional distillation.
8. It should be stable with respect to radiation, temperature and chemicals employed, such as nitric acid.
9. It should be cheap.

In Table 2 are listed some extractants which can be used in processing nuclear fuels. Of the organic solvents, ketones generally give the most efficient extraction, followed by ethers, ether-esters, esters, alcohols, aldehydes and nitroparaffins in descending order of efficiency. Hydrocarbons and halogenated hydrocarbons give neglible extraction when no complexing agents are present.

The solvents most frequently used in processing nuclear fuels are methyl isobutyl ketone (Hexone), dibutyl carbitol (Butex) and tributyl phosphate (TBP). The important "Purex" solvent extraction involves the use of TBP, and this method will be described more extensively in Chapter 8.1. TBP meets many of the above-mentioned requirements except requirement 5 and partly 3, 7 and 8. In order to reduce viscosity and density and improve stripping properties, TBP is generally diluted with a saturated hydrocarbon, such as kerosene. The main reasons for the use of TBP is its remarkable selectivity and

the fact that it employs a liquid "salting" agent, nitric acid, which is recoverable.

5.3. Aqueous Chemistry

The aqueous chemistry of the elements present in irradiated fuels is, of course, of great importance for the understanding of the various solvent extraction processes, since these are aqueous feed solutions. The electronic configuration of some important elements is given in Table 3.

The chemical behaviour of elements is dependent on the number of electrons in the outermost shells. The transition elements start with $_{21}Sc$ when the 3d orbitals are filled, the rare earths with $_{57}La$ when 4f orbitals are filled (and 5d with one electron), the actinide series when 5f orbitals are filled (and 6d with one or two electrons). The rare earths, or the lanthanide series consists of 15 elements which have similar chemical properties. They all form trivalent positive ions in aqueous solutions. This is due to the filling of the 4f orbitals, which are too deep within the atom to have any significant influence on the chemical properties.

The chemical properties of the actinides are not so similar as those of the lanthanides, because the differences in energy levels between 7s, 5f and 6d orbitals are much smaller than for the 6s, 4f and 5d orbitals. The 5f and 6d orbitals are also further displaced from the nucleus than 4f and 5d orbitals. It is believed that these properties of the 5f and 6d orbitals may explain the great tendency of the actinides to form complexes and stable coordination compounds and undergo hydrolysis; for a more complete description see (37).

5.3.1 Hydrolysis of Ions

Uranium and plutonium may exist in oxidation states 3, 4, 5 and 6 in aqueous solutions. However, ions of the highest oxidation state are always hydrolized to form cations of the type MO_2^{2+}, according to the reaction:

$$(5.11) \quad M^{6+} + 2H_2O = MO_2^{2+} + 4H^+$$

The general hydrolysis reaction might be represented as:

$$(5.12) \quad M^{q+} + nH_2O = M(OH)_n^{(q-n)+} + nH^+$$

where n may be greater than q. The tendency towards hydrolysis

increases with the increasing ratio of charge/ionic radius (the columbic attraction forces are proportional to Z^2/r). Thus, for a given element, this tendency increases according to:

(5.13) $MO_2^+ < M^{3+} < MO_2^{2+} < M^{4+}$

or for tetrapositive ions:

(5.14) $Th^{4+} < U^{4+} < Pu^{4+} < Zr^{4+}$

The hydrolysis products may precipitate as metal hydroxides or polymerized products where the metal atoms are bonded together by oxygen or hydroxyl bridges. The polymerization is often irreversible and it may require prolonged heating with concentrated acid to dissolve the polymerization products. With a low degree of polymerization the hydrolytic products often exist as colloids. The hydrolytic behaviour is somewhat unpredictable and it quite often causes difficulties in the separation of the metals.

5.3.2 Complex Formation

The tendency of cations to form complexes in aqueous solutions is in certain respects analogous to the tendency towards hydrolysis. Thus, the complexing tendency of a metal ion is greater the greater its charge and the smaller its radius. This similarity becomes more apparent when the following reactions are compared:

(5 15) $M^{4+} + A^- = MA^{3+}$

(5.16) $M^{4+} + OH^- = M(OH)^{3+}$

(5.17) $M^{4+} + HA = MA^{3+} + H^+$

(5.18) $M^{4+} + H_2O = M(OH)^{3+} + H^+$

where HA is the acid of a complexing anion A^-

The tendency of anions to complexes increases in the order

$$ClO_4^- < Cl^- < NO_3^- < SO_4^{--} < PO_4^{3-} < F^-$$

The presence of such anions as F^-, PO_4^{3-} and SO_4^{--} complexe uranium and plutonium so strongly that they inhibit the extraction of these metals with organic solvents. Comprehensive tables of the stability

constants of the complexing of metals with organic and inorganic ligands have recently been issued (13).

5.3.3 Oxidation-Reduction Properties

In the Purex processes it is of utmost importance to keep the various elements in the proper valence state, e.g. in the first solvent contactor plutonium must be tetravalent and uranium hexavalent, whereas in the second contactor, plutonium must be trivalent and uranium hexavalent.

The oxidation-reduction behaviour can be calculated if the oxidation-reduction potentials of the half-couples are known. The following red-ox potentials are very important in reprocessing (14):

(5.19) $Pu^{3+} = Pu^{4+} + e^-$, $E^0 = -0,9819$ volts

(5.20) $Fe^{2+} = Fe^{3+} + e^-$, $E^0 = -0,7714$ volts

(5.21) $U^{4+} + 2H_2O = UO_2^{2+} + 4H^+ + 2e^-$, $E^0 = -0.334$ volts

Pu^{3+} has the largest negative potential of the three elements, which means that Pu^{4+} is more easily reduced than Fe^{3+} which again is more easily reduced than UO_2^{2+}. Therefore, by employing Fe^{2+} as a reducing agent, Pu^{4+} will be reduced but not UO_2^{2+}. The overall reaction of this reduction is:

(5.22) $Pu^{4+} + Fe^{2+} = Pu^{3+} + Fe^{3+}$

The equilibrium constant is:

$$(5.23) \quad K = \frac{[Pu^{3+}]\,[Fe^{3+}]}{[Pu^{4+}]\,[Fe^{2+}]}$$

This constant can be calculated from the Gibbs-Helmholz equations:

(5.24) $RT \ln K = -\Delta F^0 = nFE^0$

where ΔF^0 is the change in standard free energy, F is Faraday's constant and n is the number of electrons transferred.

The standard potential of reaction (5.22) is 0,9819 - 0.771 = 0,211 volts which gives a reaction equilibrium constant of K = 3700. In 1 M nitric acid this constant is equal to 330(1).

6. Solvent Extraction Processes

Richards has divided the aqueous reprocessing procedure as follows (15):

1. Following irradiation, arrangements must be made to deliver irradiated elements to separations facilities.
2. Processing starts by removing the cladding, dissolving the metal, and preparing the feed for separation and decontamination.
3. Separation of the key elements and their decontamination from fission products.
4. Concentration and purification of products, usually involving a reduction in volume.
5. Conversion to salts and/or metal, completing the cycle to the metal.
6. Refabrication into fuel for re-use.
7. Disposal of gaseous, liquid, and solid wastes.

The dissolution step, step 2, has already been described in this course by A. Hultgren. Preparing and conditioning of the feed for solvent extraction will be discussed in the following chapter and in connection to the various flowsheets. It is assumed that the uranium core material has been dissolved in nitric acid. Step 3 will be treated under the description of various processes. Steps 4 and 5 will be discussed very briefly in chapter 7, and steps 6 and 7 are beyond the scope of this lecture. The tail-end purification of plutonium will be further discussed by Chesnè.

6.1. Feed Conditioning

After dissolution in nitric acid the uranium core material will be in the form of nitrates. The solution may contain metal ions from the alloy metals, from the canning material, and the bonding agent, if the uranium is alloyed or the canning dissolved together with the core. The feed solution must be pretreated and adjusted for the particular extraction process to be used.

All solid particles should be removed from the feed solutions in order to avoid troubles in feed lines, pumps, valves, and phase separation (emulsification, crud). These particles may be corrosion products or siliceous residues originating from the bonding between core and canning or from silisium originally present in uranium. The

particles may be removed by filtration, e.g. by sandfilters. However, the siliceous precipitates are slimy or gelatinous and they easily plug the filters. To increase filterability, gelatin might be added (34). Blanco reports removal of these residues by centrifugation at 1500 r.p.m. (16).

The feed solution must be adjusted for the content of uranium, free acid and salting agents (if such are used). In some processes, the feed solution is made acid-deficient, i.e. the acidity is less than that resulting from the hydrolysis of the main metal constituents in the solution, e.g. uranium and aluminium (salting agent). The solution can be made acid-deficient by the addition of a base or by destruction of nitric acid by heating. Also, it is imperative to adjust the valence state of plutonium before extraction. In the Redox process all plutonium is oxidized to the hexavalent state, i.e. PuO_2^{2+}, to prevent hydrolysis and increase extractability of this element. At the same time, the feed-solution is made acid-deficient to allow elements like zirconium and niobium to hydrolize to less extractable species. In the Purex process, plutonium is maintained in the tetravalent state as Pu^{4+} forms the most extractable compound with TBP. This is achieved by the addition of nitrite ion (HNO_2 or $NaNO_2$), according to the reactions:

(6.1) $Pu^{3+} + NO_2^- + 2H^+ \longrightarrow Pu^{4+} + NO + H_2O$

(6.2) $PuO_2^{++} + NO_2^- + 2H^+ \longrightarrow Pu^{4+} + NO_3^- + H_2O$

The pretreatment of the feed solution may also give partial decontamination from fission products. Harmon and Culler describe processes in which permanganate is added to coprecipitate fission products, notably Zr and Nb (17), (18). By heating and by the intense radiation the permangate is reduced to a MnO_2-precipitate, which removes 90-99% of both Zr and Nb, 1-10% of Ru and 40% of Ce, but not UO_2^{2+} and Pu^{2+}. The precipitate is separated from the feed by a centrifuge. This pretreatment is also effective in scavenging fine solids.

The feed conditioning may also involve removal of ruthenium which is the most troublesome element to remove by solvent extraction. This has been accomplished by oxidation with ozone or permanganate which oxidizes Ru to RuO_4 which is volatile (B.p $\sim 101^\circ C$) and can be

removed by sparging with air (or N_{21}, steam) at 90° or by boiling of the solution. The RuO_4 is stripped from the gas by scrubbing with 10-20% NaOH. This treatment will remove up to 95% of the ruthenium present in the feed. Of course, the removal and safe disposal of RuO_4 will introduce additional problems.

6.2. Purex and TBP Processes

The Purex process was developed for the separation of plutonium, uranium and fission products in natural uranium fuel elements (19), (24). The process employs tributyl phosphate (TBP) as solvent and nitric acid as salting agent. Therefore, it is often referred to as the TBP process. Modified versions of the process are now being used for reprocessing of enriched uranium fuels (18), uranium-aluminium alloy fuels (20) and uranium-zirconium alloy fuels (21). Detailed descriptions of the Purex process are also given by Irish and Reas (22) and Irish (23).

The standard Purex flow sheet according to Flanary (19) is shown in fig. 1. In the first cycle, uranium and plutonium are separated from the fission products by contacting the feed with TBP (in a diluent) in the first extraction column. The aqueous raffinate, containing the bulk of the fission products, is drawn off at the bottom as waste. The organic phase, nearly saturated with uranium, is scrubbed in the upper part of the column with a nitric acid solution to backwash any fission products, and led to the partition column. In this column, the organic stream is contacted with dilute nitric acid containing a reducing agent, such as ferrous sulphamate or hydroxylamine. Plutonium is thus reduced to the much less extractable trivalent state which is stripped from the phase. The organic product from the partition column is scrubbed with water in the stripping column to strip out uranium.

For further decontamination, both the uranium and plutonium product from the first cycle are passed through a second cycle, as shown in fig. 1. The final decontamination is accomplished by passing the uranium stream through a silica gel column and the plutonium stream through a cation exchange resin.

Decontamination factors obtained by the Purex process with a 2-cycle flow sheet, are given by Flanary (19) as follows:

	U	Pu
Gross : γ	$2,7 \times 10^6$ ($6,5 \times 10^6$)	2.0×10^6 (1.6×10^7)
Gross : β	6.6×10^6 (9.9×10^6)	$7,7 \times 10^6$ ($3,2 \times 10^7$)

The numbers in parenthesis refer to decontamination after silica gel treatment of uranium and ion exchange treatment of plutonium.

A simplified Purex flow sheet is shown in fig. 4. This is a one-cycle process which is going to be used in the reprocessing pilot plant at Kjeller. The flow sheet gives more detailed information on process conditions and flow compositions The solvent is 20% TBP in Shellsol. With a flow ratio solvent: feed of 4,5: 1 and a uranium concentration of 1,25 M this corresponds to 76% uranium saturation of the solvent, i.e. percentage TBP needed to complex uranium in the feed to $UO_2(NO_3)_2 \cdot 2TBP$. It has been shown by several investigators that the distribution coefficients of the fission products will decrease with increasing uranium saturation of the solvent. The concentration of nitric acid employed in the feed solution of fig. 4 is 3.0M HNO_3. The distribution coefficients for the various fission products will increase with increasing acid strength, except for ruthenium; see ref (26) which gives a comprehensive survey of distribution data. For the extraction column I (fig. 4), which contains 5 theoretical stages, it is calculated that the distribution coefficient (org/aq) will increase from the feed-stage to the bottom stage as follows: Du from 1,36 to 30, D_{Pu} from 0,5 to 10, D_{Ru} from 0,0015 to 0,06 and D_{Zr} from 0,0042 to 0.05.

There now exist quite a variety of TBP processes adapted for the specific type of fuel elements. Ref (8) gives extensive descriptions of the reprocessing facilities at Hanford (less than 5% U^{235}), Idaho (highly enriched),Savannah River and Oak Ridge. Among the fuel types to be treated are (cladding material in parenthesis): U (Al), U-Al(Al), U-Zr(Zr), UO_2-SS(SS), UO_2(Zr), UO_2(Al), and U-Mo(Zr).

As may be expected, major improvements have been achieved in the TBP processes in recent years. Among these might be mentioned:

back-cycling of aqueous waste streams (27), dual-temperature TBP process (28), anion-exchange purification of plutonium (29).

6.2.1 Solvent Purification

Tributyl phosphate is an ester which may hydrolize to form dibutyl (DBP) and monobutyl (MBP) phosphates and butanol. Small concentrations of these degradation products will cause difficulties in the extraction operations (F.P. rentension) DBP and MBP have active hydrogen and oxygen (electron donor) atoms and they are strong chelating agents. DBP forms strong, organic-soluble complexes with fission product, especially Zr_1, which are difficult to scrub out from the organic phase. MBP forms precipitates with uranium and plutonium

The rate of hydrolysis of TBP is mainly determined by hydrogen ion concentrations and temperature and radiation, but traces of DBP and MBP are also present in commercial TBP. Fortunately, they are acids and can be removed by washing with sodium carbonate solution, preferentially at higher temperatures ($45^{o}C$). Traces of complexed fission products are removed at the same time. However, radio colloids are often formed. Therefore, manganese dioxide is often used as a scavenging agent. Finally, the solvent is washed with dilute nitric acid to remove dissolved alkalies.

6.3. Redox Process

The Redox process employs hexone (methyl-isobutyl ketone) as solvent and $Al(NO_3)_2$ as salting agent. Hexone is not stable to high concentrations of nitric acid, which, therefore, cannot be used as the sole salting agent. As the name Redox implies, a reduction-oxidation cycle is used for the separation of uranium and plutonium.

The process is very similar to the Purex process. The principal separations are performed in three extraction columns as in the first Purex cycle. However, as mentioned earlier, plutonium is oxydized to the hexavalent state by addition of sodium dichromate, because this valence state is best extracted by hexone. Also, the feed solution is made acid deficient to form hydrolized species of the fission products (Nb, Zr).

The salting agent is added in the scrub as a 2.0 M solution. The feed is generally of following composition: 2.0 M $UO_2(NO_3)_2$, 0,2 M HNO_3, 0,1 M $Na_2Cr_2O_7$ and 0,38 M $NaNO_3$ (30).

The decontamination factors obtained are generally of the same order as in the Purex process, with the exception of the decontamination from ruthenium. The main disadvantage of the Redox process is the use of a metal salt as salting agent. This sets a limit for the reduction in volume of the fission product waste.

6.4. Other Processes

A variety of other solvent-extraction processes have developed. They differ mainly from the TBP-processes and Redox-process in the use of solvent, such as dibutyl carbitol (Butex), dibutyl ether or thenoyl-trifluoracetone (TTA-chelation process).

The Butex process was developed at Windscale and it is described in ref (2). This method uses a 3-column extraction process with plutonium reduction in the second one. Nitric acid is used as salting agent, employing a feed 3N in nitric acid. Thus, the process is very similar to a one-cycle TBP process. However, the decontamination from Ru and Zr is reported to be low.

The Russian dibutyl ether process is described by Vdovenko and Kovalskaia (31). The solvent is an explosion-proof mixture of dibutyl ether (85 mls/100 mls) and carbon tetrachloride, and calcium nitrate is used as salting agent. A 3-cycle extraction is employed with the common ox-red cycle for plutonium. Decontamination factors of $1{,}2 \times 10^6$ for the uranium product and 8×10^4 for the plutonium have been achieved (31). In recent laboratory studies, a decontamination factor of 2×10^7 has been obtained (32).

The TTA-chelation process uses a solution of TTA in benzene as solvent (18). TTA is a substituted diketone, the enol form of which is a weak acid (HK) and strong chelating agent. The chelation of Pu^{4+} (or Zr^{4+}) may be represented schematically as follows:

$$Pu^{4+} + 4HK = PuK_4 + 4H^+$$

It can be shown that the distribution ratio for plutonium is:

$$(6.4) \qquad D_{O/W} = \frac{K_f \left[HK\right]_O^4}{\left[H^+\right]_W^4}$$

where K_f is the equilibrium constant or stabilibility constant for reaction (6.3).

In this process Pu^{4} and Zr^{4+} are extracted into the solvent, but not UO_2^{2+} at the employed acid strengths. Plutonium is stripped with nitric acid containing Fe^{2+} and zirconium with oxalic acid. Uranium is separated from the fission products by extracting with TTA at lower acidities and back-extracted with nitric acid. The disadvantage of this process is that the rate of chelation is slow, which necessitates large contacting equipment.

7. TAIL-END TREATMENT AND RECOVERY

After solvent extraction decontamination the plutonium and uranium must be further purified. For plutonium this is done by ion exchange, and for uranium by sorption on cation resins or silica gel(33).

Cation exchange was originally used in the Purex for further decontamination of plutonium (18). The feed to the ion exchange column is the weak HNO_3 solution (acidity varies from 0.15 M to 0,5 M) that has been used to strip the Pu from the organic solvent. The Pu concentration may be as low as 0,1 and as high as 10 g/l. The feed contains hydroxylamine, which was added to reduce the Pu(IV) to Pu(III). Principal impurities are U, fission products (Zr/Nb, Ru and Ce) and corrosion products. The solution is passed through a cation resin column (Dowex-50) where the Pu is adsorbed in a band above the U. The U is eluted downwards with 0.25 M H_2SO_4 containing some hydroxylamine to maintain the Pu in the trivalent state. The Pu is then eluted upwards by 5.7 M HNO_3 - after a "spacer wash" - containing some sulphamic acid (0,3 M) to inhibit the ox. of Pu(III) to Pu(IV) by the acid.

The concentration of the Pu in the product is about 50 g/l. This product is now ready for further treatment in α -glove boxes.

Recently, an anion exchange method has been described by Ryan and Wheelwright (29) which is applicable to plutonium containing effluents. In this process, a strong acid solution (7.2 M) is passed through the resin, where Pu(IV) is adsorbed as nitrato anionic complex, whereas most of uranium and fission products pass through. In principle, the method is identical to that described in

(10). However, by operating at elevated temperatures (50 to 60°C) and by proper choice of anion exchange resins, throughputs may be increased considerably, product concentration is increased, decontamination improved, and the use of reagents other than HNO_3 eliminated. Pu is eluted from the column using 0.3 - 0.8 M HNO_3 (depending on the type of resin used) instead of hydroxylamine used in (10). Adsorption and elution flow rates as high as 80 mg Pu/min/cm^2, decontamination factors of greater than 5×10^3 for fission product and greater than 5×10^4 for U and other metallic impurities, and product concentrations of above 50 g Pu/l are readily attainable in a single anion exchange cycle under proper operating conditions. The method is both chemically and mechanically simple.

The various aqueous effluents from solvent extraction processes mentioned in chapter 6 all contain nitric acid. Dilute solutions can easily be concentrated in nitric acid by evaporation. At higher concentrations, nitric acid becomes more volatile and can be recovered, e.g. by evaporating the waste fission product solution.

The final step in aqueous reprocessing of uranium fuels is the conversion of uranium and plutonium nitrate salts to the metal or oxide. Plutonium is not recovered from highly enriched uranium fuels. The conversion chemistry of plutonium nitrate has recently been reviewed by Harmon and Reas (35). The dilute Pu-nitrate solution is first concentrated up to 10-100 g Pu/litre by evaporation, ion-exchange or solvent extraction. Plutonium is then precipitated from this solution as Pu(III) or Pu(IV) oxalate or peroxide. These salts are then converted to PuF_4 by calcining the precipitates to PuO_2 and hydrofluorination by HF. The final reduction is accomplished by reacting with calcium metal at temperatures up to 1600°C. Plutonium may also be precipitated as PuF_3 or $CaPuF_6$ which can be reduced directly to metal with calcium.

Uranium is converted to the metal by methods similar to those described for plutonium, or methods used in the production of uranium from ores. Uranium is usually precipitated from the nitrate solution as peroxide (UO_4) or ammonium diuranate $(NH_4)_2 U_2O_7$). These compounds are then calcined to UO_3, which may also be obtained by direct calcination of uranyl nitrate. UO_3 is then reduced to UO_2 by hydrogen

or ammonia gas. UO_2 is converted to UF_4 by reacting with HF. The uranium metal is obtained by reduction of UF_4 with calcium or magnesium. By the recently developed "Flurex" method (36), uranyl nitrate may be directly converted to NH_4UF_5 by electrodialysis which is easily decomposed to UF_4.

Before this lecture is concluded it is mentioned that description of equipment has been omitted in the present notes. There will be arranged an excursion to the reprocessing pilot plant here at Kjeller, and a description of the equipment will be included.

8. References.

I. General References.

1) M. Benedict and T.H. Pigford: Nuclear Chemical Engineering . Chapters 3, 6, 7 and 8. McGraw-Hill Book Co., Ltd., New York. 1957.

2) F.S. Martin and G.L. Miles: Chemical Processing of Nuclear Fuels . Butterworths Scientific Publications, London, 1958.

3) TID - 7534. Symposium on the Reprocessing of Irradiated Fuels. Brussels, May 20-25, 1957. Book 1, 2 and 3.

4) Proceedings Geneva Conference, August 8 - 20, 1955, Volume 9.

5) Proceedings 2nd Geneva Conference September 1-13, 1958, Volume 17.

6) Progress in Nuclear Energy, Series III, Process Chemistry, Volume I, Pergamon Press Ltd., London 1956.

7) Ibid, Volume II, Pergamon Press Ltd, London 1958.

8) TID - 7583. Symposium on the Reprocessing of Nuclear Fuels, Richland, Washington, U.S.A., 1959.

II. Special references.

9) G.T. Seaborg: The Transuranium Elements , Ch.1. The Plutonium Story p.p. 19 - 29. Yale University Press, 1958. Addison-Wesley Publishing Co, Reading, U.S.A.

10) Aikin,A.M: An Ion Exchange Process for the Recovery of Plutonium from Irradiated Fuels. 57 - NESC - 100 (1957).

11) Å. Hultgren and E. Haeffner: Plutonium Separation Using a Silica Gel Column . Geneva Conference, 1958, Volume 17, P/144.

12) R.E. Treybal: Liquid Extraction . McGraw-Hill Book Co, Inc., New York 1951.

13) J. Bjerrum, G. Schwarzenback and L.G. Sillén Stability Constants of Metal-ion Complexes. Par. I and II. The Chemical Society, London 1957.

14) W.F. Fullwood and F.R. Harris. R & DB (W) TN-16, 1952, UKAEA.

15) R.B. Richards: Aqueous Reprocessing - An Introduction, page 3, book 1 of ref.(3).

16) R.E. Blanco: Dissolution and Feed Adjustment, page 22, book 1 of ref. (3).

17) Merle K. Harmon: Removal og Fission Products from Feeds, page 262, book 1 of ref. (3).

18) F.L. Culler: Reprocessing of Reactor Fuel and Blanket Materials. Geneva Conference 1955, Vol. 9, Document P/822, page 464.

19) J.R. Flanary: Solvent Extraction Separation of Uranium and Plutonium from Fission Products by Means of Tributyl Phosphate, Geneva Conference 1955, Vol 9, Document P/539, page 528.

20) F L. Culler and F.R. Bruce: The Processing of Uranium-Aluminium Reactor Fuel Elements. Geneva Conference 1955, Vol. 9, Document P/541, page 484.

21) P.G. Reid, C.E. Stevenson, R.B. Lemon and F.K. Wrigley: Reprocessing of Fuel Containing Zirconium. Geneva Conference 1958, Vol. 17, Document P/526, page 145.

22) E.R. Irish and W.H. Reas. The Purex Process - A Solvent Extraction Method for Irradiated Uranium, page 83, book 1 of ref. (3).

23) E.R. Irish: Description fo Purex Plant Process. HW-60116, May 19, 1959 (Hanford).

24) B. Goldschmidt, P. Regnant and I. Prevot: Solvent Extraction of Plutonium from Uranium Irradiated in Atomic Piles, Geneva Conference 1955, Vol. 9, Document P/349, page 492.

25) Brown, Fletcher, Hardy, Kennedy, Scargill, Wain and Woodhead: The Significance of Certain Complexes of Ruthenium Niobium, Zirconium and Uranium in Plant Process. Geneva Conference 1958, Vol.17 Document P/31,page 118.

26) N.R. Geary: Collected Partition Data for Tributyl Phosphate. Report 8142, UKAEA (1959).

27) V.R. Cooper and M.T. Walling: Aqueous Processes for Separation and Decontamination of Irradiated Fuels. Geneva Conference 1958, Vol. 17 Document P/2409, page 291.

28) D.G. Karraker: Temperature Effects on TBP Solvent Extraction Processes. Geneva Conference 1958, Vol. 17, Document P/519, page 333.

29) J.R. Ryan and E.J. Wheelwright: Geneva Conference 1958, P/1915, page 137 see also same authors: HW-55893, Jan 2, Hanford (1959).

30) S. Lawroski and M. Levenson: Redox Process, page 45, book 1 of ref. 3.

31) V.M. Vdovenko and M.P. Kovalskaia: Separation of Uranium and Plutonium from Fission Products by Extraction with Dibutyl Ether. Geneva Conference 1958, Vol. 17, Document P/2216, page 329.

32) H.J Born and S. Krawczynski: Some Remarks on the Dibutyl Ether Solvent Extraction Process. Proceedings of the EAEA Symposium on Solvent Extraction, Madrid, 1959, page 355.

33) F.R. Bruce: Ion Exchange Isolation Processes, page 303, book 1 of ref. (3).

34) B.J. Newby and B.E. Paige: A Gelatin-Filtration Headend for Fuel Reprocessing Solutions. IDO-14468, July 24, Idaho (1959).

35) K.M. Harmon and W.H. Reas: Conversion Chemistry of Plutonium Nitrate, page 332, book 1 of ref. (3).

36) W.W. Schulz et. al.: Electrodialytic Conversion of Uranyl Nitrate of Uranyl Nitrate to Uranic Fluoride Salts. Ind.Eng.Chem. 50, 1768 (1958).

37) A.E. Comyns: The Coordination Chemistry of the Actinides Chemical Reviews 60 (2) 115 - 147 (1960).

TABLE I

Approximate composition of 1 tonne U fuel after 1000 MWd/t irradiation, cooled for 100 days (irradiation time 300 days)

Element	Approx. weight, g.	Activity β +γ curries(a)
U	998×10^3	-
Pu	800	-
Cs	110	13.100
Sr	40	41.500
Ba	40	4.200
Y	20	51.000
La	40	-
Ce	100	174.000
Pr and other rare earths	155	15.000
Zr	115	112.000
Nb	5	203.000
Mo	85	-
Tc	25	-
Ru	55	37.000
Rh	12	-
Other elements	40	2.000
Total activity		.. .. 652.800

(a) The activity from short-lived daughters of Cs^{137}, Sr^{90}, Ce^{144}, Ba^{140} and Ru^{106} is included with the parents.

TABLE II

Extractants used in processing nuclear fuels

Extractant	Specific gravity at 20°C	Viscosity at 20°C (centi-poises)	Boil-ing point (°C)	Melt-ing point (°C)	Solubility in water at 20°C (vol. %)	Solubility of water in extrac-tant at 20°C (vol. %)	Flash point (°C)
Tributyl phosphate	0.973	3.41 (25°C)	289 (decomp.)	-80	0.6	7	146
Methyl iso-butyl ketone	0.802	0.585	116	-84.7	2.0	2.2	27
Diethyl ether	0.714	0.233	34.5	-116	11.5	0.90	-40
Dibutyl cellosolve	0.837	1.34	203.3	-69.1	0.17	0.49	85
Dibutyl carbitol	0.885	2.39	254.6	-60.2	0.26	1.2	127
Pentaether	1.125	---	327.3	-6.2	1.0	5.1	174
Cyclohexanone	0.949	2.8 (23°C)	156.7	8.5	2.4	6.5	55
Thenoyl tri-fluoracetone	0.88 (benzene solution)	---	140 (at 40 mm Hg)	43	slight	---	---

TABLE III.

ELECTRONIC CONFIGURATION ABOVE THE 4d ORBITALS FOR SOME ELEMENTS.

ELEMENT	SHELL 4	SHELL 5				SHELL 6				SHELL 7
	4f	s	p	d	f	s	p	d	f	s
$_{56}Ba$		• •	• • • • •			• •				
$_{62}Sm$	• • • • • •	• •	• • • • •			• •				
$_{72}Hf$	• • • • • • • •	• •	• • • • • •			• •				
$_{92}U$	• • • • • • • •	• •	• • • • • • • • • • • • • •			• • • • •				• •
$_{94}Pu$		• •	• • • • • •			• • • • •				• •
$_{94}Pu^{4+}$		• •	• • • •			• • • •				

Increasing energy levels of orbitals:

1s 2s 2p 3s 3p 4s <u>3d</u> 4p 5s 4d 5p 6s <u>4f</u> 5d 6p 7s <u>5f</u> 6d 7p 8s

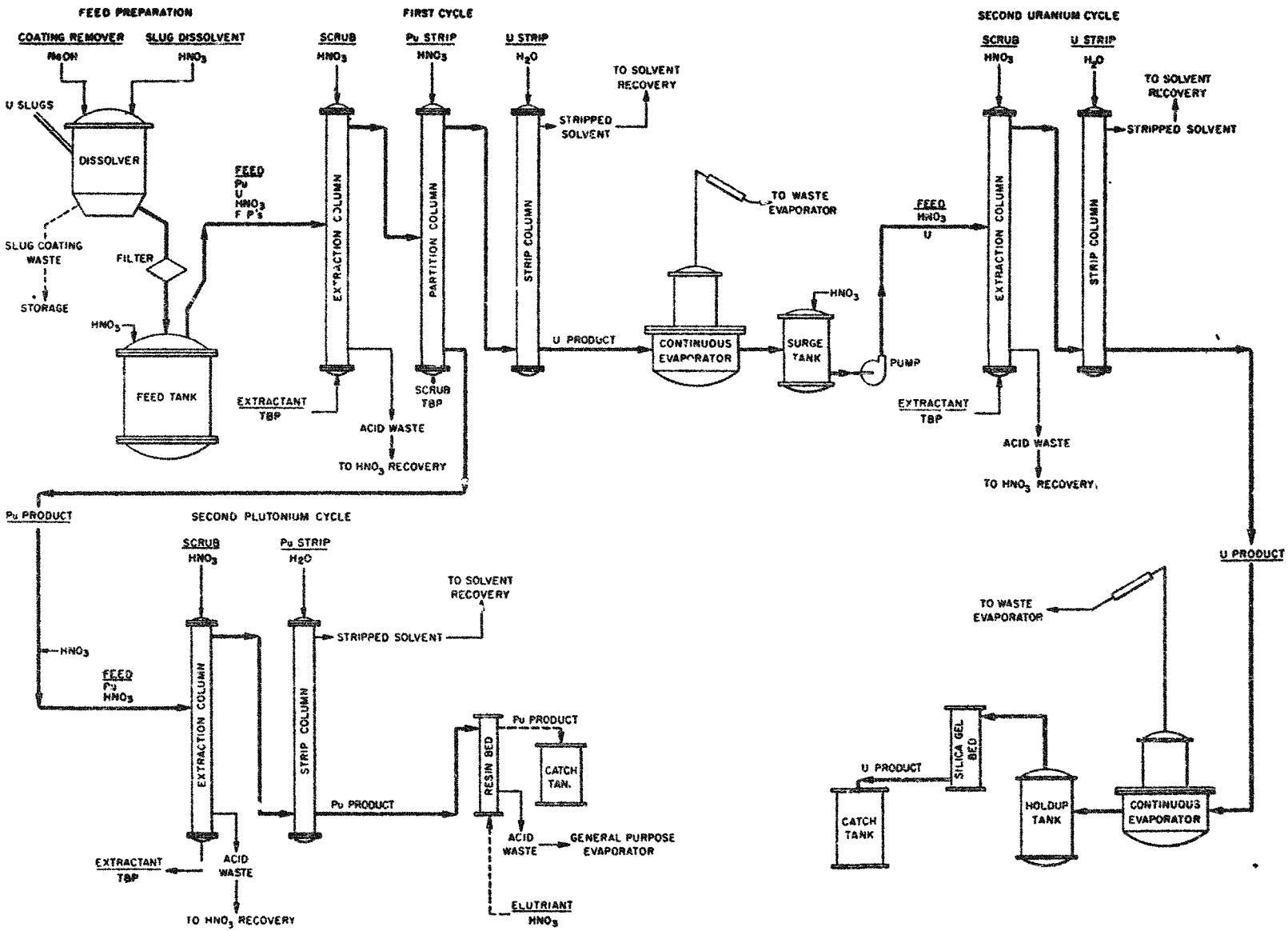


Figure 1. Flowsheet of tributyl phosphate solvent extraction recovery of uranium and plutonium from irradiated uranium

Fig. 2. Countercurrent Solvent Extraction.

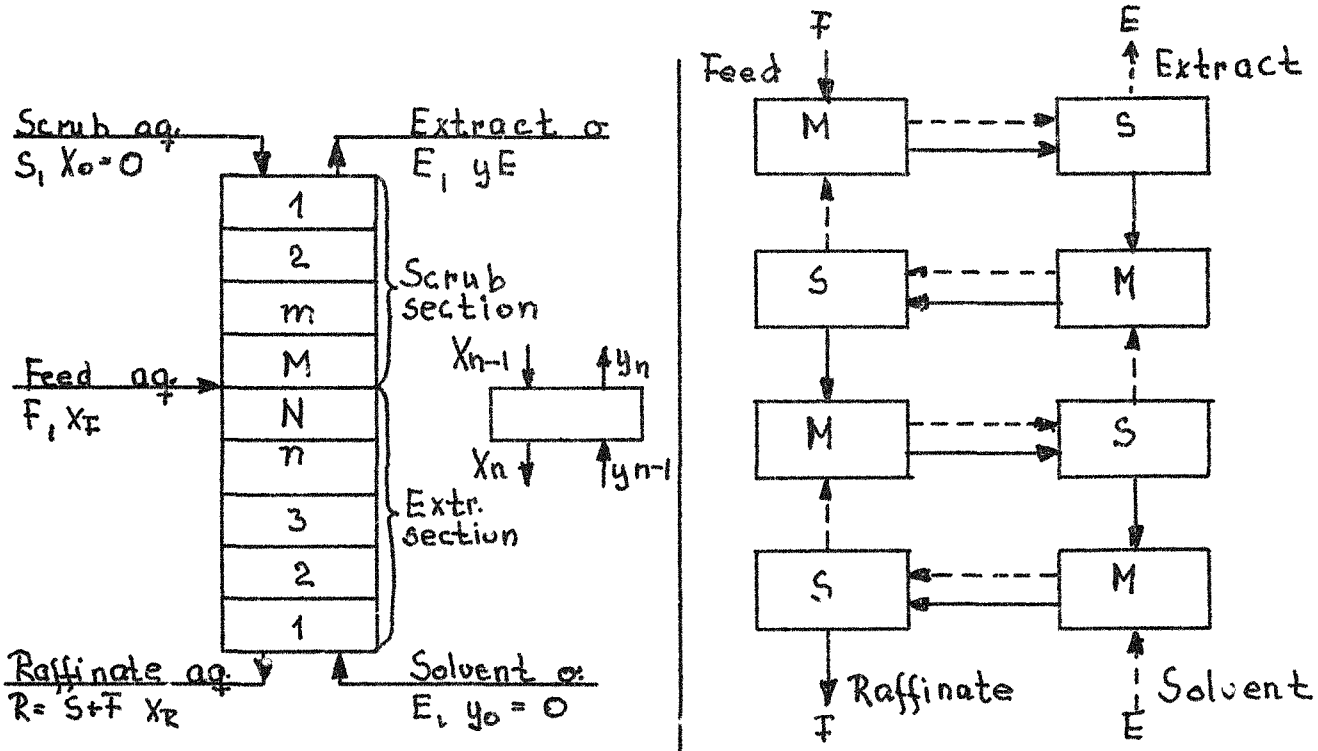


Fig. 2c. No. of stages by Mc Cabe Thiele Method.

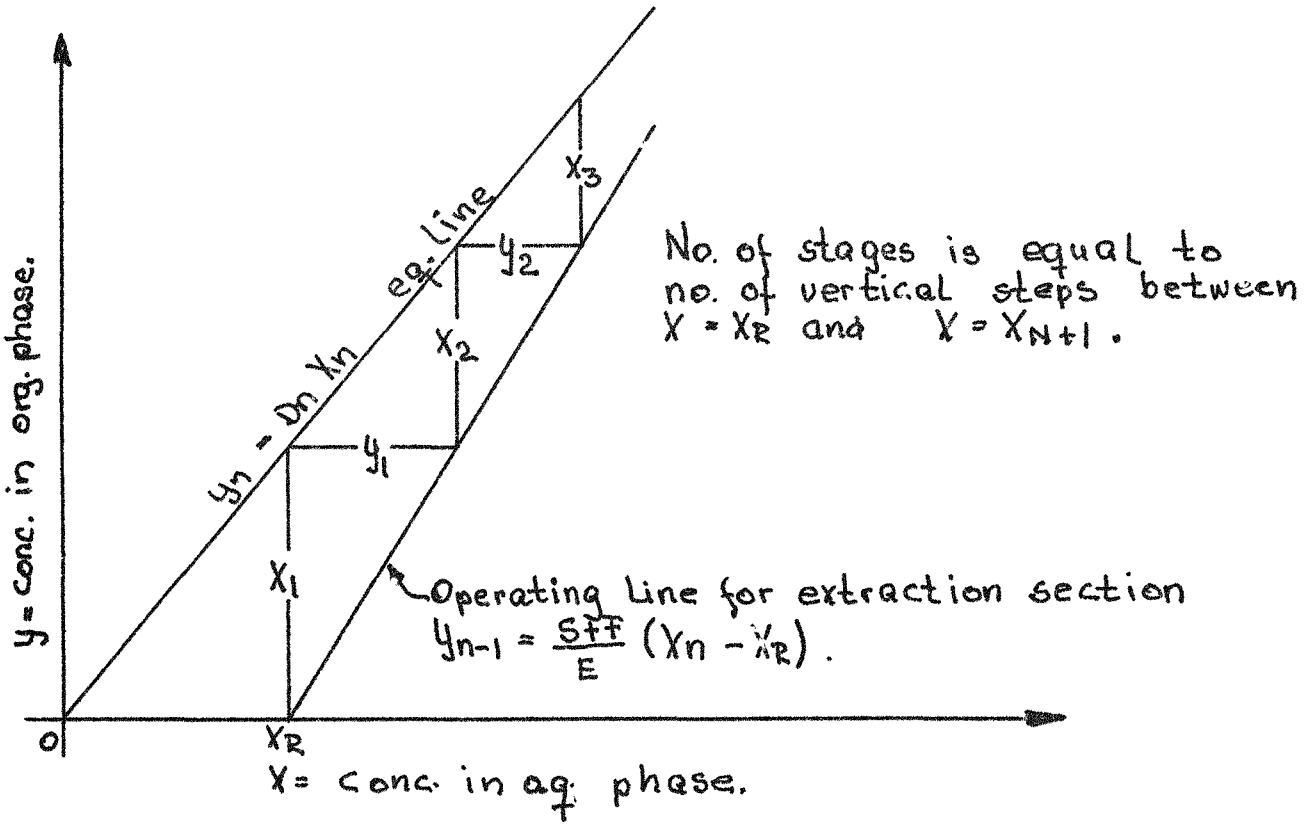
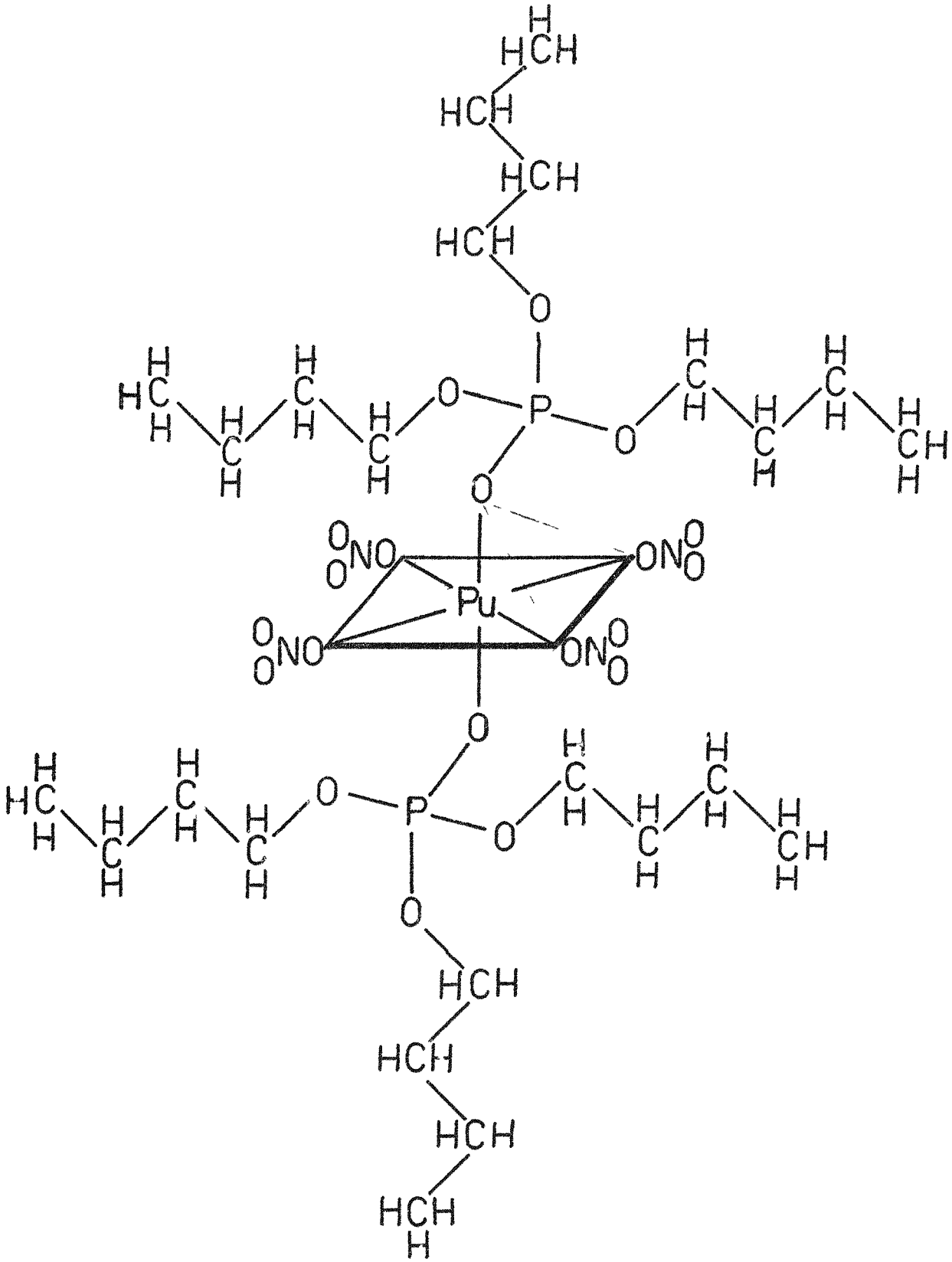
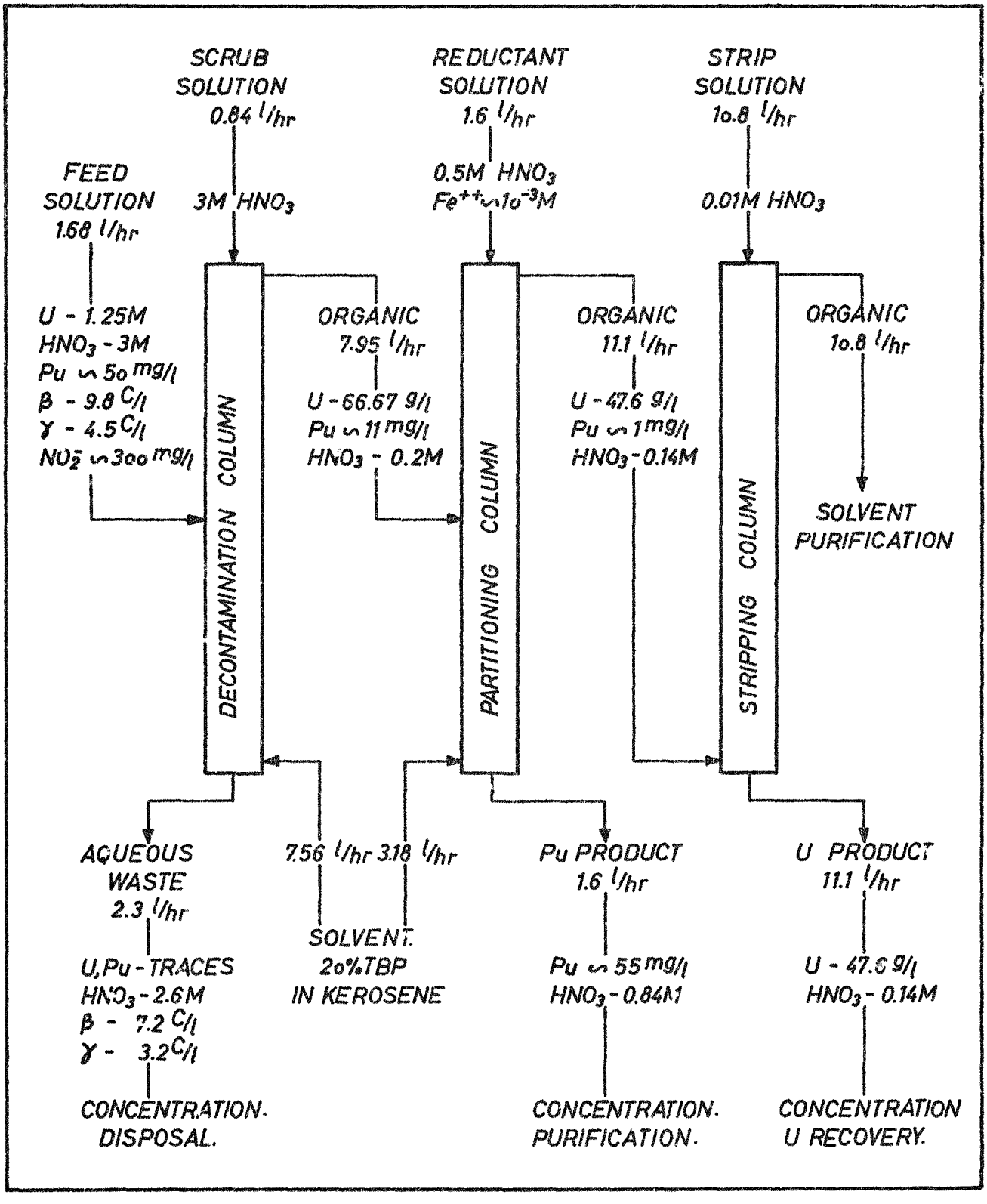


Fig. 3. Suggested Structure of $Pu(NO_3)_4 \cdot 2\,TBP$



Orbitals which might be used in the octahedral bonding of Pu:

$6d^2\,7s\,5f^3$



FLOW SHEET OF EXTRACTION PROCESS IN N-D PLANT
(FLOW RATES BASED ON 500 gU/hr).

Fig. 4

THE ADVANCED SUMMER INSTITUTE AT KJELLER

Section II

AQUEOUS REPROCESSING OF URANIUM BY AMINE EXTRACTION

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S O M M A I R E

AQUEOUS REPROCESSING OF URANIUM BY AMINE EXTRACTION

by

A. CHESNE

I. INTRODUCTION

Depuis plus de dix ans, les techniques d'extraction par solvant se sont imposées dans le domaine du retraitement chimique des combustibles par voie aqueuse. En effet, à leur efficacité pour la récupération et la purification des matériaux fissiles et fertiles s'ajoute leur grande souplesse d'utilisation.

Spécialement adaptées au cas des combustibles à l'uranium naturel dans lesquels la teneur en plutonium ne dépassait pas quelques grammes par kilogramme d'uranium, ces techniques ont dû évoluer quelque peu dans le cas du traitement chimique des nouveaux combustibles.

Les caractéristiques de ceux-ci sont liées au développement des réacteurs de puissance dans lesquels l'énergie libérée est élevée ainsi que le degré de burnup et où le coût du traitement chimique ne doit pas être prohibitif.

En conséquence, aux combustibles uranium naturel sous forme métallique, on a souvent préféré de l'uranium plus ou moins enrichi employé sous forme d'alliage (U - Zr par exemple) ayant une meilleure tenue mécanique ou employé sous forme de "pellets" d'oxyde UO_2 fritté ou encore d'oxyde dispersé dans des métaux tels Zirconium ou acier inoxydable. L'emploi de plutonium (oxyde ou alliage) comme combustible est à considérer également.

Les matériaux de gainage doivent etre capable de résister dans les conditions de marche du réacteur et le choix s'est porté généralement sur le zirconium ou le zircaloy (Zr à 2% de Sn) ou sur l'acier inoxydable.

La nécessité de diminuer l'importance des frais de stockage du matériau irradié a conduit à envisager la réduction du temps de refroidissement des cartouches brûlées et par voie de conséquence exige un traitement chimique à de hautes intensités de radiation.

Nous allons voir à la lumière de quelques exemples comment a été effectuée la première étape du traitement chimique de ces nouveaux combustibles c'est-à-dire la mise en solution.

Dans le procédé Darex on effectue conjointement la dissolution de la gaine d'acier inoxydable et du matériau fissile par action d'un mélange acide nitrique (5 M) acide chlorhydrique (2 M).

Dans le procédé Sulfex, seule la gaine d'acier inoxydable est dissoute par de l'acide sulfurique 6 N. L'oxyde d'uranium constituant le matériau combustible est ensuite dissout dans l'acide nitrique. La perte en uranium et en plutonium bien que faible lors du dégainage chimique exige cependant un traitement de récupération de la solution résultante.

Le procédé Zirflex est adapté au traitement des combustibles ou des gaines à base de zirconium. L'attaque de ce métal ou de l'alliage riche en zirconium s'effectue au moyen d'acide fluorhydrique ou de fluorure d'ammonium.

Rappelons que dans les cycles classiques d'extraction type Redox ou Purex, il était nécessaire que la solution à extraire soit une solution de nitrate. Donc pour adapter les procédés classiques à la purification de ces solutions de dissolution, celles-ci doivent être traitées spécialement: entraînement de l'acide chlorhydrique des solutions Darex, addition de nitrate d'aluminium aux solutions Zirflex (action complexante des ions Al^{+++} et rapport de nitrates).

Enfin la récupération des traces d'U et Pu des solutions de dégainage Sulfex présente de grosses difficultés par les extractions classiques au TBP ou à l'hexone.

Très grave est également l'objection faite à l'emploi du TBP pour le traitement chimique de combustibles ayant été refroidis peu de temps.

Des évaluations de la dose moyenne reçue par le TBP dans un cycle classique lors du retraitement des combustibles de réacteur de puissance ont été faites. Elles diffèrent sensiblement selon les auteurs. Certains pensent qu'un refroidissement de 10 jours et un temps de séjour moyen de 10 minutes dans l'extracteur conduirait à des doses de 20 à 30 watt-heure par litre. D'autres estimations indiquent, pour un temps moyen de séjour de 5 minutes des doses d'irradiations beaucoup plus faibles (fig. 1).

Les produits de dégradation du TBP par radiolyse ou par hydrolyse chimique sont principalement: le DBP, le MBP, le butanol. La conséquence de la formation de ces produits est:

1) Une formation de complexes solubles en phase organique en milieu peu acide. Ces complexes sont formés avec l'uranium, le plutonium, le thorium et certains produits de fission. En conséquence, les pertes en U, Pu, Th peuvent devenir importantes (fig. 2 - 3 et 4). D'autre part, le solvant devant être recyclé doit être décontaminé par des lavages successifs. Enfin la purification des produits finaux U - Pu - Th est moins bonne.

2) Une conséquence technologique celle-là est la formation d'émulsion très gênante dans les appareillages d'extraction. On cite en particulier la formation d émulsions dûes au dibutyl phosphate de thorium dans le procédé Thorex. On peut penser qu'il en sera de même dans la manipulation de solutions riches en zirconium.

Le tableau de la figure 5 résume l'influence des radiations dans les procédés au TBP

La recherche des nouveaux solvants a eu comme idée directrice l'utilisation de corps organiques possédant les qualités suivantes:

- Plus grande sélectivité permettant d'améliorer les séparations et les facteurs de décontamination donc de diminuer si possible le nombre de cycles et le coût des opérations.

- Résistance convenable aux effets chimiques ou radiolytiques des solutions à traiter.

De plus les possibilités d'emploi de ces solvants dans des milieux autres que le milieu nitrique devrait permettre une plus grande souplesse dans les traitements chimiques qui concernent des matériaux variés (Zr, acier inox, etc...) et également une récupération des sous-produits intéressants (ex. Np^{237}, Am^{241}).

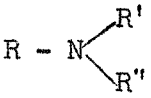
Les travaux d'un certain nombre de chercheurs ont permis d'obtenir des indications utiles concernant ces nouveaux solvants et à l'heure actuelle deux types principaux de composés organiques semblent prometteurs. Il s'agit des composés organo-phosphorés et des alkylamines.

C'est de ces derniers composés qu'il va s'agir dans ce qui suit.

II. PROPRIETES GENERALES DES AMINES

Les amines aliphatiques à longue chaîne ont été citées pour leurs propriétés extractives dès 1948 par des chercheurs britanniques qui les ont utilisées pour extraire des acides faibles. Ils ont noté la possibilité d'extraction d'espèces anioniques. Plusieurs séparations analytiques se basant sur cette prorpiété générale ont été utilisées - séparation Nb - Ta, Pa - Th, Sn - Sb, etc...

La structure de ces composés est la suivante:



ou R et R' représentent soit un atome d'hydrogène, soit un radical alkyl, R" étant un radical alkyl.

On a donc la possibilité d'avoir trois groupes principaux:

$R'' - N H_2$	$R' \; N \; H$ R''	$R - N - R''$ R'
amine primaire	secondaire	tertiaire

Dans ce qui suit, et pour raison de simplicité nous ne différencierons pas les radicaux alkyls écrivant ces groupes

$R \; N \; H_2$ $\qquad$ $R_2 \; N \; H$ et $R_3 \; N$

Tous ces corps ont un caractère basique marqué et leur comportement en présence d'un acide [HA] est une réaction de salification donnant le sel d'amine:

$R_3 \; N \; H \; A$ pouvant être dissocié en $R_3 \; N \; H^+$ et A^-

La solubilité de ces sels dans l'eau est d'autant plus faible que les radicaux R comportent un nombre d'atomes de carbone plus élevé.

La solubilité dans les solvants organiques varie selon:

a) la nature du solvant et sa polarité
b) " " de l'anion A

En particulier il a été noté que la solubilité des sels de certaines amines dans le kérosène décroît dans l'ordre

sulfate - bisulfate - chlorure - nitrate

Le mécanisme de l'extraction par les sels d'amine a été assimilé à un échange d'anion selon la réaction générale.

$$n\,R_3\,N\,H\,A + B^{n-} \rightleftarrows (R_3\,N\,H)_n\,B + n\,A^-$$

B^{n-} pouvant être un anion ou un complexe anionique.

Les amines primaires, secondaires, tertiaires se comportent comme des résines échangeuses d'anions "base faible", et sont sans effet sur les complexes anioniques à pH élevé.

Comme pour les résines échangeuses d'anions, il semble que l'affinité pour l'anion décroisse dans l'ordre suivant:

$$Cl\,O_4^- > N\,O_3^- > Cl^- > H\,S\,O_4^- > F^-$$

Dans le cas des extractions en milieu acide, l'extrayant sera le sel d'amine correspondant à l'acide envisagé.

Nous passerons en revue les propriétés des trois sels d'amine suivants: sulfate, chlorure, nitrate.

III. EXTRACTION PAR LES SULFATES D'AMINE

a) Formation du sulfate

La solution organique de l'amine sous forme basique réagit avec l'acide sulfurique en donnant le sulfate d'amine suivant la réaction.

$$2\,R_3\,N + H_2\,S\,O_4 \rightleftarrows (R_3\,N\,H)_2\,S\,O_4$$

En présence d'un excès d'acide sulfurique on forme le bisulfate d'amine selon:

$$(R_3\,N\,H)_2\,S\,O_4 + H_2\,S\,O_4 \rightleftarrows 2\,(R_3\,N\,H)\,H\,S\,O_4$$

La courbe de la figure 6 montre la neutralisation de trioctylamine par l'acide sulfurique en milieu hydroalcoolique. On constate la présence de deux points équivalents correspondant à la formation de sulfate et de bisulfate.

b) Extraction de l'uranium

Un nombre considérable de travaux ont été effectués pour extraire l'uranium de solutions sulfuriques obtenues lors du traitement des minerais.

Cette extraction peut s'écrire de la façon suivante

UO_2^{++} (a) + 2 SO_4^{--} (a) $\rightleftarrows$ $UO_2(SO_4)_2$ (a) qui est la réaction de formation d'un complexe en phase aqueuse, puis

$UO_2(SO_4)_2^{--}$ (a) + $(R_3NH)_2SO_4$ (o) $\rightleftarrows$ $(R_3NH)UO_2(SO_4)_2$ + SO_4^{--} (a)

Certains auteurs signalent que l'extraction du complexe non chargé UO_2SO_4 s'effectue probablement parallèlement suivant

UO_2SO_4 (a) + $(R_3NH)_2SO_4$ (o) $\rightleftarrows$ $(R_3NH)_2UO_2(SO_4)_2$ (o)

Ces deux voies également possibles conduisent de toutes façons à la formation en phase organique du complexe cité plus haut.

c) Extraction d'autres éléments

D'autres éléments sont connus comme donnant des complexes sulfuriques négatifs en phase aqueuse. Citons parmi eux: Fe^{+++}, Th^{4+}, Pu^{4+}, etc...

Nous allons passer en revue l'extraction de ces éléments, comparée à celle de l'uranium en fonction de la structure des amines employées. En particulier, nous verrons l'influence des radicaux liés à l'atome d'azote et de leur degré de ramification.

La figure N° 7 nous montre que le pouvoir d'extraction décroît des amines primaires aux secondaires et aux tertiaires pour les éléments trivalents tels Fe, V, terres rares et les éléments tétravalents Ti, Zr, Th et U.

Pour tous ces éléments les ramifications des chaînes alkyl ont un effet néfaste sur l'extraction.

Le phénomène semble inversé pour le vanadium pentavalent l'uranium et le molybdène hexavalent. Des ramifications trop voisines de l'atome d'azote amène comme précédemment une diminution du pouvoir d'extraction.

INFLUENCE DU DILUENT SUR L'EXTRACTION

Une autre variable importante influant sur les coefficients d'extraction est le diluant. Son effet a été particulièrement étudié dans le cas de l'uranium. La figure 8 rapporte les résultats expérimentaux concernant l'extraction de l'uranium par diverses amines diluées soit dans du kérosène, soit dans du benzène ou enfin dans du chloroforme. Remarquons que le choix de ces trois diluants correspond à une variation de polarité des molécules, polarité croissante du kérosène au chloroforme.

Le diluant le plus polaire permet les meilleurs coefficients d'extraction avec les amines primaires, avec les amines secondaires à chaînes droites ou peu ramifiées.

Le diluant le moins polaire favorise au contraire l'extraction dans le cas des amines secondaires à chaînes relativement courtes et très ramifiées et des amines tertiaires ramifiées.

On constate donc non pas une séparation nette entre les propriétés des trois groupes d'amine: primaire, secondaire et tertiaire, mais plutôt un recouvrement partiel.

Les amines secondaires ramifiées se comportent comme les tertiaires symétriques et non ramifiées.

Les primaires ramifiées se comportent comme les secondaires non ramifiées.

L'addition d'un corps polaire (alcool lourd par exemple) à du kérosène améliore l'extraction de l'uranium dans le cas des amines secondaires peu ramifiées et des tertiaires à chaîne droite. L'effet est inverse quand les ramifications sont abondantes.

On n'a malheureusement pas noté une généralité de ces effets, certains autres complexes métalliques réagissant de façon différente. Par exemple l'addition à du kérosène de 5% en volume de tridécanol fait décroître considérablement l'extraction du fer dans la di(tridecyl)amine alors que l'extraction de l'uranium n'est pas affectée.

AUTRES FACTEURS AGISSANT SUR L'EXTRACTION

a) Autres anions ou complexes extractibles

La figure 9 montre l'influence néfaste de l'acidité sur les coefficients d'extraction de l'uranium. Cet effet peut être interprété en considérant que le complexe sulfurique de l'uranium est en compétition avec l'anion bisulfate formé par diminution du pH.

La compétition de l'ion sulfate lui-même tendant à déplacer l'équilibre

$$(R_3\,N\,H)_2\,S\,O_4 + U\,O_2\,(S\,O_4)_2^{--} \rightleftarrows (R_3\,N\,H)_2\,U\,O_2\,(S\,O_4)_2 + S\,O_4^{--}$$

de la droite vers la gauche est visible sur la figure 11. Sur la figure 10 l'effet de la présence d'anions étrangers est toujours défavorable. Ces anions peuvent agir selon deux mécanismes:

- Ou un effet de compétition se rapportant à l'extraction en phase organique par le sel d'amine, comme dans les cas précédents des sulfates et bisulfates.

- Ou un effet de compétition se rapportant à la formation d'un complexe avec l'ion UO_2^{++} en phase aqueuse.

- Ou un effet double comprenant les deux effets précédents. Cette action des ions étrangers est utilisée lorsque l'on désire réextraire l'uranium de la phase organique dans la phase aqueuse.

b) Température

L'accroissement de température fait décroître l'extraction de l'uranium.

c) Concentration en amine

Le degré d'association des atomes d'uranium et des molécules d'amine a été trouvé variant de 4 à 6 (4 à 6 molécules par atome d'uranium).

La courbe représentant le logarythme du coefficient d'extraction de l'uranium en fonction du logarythme de la concentration en amine est une droite de pente 1. Ceci suggère que l'activité du sel d'amine est constante quelle que soit la concentration de l'amine dans le diluant et l'on a émis l'hypothèse que ce sel est sous forme d'agrégat colloïdal dans le diluant formant une seconde phase de composition constante.

APPLICATION AU CAS DES COMBUSTIBLES IRRADIES

Nous venons de voir ce qui concerne l'extraction de l'uranium. Le plutonium, comme les autres éléments tetravalents Zr, Th, etc., est extrait nettement mieux par les amines primaires que par les secondaires et tertiaires.

En milieu sulfurique 3 M, l'amine Primène JT fournit des coefficients d'extraction supérieurs à 1000 tandis que la tri n octylamine donne des coefficients inférieurs à 0,1.

L'extraction de l'uranium tetravalent étant aussi excellente, l'amine Primène JT a été proposée pour récupérer l'uranium et le plutonium des solutions de dégainage dans le procédé Sulfex.

Ce procédé doit être installé à Oak Ridge National Laboratory pour traiter les fuels des réacteurs de puissance.

La figure 12 indique le flowsheet adopté pour ces opérations.

Bien que des résultats d'exploitation ne soient pas encore fournis, on peut envisager des possibilités intéressantes d'emploi des amines dans le cas des solution sulfuriques provenant du traitement des combustibles des réacteurs de puissance.

IV. EXTRACTION PAR LES CHLORURES D'AMINE

En se basant sur le mécanisme d'échange anionique des sels d'amine, l'extraction en milieu chlorhydrique d'éléments lourds se déduit des études faites dans ce même domaine au moyen de résines échangeuses d'anions.

En particulier des séparations ont été obtenues entre l'uranium et le thorium. D'autre part, la fixation du complexe chlorhydrique du plutonium tetravalent sur résines échangeuses d'anion est connue.

Bien que principalement axée sur des buts analytiques, l'extraction par les chlorures d'amines peuvent offrir des possibilités intéressantes dans le cas de traitement de combustibles irradiés.

Nous nous limiterons cependant dans ce chapitre à des indications générales qui pourront être utiles dans le cas d'une éventuelle utilisation.

1) La formation du chlorure d'amine peut s'écrire:

$$R_3 N_{(o)} + H^+_{(a)} + Cl^-_{(a)} \rightleftarrows R_3 N H Cl_{(o)}$$

la constante K de cet équilibre fournissant pK = 4.

La solubilité des chlorures d'amine tertiaire est souvent faible dans le kérosène et la chloruration de l'amine donne souvent lieu à des précipatations ou des phénomènes de troisième phase. Généralement on a utilisé des diluants du type xylène. Cependant même avec le xylène des formations de gels ou de 3ème phase lors de l'extraction de complexes métalliques peuvent être observés. On évite ces phénomènes gênants soit:

- En augmentant l'acidité de la phase aqueuse.
- Par l'addition ou l'utilisation de diluants plus polaires que le xylène (la méthylisobutylcétone est signalée comme donnant d'excellents résultats soit utilisée seule soit en mélange avec kérosène, xylène, CCl_4).

2) Extraction de l'uranium

La courbe de la figure 13 donne le pourcentage d'uranium extrait en fonction de l'acidité chlorhydrique de la phase aqueuse, le solvant étant de la tri iso octylamine à 5% dans du xylène. On voit que dès 2 N l'extraction de l'uranium commence à devenir importante.

D'autre part les faibles pourcentages d'extraction en milieu moins acide indiquent la possibilité de réextraire l'U en phase aqueuse aisément.

L'équation générale d'extraction peut s'écrire:

$$2\ R_3\ N\ H\ Cl\ _{(o)} + U\ O_2^{++}\ (a) + Cl^-\ (a) \rightleftarrows (R_3\ N\ H)_2\ U\ O_2\ Cl_4$$

La constante K de cet équilibre est telle que pK = 1,5 ± 0,3.

Quant au phénomène d'extraction lui-même, il peut être envisagé comme une association ionique entre 2 $R_3\ N\ H^+$ et $(U\ O_2\ Cl_4)^{--}$ ou une association moléculaire entre 2 $R_3\ N\ H\ Cl$ et $U\ O_2\ Cl_2$ ou probablement un mélange des deux.

3) Extraction des autres éléments (fig. 14)

Quelle que soit l'acidité, le thorium n'est pas extrait de façon sensible.

L'extraction du zirconium est faible jusqu'à 6, 5 N, et celle du niobium faible jusqu'à 5 N. Le ruthenium par contre est extrait dès les très faibles concentrations en acide chlorhydrique.

Le protactinium se comporte comme le couple Zr - Nb et est extrait facilement dès que la concentration en H Cl dépasse 4 N.

Le cas du plutonium mérite d'être considéré à part, étant donné ses nombreux états de valence.

Le Pu trivalent se comporte comme les terres rares, c'est-à-dire qu'il n'est pas extrait quelle que soit l'acidité.

A l'état tétravalent, l'extraction est similaire de celle du niobium, c'est-à-dire qu'elle devient sensible vers 5 N acide chlorhydrique.

A l'état hexavalent, le comportement du plutonium est identique à celui de l'uranium.

Le neptunium se comporte comme le plutonium à état de valence comparable.

APPLICATION A CERTAINS CAS DE SEPARATION

Des séparations U - produits de fission sont possibles. L'uranium est extrait par le chlorure d'amine en 4 N acide chlorhydrique, (séparation de Zr - Nb des terres rares, Th), puis réextrait en acide dilué (séparation Ru); moins de 1% du Ru est entraîné.

En présence de protactinium un lavage de la phase organique après extraction de l'uranium par un mélange H Cl - H F permet une bonne séparation U - Pa. La séparation U + Pu des produits de fission exige l'emploi d'un oxydant énergique pour amener le plutonium à l'état hexavalent. Le bichromate peut être utilisé. Il est bon de noter que dans ce cas le comportement du ruthenium peut être different de celui envisagé précédemment.

V. EXTRACTION PAR LES NITRATES D'AMINE

L'utilisation des amines comme agent d'extraction en milieu acide nitrique a sans doute été plus développée que l'utilisation des sulfates et des chlorures en ce qui concerne le reprocessing des combustibles irradiés.

La réaction de formation du nitrate est la suivante:

$$R_3 N\ (o) + H^+(a) + NO_3^-\ (a) \rightleftarrows R_3 NH\ NO_3\ (o)$$

L'acide nitrique en excès est partiellement extrait dans le nitrate d'amine. L'espèce extraite en phase organique peut être écrite

$$R_3 NH\ NO_3 H,\ x\ NO_3 H$$

x étant un coefficient qui dépend de la teneur de la phase aqueuse en équilibre avec le solvant. Notons que sa valeur peut être supérieure à 2, comme le montre la figure N° 15.

Comme dans le cas des sulfates et des chlorures la solubilité de ce sel dans la phase organique dépend de l'amine utilisée ainsi que du diluant. Des phénomènes de troisième phase se produisent et seront étudiées plus loin.

PROPRIETES EXTRACTIVES

Nous allons passer en revue différents éléments qui seront groupés par état de valence. Les figures 16 - 17 et 18 se rapportant à des extractions effectuées avec une amine tertiaire la tri n octylamine diluée dans du xylène (10% en volume d'amine).

1) Eléments tétravalents

Les courbes de la figure 16 concernant le Th, le Pu, le Np. On remarque que l'extraction s'effectue dans l'ordre du numéro atomique.

Si l'on étudie la variation du logarythme du coefficient de partage de ces éléments en fonction du logarythme de la concentration de l'amine (fig. 17), on constate que les droites obtenues ont une pente 2 ce qui indique que deux molécules d'amine sont liées à un atome d'éléments. On est donc amené à adopter le mécanisme d'extraction suivant:

$$M^{4+} + 6\,NO_3^- \rightleftarrows M(NO_3)_6^{--} \quad \text{formation de complexe}$$

$$M(NO_3)_6^{--} + 2\,R_3NH\,NO_3 \rightleftarrows (R_3NH)_2\,M(NO_3)_6 + 2\,NO_3^-$$

Les éléments tetravalents seraient donc extraits dans la phase amine à l'état de complexe hexanitrato.

2) Eléments hexavalents

Sont étudiés ici l'uranium, le neptunium, le plutonium. On constate (fig. 18) une grande différence entre la valeur des coefficients de partage obtenus et de celle des éléments tetravalents.

La détermination du nombre de molécules d'amine entrant dans la composition de ces complexes donne des valeurs comprises entre 1 et 2.

3) Eléments penta et trivalents

La valeur des coefficients de partage de ces éléments est d'un ordre de grandeur inférieur. Elle décroît dans l'ordre Pa Pu^{III} Np^{V} Am^{III}.

Des courbes précédentes on peut déduire que:

- La forme générale de ces courbes indique un maximum d'extraction lorsque la teneur de la phase aqueuse est voisine de 6 M.
- Des possibilités de séparation du plutonium et du neptunium des autres éléments semblent applicables à condition de maintenir des éléments à l'état tétravalent.

Ceci est résumé dans le tableau des coefficients de séparation (fig. 19) obtenus en milieu acide nitrique 2 N avec une amine tertiaire symétrique la trilaurylamine 0,15 M dans le dodécane.

ROLE DE CERTAINES VARIABLES SUR L'EXTRACTION DU PLUTONIUM PAR LES AMINES

1) Nature de l'amine

Des études ont été faites dans le but d'étudier le comportement de différents types d'amine.

La figure 20 indique la valeur relative de certaines amines tertiaires pour de l'extraction du plutonium. On ne peut déduire des chiffres cités, une loi générale concernant l'influence des radicaux liés à l'atome d'azote. De même les amines à haut poids moléculaire donnent en général des résultats plus satisfaisants sans doute à cause de leur plus faible solubilité dans la phase aqueuse. Les amines tertiaires semblent présenter des coefficients d'extraction plus favorables que les amines primaires et secondaires.

2) Température

Certains auteurs ont noté que l'augmentation de température a une action défavorable sur le coefficient de partage du plutonium mais surtout sur celui du zirconium permettant d'accroître le coefficient de séparation entre ces deux éléments.

3) Action d'autres anions extractibles

On peut interpréter les maxima des courbes d'extraction d'actinides en fonction de l'acide nitrique présent en phase aqueuse comme un effet dû à la compétition entre l'extraction du complexe métallique et de l'acide nitrique.

Plus important est l'effet dû à la présence d'uranium. Malgré son faible coefficient de partage, l'uranium gêne l'extraction du plutonium d'autant plus que le rapport $\frac{U}{Pu}$ est grand.

Le tableau de la figure 21 montre l'ordre de grandeur des effets que nous venons de citer.

4) Action d'anions complexants

Tous les anions capables de donner un complexe avec le plutonium peuvent gêner. Parmi ceux-ci: SO_4^{--}, Cl^-, etc...

CHOIX DU DILUANT - PHENOMENES DE TROISIEME PHASE

Dans le but d'une application de l'extraction par les amines au cas du traitement des combustibles irradiés, le diluant joue un grand rôle. Les qualités exigées comportent des impératifs physiques tels que: solubilité faible dans l'eau, densite, viscosité convenable, point d'inflammation élevé, etc... Le choix, dans le cas d'une utilisation du TBP s'est porté sur les solvants du type kérosène qui présentent bon nombre des qualités sus-indiquées.

Une tentative identique a été effectuée avec les amines. La solubilité de celles-ci à l'état de base, dans le kérosène est excellente. Par contre, la solubilité de ses sels et des sels complexes est beaucoup moins favorable.

Au-dessus d'une certaine concentration en complexe métallique, la phase organique se sépare en deux parties: l'une lourde contenant l'amine complexée et le sel d'amine, l'autre légère contenant principalement le diluant.

Etant donné les risques que ces troisièmes phases font courir lors d'un traitement chimique, il est intéressant d'examiner de plus près les conditions de formation et les moyens dont nous disposons pour les éviter.

Parmi les risques cités plus haut, il convient de mettre l'accent sur les risques de criticalité et les perturbations amenés dans la purification des produits.

FACTEURS AGISSANT SUR LA FORMATION DE TROISIEME PHASE

1) Nature du sel d'amine

Le radical organique et l'anion minéral influent: Certains auteurs ont montré que diverses amines diluées dans la décaline présentaient une tendance décroissante à la formation de la 3ème phase en passant de NO_3^- à Cl^-.

2) Nature du diluant

Le tableau de la figure 22 montre l'action de quelques diluants sur la charge admissible, de plutonium dans l'amine. D'une façon générale, la polarité du diluant et un facteur favorable pour la suppression des troisièmes phases.

3) Nature du complexe extrait

La figure 23 se rapporte à l'extraction des trois cations Th, Pu, U dans la trilaurylamine 10% - dodécane. On note une identité de comportement entre les deux éléments tétravalents et une charge admissible plus importante pour l'uranium.

FACTEUR PERMETTANT D'EVITER OU DE LIMITER CE PHENOMENE

1) Température (voir figure 23)

2) Addition d'adjuvants polaires

Les alcools lourds ont été utilisés largement à l'échelle du laboratoire. En présence de 2% d'alcool octylique, la teneur limite en Pu dans la TLA 0,15 M/Amsco est de 0,8 g/l-10% d'alcool permettent d'obtenir 5,2 g/l.

Avec 0,15 M TLA/dodécane, on a obtenu à:
0% alcool octylique 2 g/l Pu
5% " " 10 g/l Pu

REEXTRACTION DU PLUTONIUM EN PHASE AQUEUSE

Divers modes de réextraction peuvent être envisagés qui résultent de ce que nous avons dit précédemment.

La première possibilité est le déplacement du complexe métallique par un anion ayant une plus grande affinité pour l'amine. L'ordre d'affinité cité auparavant était, rappelons-le: $Cl\,O_4^- > NO_3^- > Cl^-$, etc...

Une solution d'acide perchlorique peut donc servir comme liqueur de réextraction.

La formation de complexe de plutonium peu extractible est mise à profit dans le cas de la réextraction de la trilaurylamine par une solution sulfurique.

De plus, dans le cas du plutonium, la possibilité d'un changement de valence permet une réextraction facile. En particulier, le passage de Pu^{4+} à Pu^{3+} fait passer le coefficient d'extraction de 100 à 10^{-3} environ. Des réducteurs tels Fe^{++}, U^{IV}, hydrazine, hydroxylamine peuvent être utilisés.

APPLICATION AU CAS DES COMBUSTIBLES IRRADIES

Certains résultats d'extraction ont été indiqués lors de la Conférence de Geneve, 1958, in particulier, l'extraction du plutonium par une amine tertiaire la trilaurylamine diluée dans l'Amsco et contenant 2% d'alcool lourd.

On met ici à profit la sélectivité de ce solvant pour le complexe hexanitraté du plutonium le séparant ainsi des produits de fission et de l'uranium. L'adaptation de ces propriétés au cas des combustibles des réacteurs de puissance peut être vu sous l'angle suivant.

L'uranium contenu dans le fuel est très appauvri et peut etre rejeté, le seul élément de valeur étant le plutonium. On éviterait un cycle de partition comme il en existe dans les procédés au TBP.

La figure 24 donne un flowsheet possible s'appuyant sur les résultats publiés en 1958.

Les séparations U - Pu sont bonnes et peuvent être augmentées en accroissant l'efficacité du lavage. La séparation Pu - produits de fission est excellente.

On doit noter que lors de l'operation de réextraction une nouvelle décontamination est obtenue, le solvant restant contaminé par une activité γ dûe probablement au couple Zr-Nb. Alors se pose le problème de recyclage du solvant. La solution de ce problème peut être un lavage par un agent complexant ou par l'action d'une solution sodique agissant ainsi:

$$R_3 N H N O_3 + O H^- \rightleftharpoons R_3 N + H_2 O + N O_3^-$$

En plus des résultats intéressants concernant la purification et la décontamination du plutonium on doit noter que la valeur élevée des coefficients de partage du plutonium permet d'atteindre un troisième but qui est la concentration.

La figure 25 retrace un flowsheet correspondant à des expéricnces menées avec des solutions de plutonium 10^{-3M} contentant 10^{-2M} d'uranium. Le facteur de concentration obtenu est 100, les facteurs de décontamination sont 10^5 pour l'uranium, 10^4 pour Zr-Nb.

Les résultats rapportés à ce jour représentent malheureusement uniquement des essais à l'échelle du millilitre, ne faisant pas intervenir un nombre de recyclages suffisants pour tester la stabilité du solvant.

Des essais d'irradiation de trilaurylamine dans des flux γ et prolongés jusqu'à atteindre 40 et 140 wh/l ne montraient pas de variation dans les performances d'extraction. On doit en déduire que les éléments formés par dégradation n'apporteront aucune gêne dans le traitement chimique, ce qui constitue pour les amines un grand avantage sur le TBP.

Ces solvants utilisés soit en complément de méthodes classiques, soit comme méthode directe, semblent prometteurs pour le traitement des fuels provenant des réacteurs de puissance.

VI. OUVRAGES A CONSULTER

GENERAL:

F.R. BRUCE - R.E. BLANCO - J.C. BREESE — O.R.N.L. 58-11-91

V.R. COOPER - M.T. WALLING Jr. — Sec. Geneva Conf. P/2409

E.L. SMITH - J.E. PAGE — Jour. of Soc. of Chem. Ind. 67 48-51 (1948)

EFFET DE L'IRRADIATION SUR LE TBP:

L.L. BURGER — Progress in Nuclear Energy Vol. 2 série 3

T. RIGG - W. WILD — Progress in Nuclear Energy Vol. 2 série 3

STRUCTURE MECANISME D'EXTRACTION:

J. BIZOT - B. TREMILLON — Bull. Soc. Chim. France 1 122-6 (1959)

C. BOIRIE — Rapports C.E.A. N^{os} 934-941 1262

J.A. BROTHERS et al — J. Inorg. Nucl. Chem. 7 85-95 (1958)

D.J. CAPSWELL - J.J. LAWRENCE — J. Inorg. Nucl. Chem. 11 69-74 (1958)

C.F. COLEMAN - K.B. BROWN
J.G. MOORE - K.A. ALLEN — Sec. Geneva Conf. P/510 and the numerous ORNL reports cited in this paper

W.E. KEDER - J.C. SHEPPARD - A.S. WILSON — HW 60-300

E.A. MASON - V.C. VAUGHAN — A.E.C.U. 4239 and 4351

SEPARATIONS:

U. BERTOCCI — A.E.R.E. R. 2933

E. CERRARI - C. TESTA — Energia Nucleare 6 707-16 (1959)

C.F. COLEMAN et al — Sec. Geneva Conf. P/510

G.W. LEDDICOTTE - F.L. MOORE — Journ. Amer. Chem. Soc. 74 1618 (1952)

F.L. MOORE	O.R.N.L. 1314 (1952) C.F. 57-6-61 Anal. Chem. USA 29 1660-2 (1957) " " " 30 5-908-11 (1958)
J.C. SHEPPARD	H.W. 51-958-10 F 1
M. de TRENTINIAN - A. CHESNE	Rapp. CEA N° 1426
A.S. WILSON	Sec. Geneva Conf. P/544
R.S. WINCHESTER W.J. MARAMAN	Sec. Geneva Conf. P/530

St.nr. 3713

Calculated Solvent Irradiation Levels Per Cycle

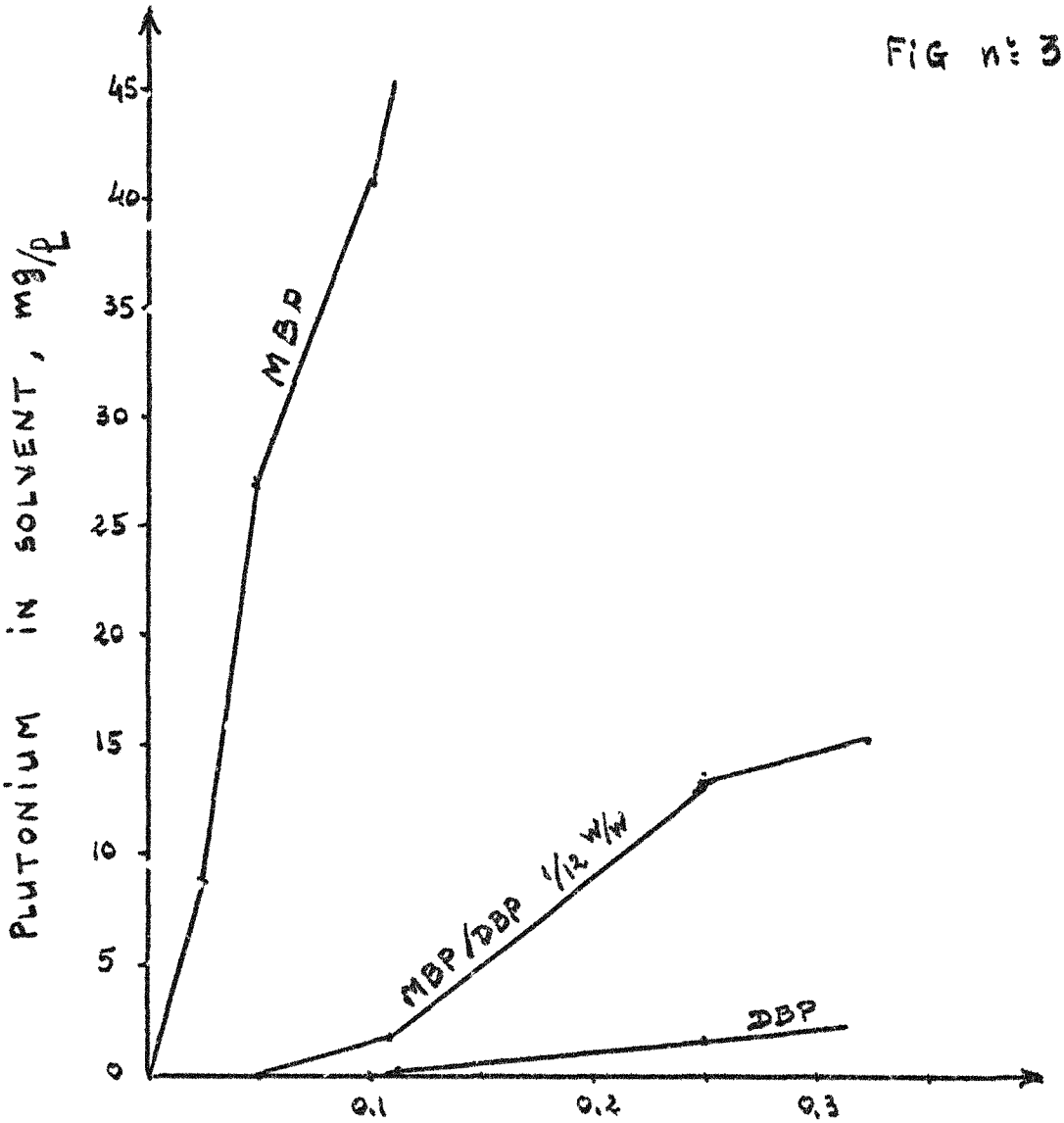
Fig n° 1

	Burn-up.	Cooling Time days	Solvent Exposure β^{wh}/ℓ
Graphite (Brookhaven) Feed 320 g/ℓ U	588 Mwd/t	90	0.01
Thermal Power Fuel Feed 320 g/ℓ U	10.000 Mwd/t	10	0.48
	10.000 Mwd/t	100	0.27
Fast Power Fuel (APDA) Feed 237 g/ℓ U	5% U_{235}	10	1.9
	5% U_{235}	50	2.57
Thorex Feed 1 M Th	4000 g U_{235}/T	30	1.3

FROM : V.R. Cooper and M.T. Walling Jr.

RETENTION OF PLUTONIUM

FIG n: 3

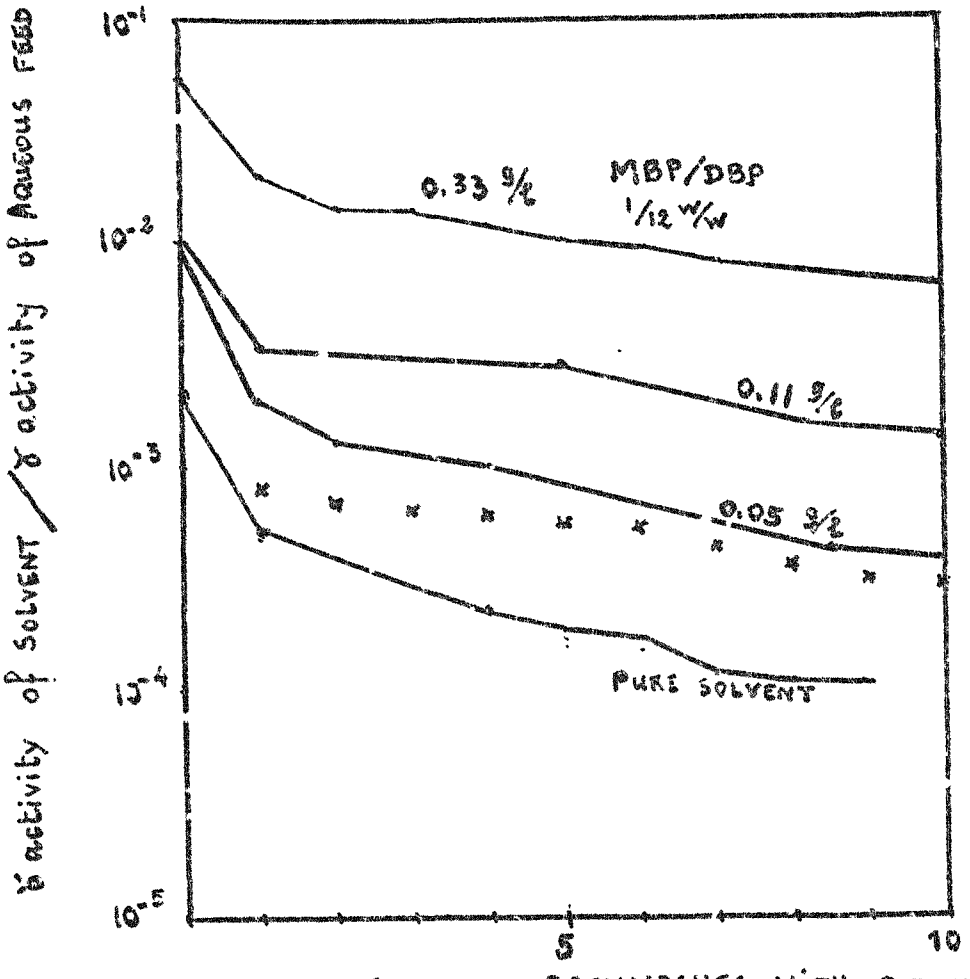


SOLVENT : 20% TBP-OK Aqueous feed 1 g/l Pu^{IV} - 200 g/l U - 3N NO_3H
BACKWASHED 3 + 2 volumes NO_3H 0.01 N

FROM T. RIGG and W. WILD

RETENTION OF FISSION PRODUCTS

FIG n° 4



SOLVENT : 20% TBP - OK Aqueous feed U 200 g/ℓ Pu 1 g/ℓ NO_3H 3M

× SOLVENT IRRADIATED TO 0.7 WATT-HOUR/LITER Fission Products

FROM T. RIGG and W. WILD

EFFECT OF RADIATION ON TBP - EXTRACTION PROCESS

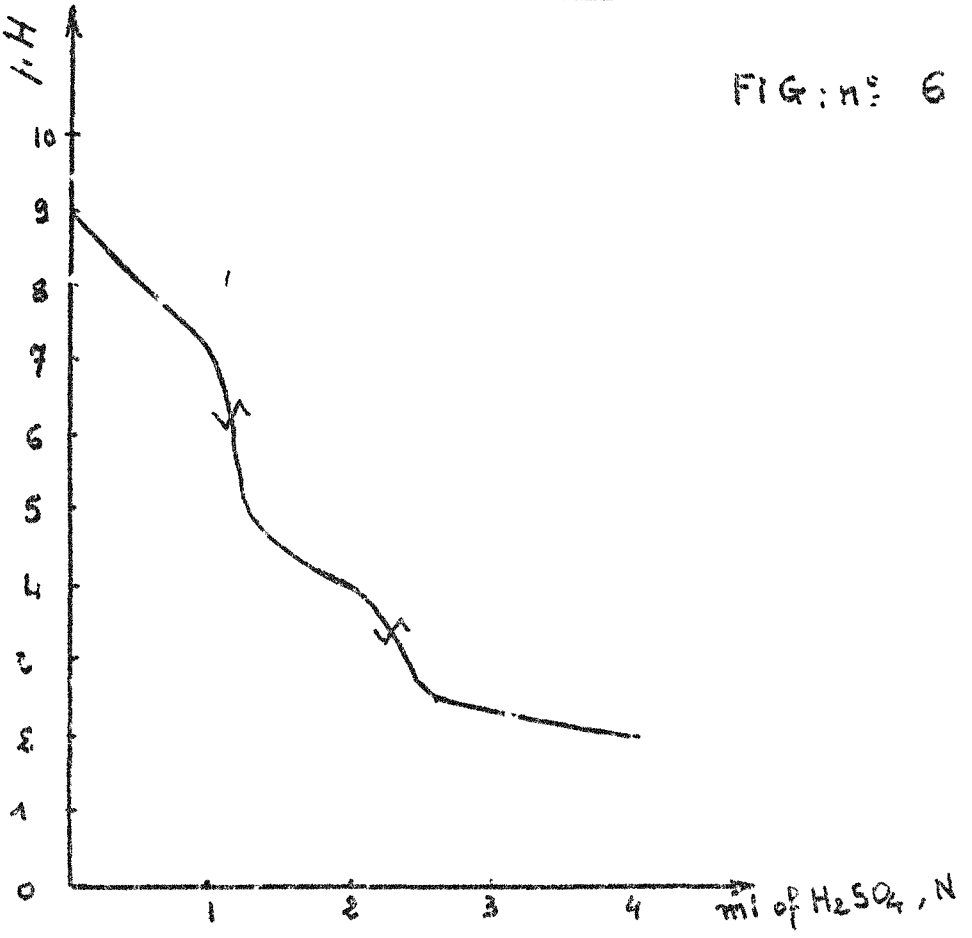
FIG n: 5

Solvent Exposure β WH/ℓ	Observed Effect
0.01	None
0.5	2-fold decrease in Ru decontamination factor (Thorex)
4.3	2-fold decrease in 25 process decontamination factor Significant Pu Loss
5 - 10	Severe Emulsions in Thorex
18	Significant U loss
24	25-fold decrease in 25 process decontamination factor

FROM : W.R. COOPER and M.T. WALLING Jr

TITRATION CURVE OF AN AMINE BY SULFURIC ACID

FIG: n° 6

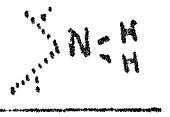
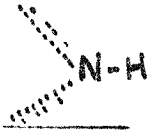


Amine: TRI-n.OCTYLAMINE
Diluent: Benzine and ethylic alcohol

FROM: C. BOIRIE

EFFECT OF AMINE STRUCTURE ON EXTRACTION OF METAL SULFATES

FIG n°: 7

METAL ION	EXTRACTION COEFFICIENT $E_a^o = [M]_o/[M]_a$		
			
Co^{II}, Ni^{II}	< 0.1	< 0.01	< 0.01
Fe^{III}	40	< 0.5	< 0.01
$R.E^{III}$	20	< 0.1	< 0.01
Zr	> 1 000	350	200
Th	> 5 000	> 500	< 0,1
Mo^{VI}	150		150
U^{IV}	40	120	90

AMINES : PRIMARY — PRIMENE JM-T
SECONDARY — DI(TRIDECYL) AMINE
TERTIARY — TRI-ISO-OCTYL AMINE

AMINE CONC: 0.1 M in aromatic diluent.

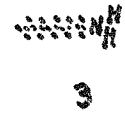
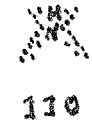
Aqueous solution 1M H_2SO_4 pH 1

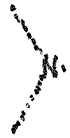
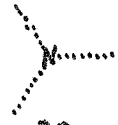
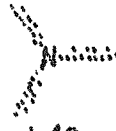
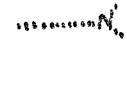
FROM : C.F. COLEMAN - K.B. BROWN - J.G. MOORE - K.A. ALLEN

EFFECT OF AMINE STRUCTURE AND DILUENT ON URANIUM EXTRACTION

Fig n° : 8

URANIUM EXTRACTION COEFFICIENT

					
Ker.	3	25		80	110
Ben.	10	40	90	120	20
Chl.	90	50	150	40	2

					
Ker.		30	140		
Ben.	50	150	60	80	<0.1
Chl.	50	5	0.3	100	20

KER. = KEROSENE
BEN. = BENZENE
Chl. = Chloroform

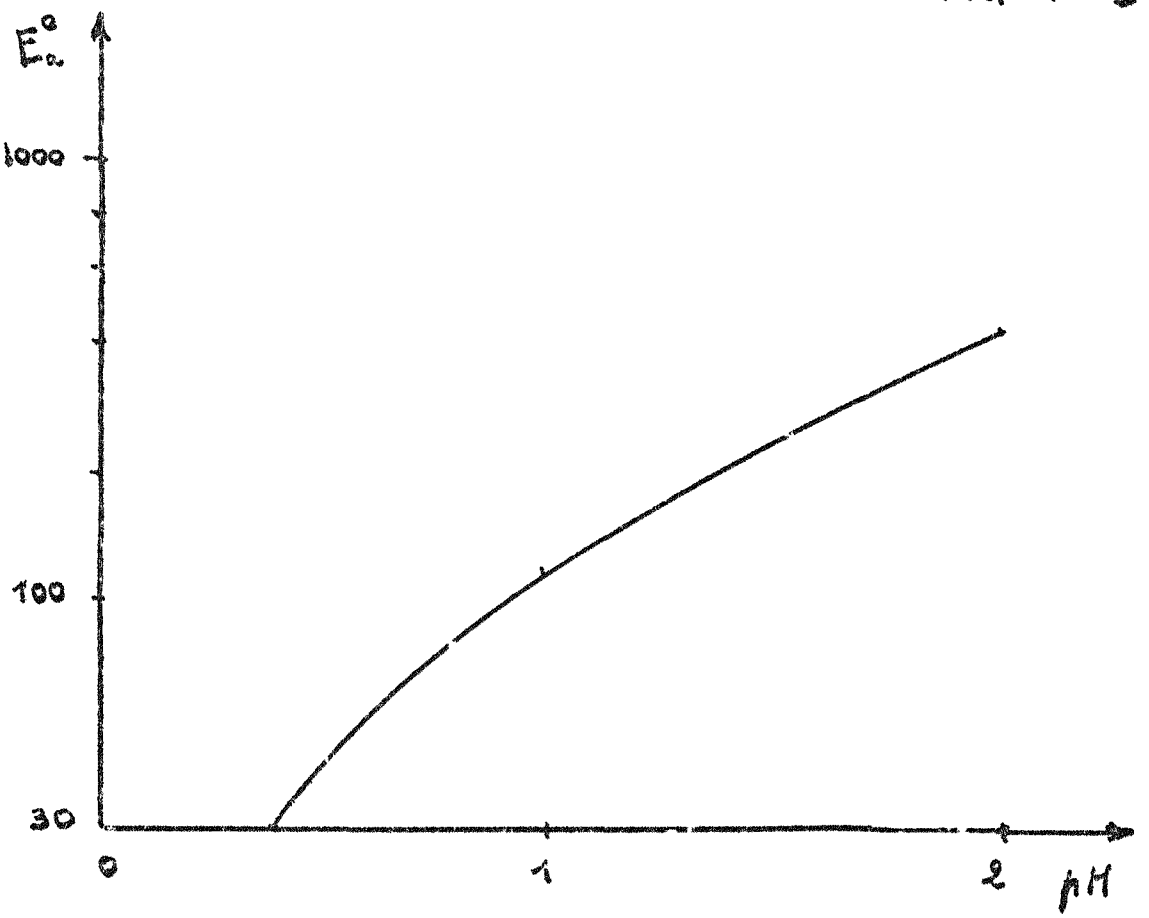
Aqueous Phase : 1 M SO_4^{--} pH: 1
0.004 M U

Solvent Phase 0.1 M amine in { kerosene / benzene / chloroform }

FROM: C.F. COLEMAN et al.

EFFECT OF THE pH ON THE URANIUM EXTRACTION COEFFICIENTS

FIG n° 9



$[SO_4]$ 0.5 M

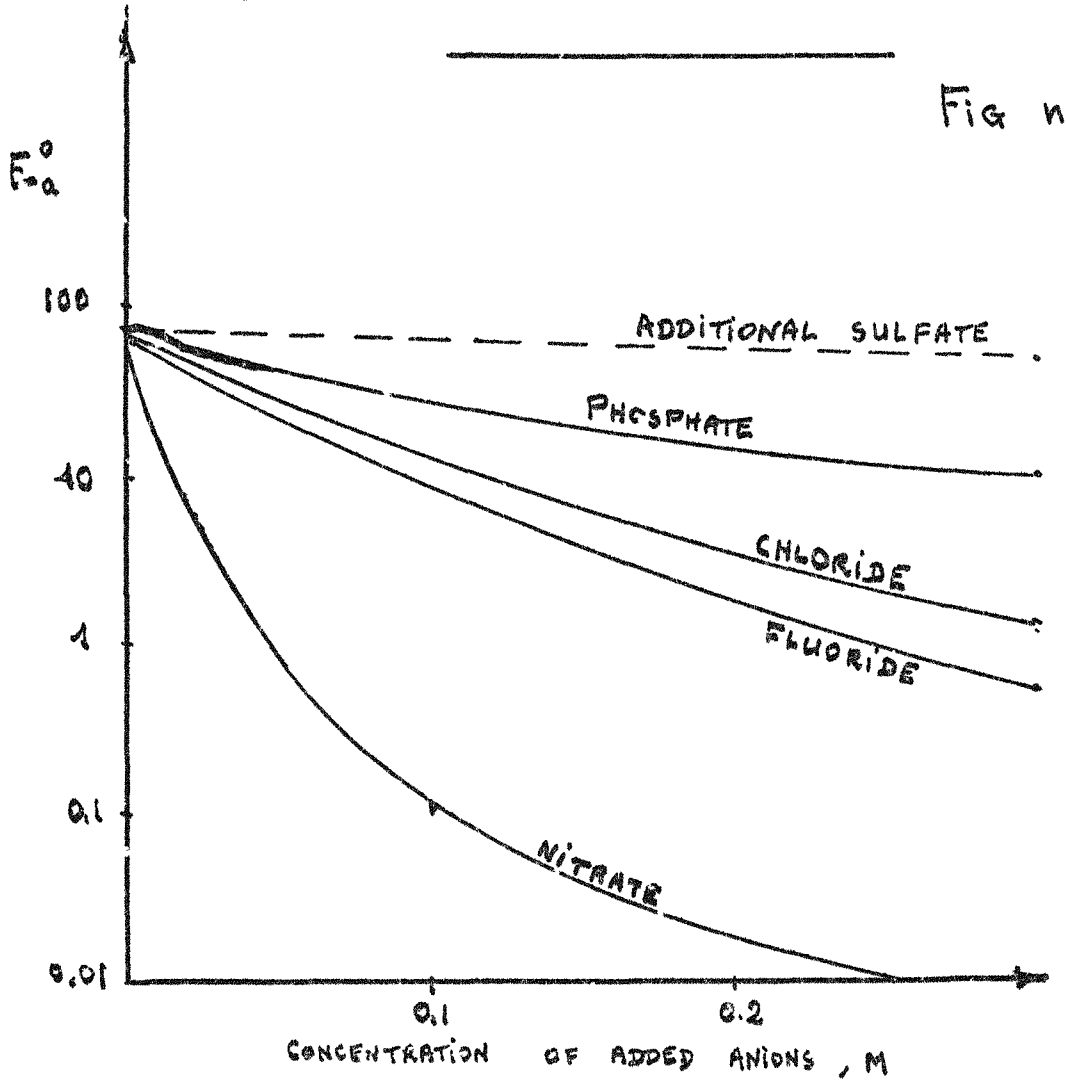
$[U]_o$ 0,1 M

Amine : 0,1 M TRI-ISO-OCTYL AMINE in AMSCO D-95

FROM : C.F. COLEMAN et al.

EFFECT OF ANIONS ON URANIUM EXTRACTION

Fig n° 10

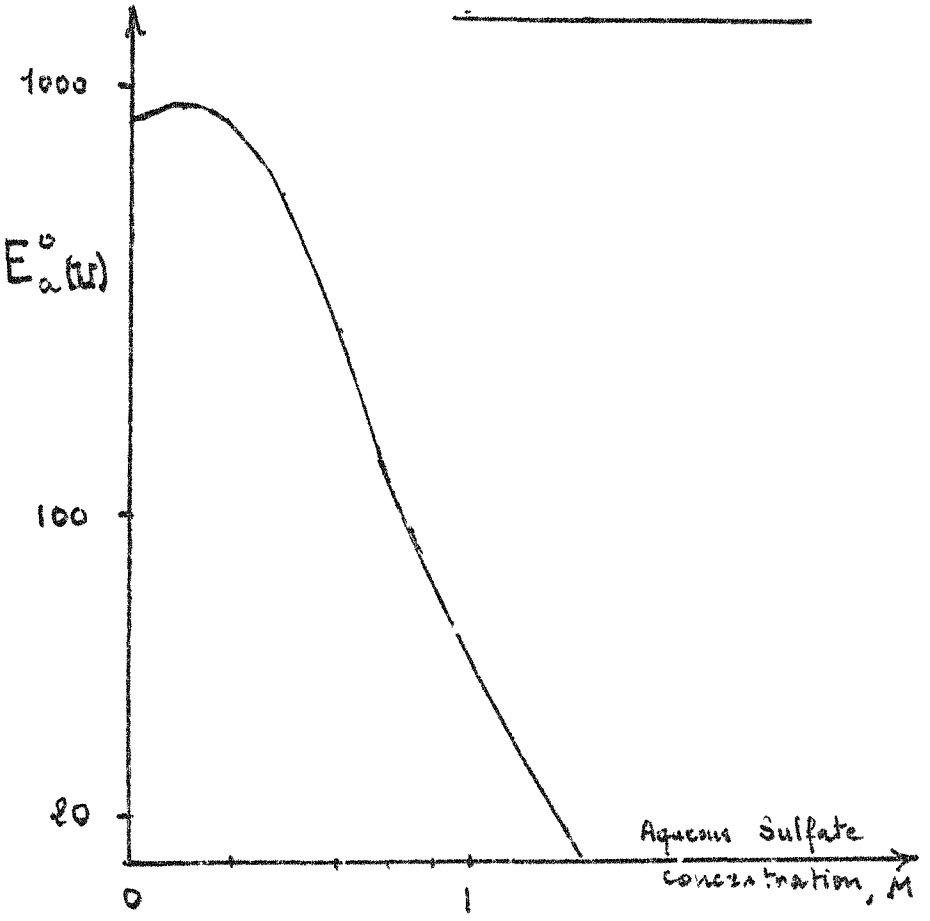


AMINE : 0.1M TRI-N-OCTYLAMINE IN AMSCO D-95
AQUEOUS SOLUTION 1M SO_4 pH 1

FROM : CF COLEMAN et al.

EFFECT OF AQUEOUS SULFATE CONCENTRATION ON URANIUM EXTRACTION

FIG n° 11

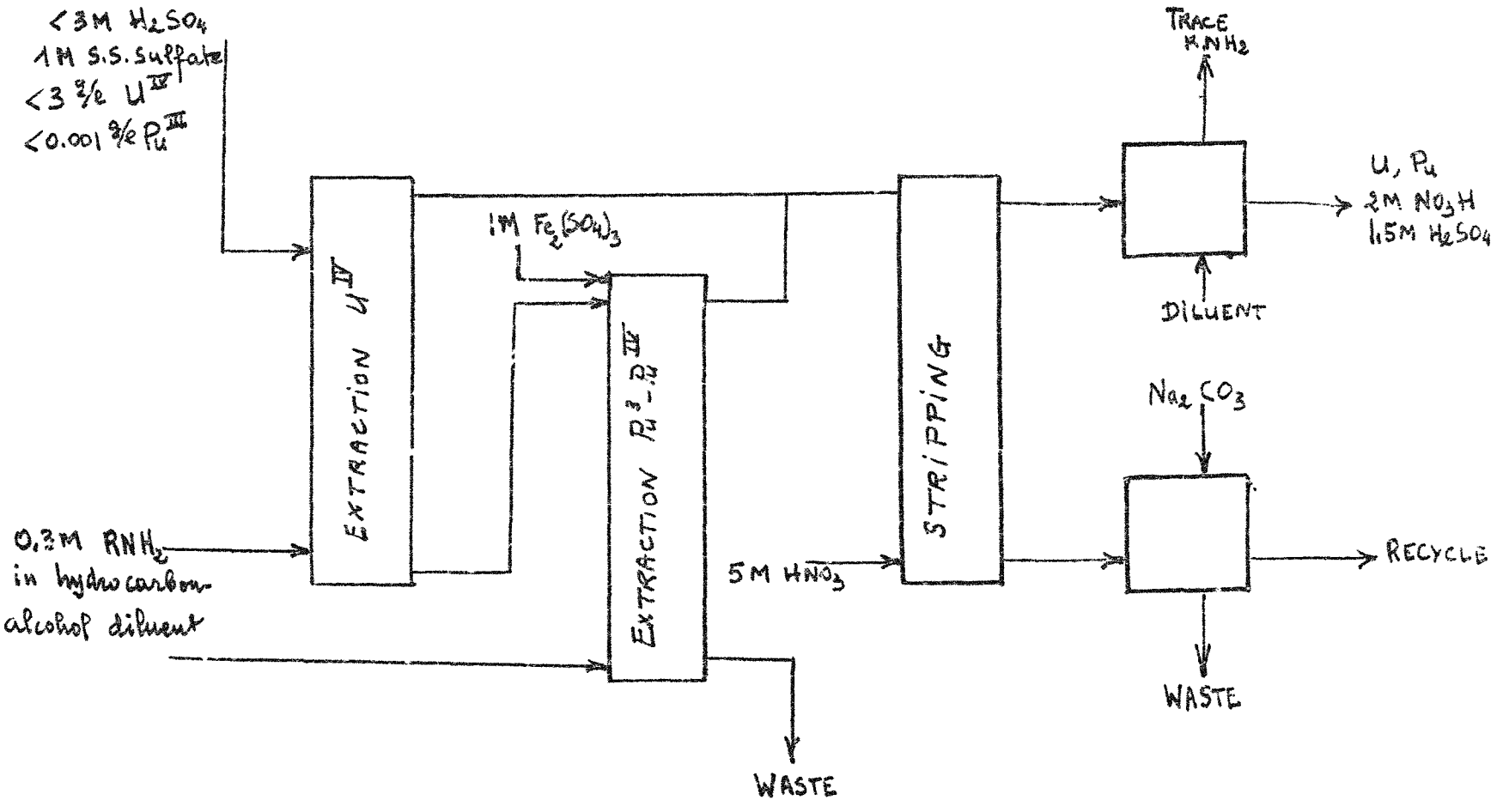


Solvent : 0,1 M TRI-n-OCTYLAMINE in AMSCO D 95
0,01 M U in organic phase
pH 1

FROM : C.F. COLEMAN et al.

RECOVERY OF URANIUM AND PLUTONIUM FROM SULFEX DECLADDING SOLUTIONS

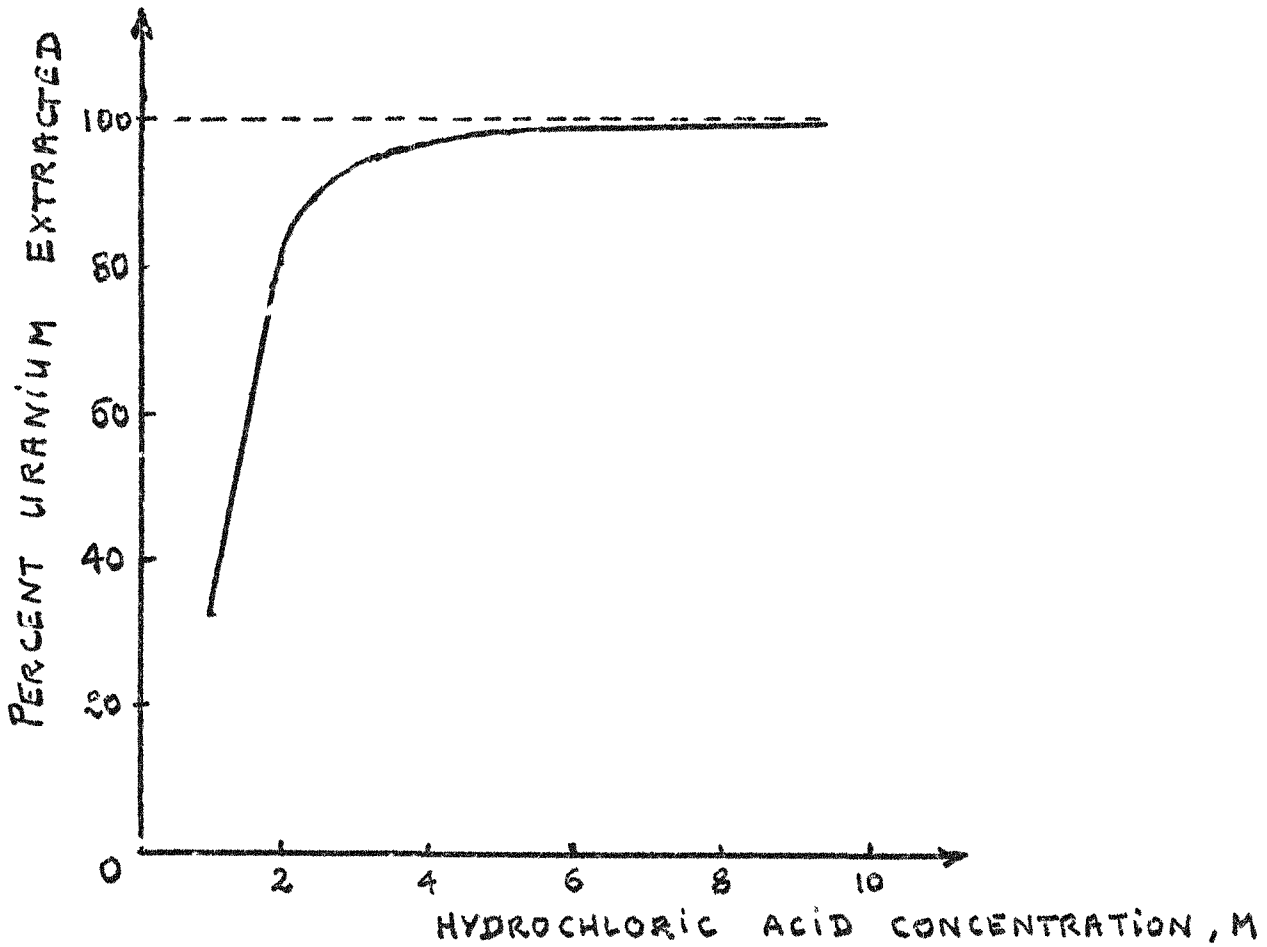
FIG : n° 12



FROM: F.R. BRUCE . R.E. BLANCO - J.C. BREESE

EXTRACTION OF URANIUM

Fig nº 13



SOLVENT TRI-ISO-OCTYLAMINE 5% IN XYLENE

FROM : F. L. MOORE

EXTRACTION OF FISSION PRODUCTS

FIG n° 14

Element	HCl, M	Tracer Extracted %	Element	HCl, M	Tracer Extracted %
Nb^{95}	2.2	0.3	Sr^{85}	2.1	0
	4.4	3.1		4.2	0
	4.6	6.2		6.4	0
	4.8	9.5		8.5	0
	5.0	17.4		10.6	
	6.5	90.2	Ru^{106}		
	6.8	96.8		0.1	82.3
	9.0	99.2		0.2	77.7
				1.1	75.0
Zr^{95}	2.1	0.02		2.1	74.3
	4.2	0.4		4.2	72.5
	6.3	0.7		6.4	69.8
	8.4	89.6		8.5	58.6
	10.5	99.0		10.6	29.4

Solvent : Tri.iso-octyl-Amine 5% in XYLENE

FROM : F. L. MOORE

Extraction of nitric acid by a tertiary amine

FIG n° 15

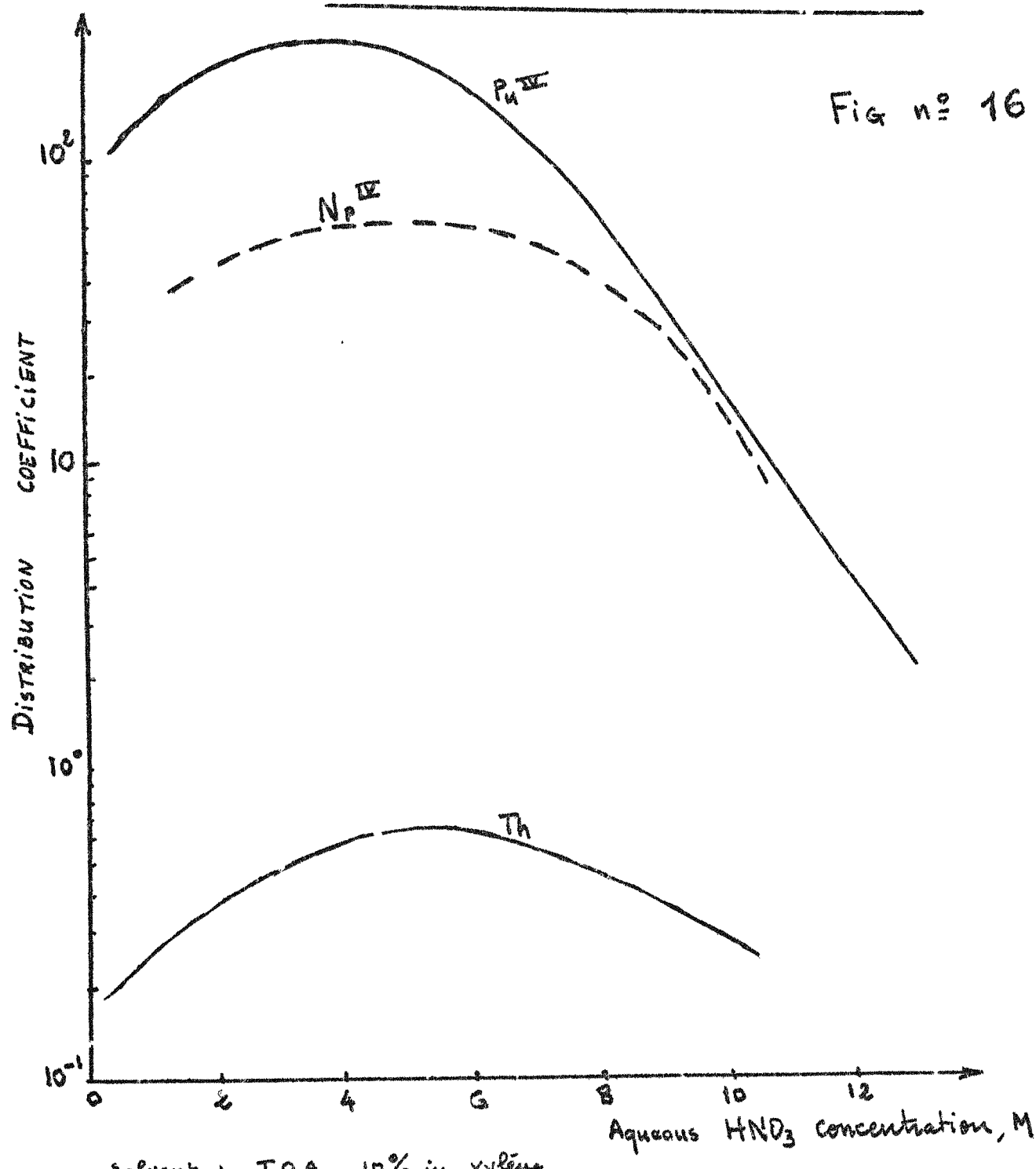
$\|HNO_3\|_a$	$\|TNA\|_o$	$\|HNO_3\|_o$	$\|HNO_3$ free$\|_o / \|TNA\|_o$
2	0.262	0.355	0,35
4	0.262	0,443	0,69
6	0.262	0,516	0,97
10	0.262	0.678	1.59

amine : TRi-nonyl amine
diluent : xylène

deduced from U. BERTOCCI

EXTRACTION OF TETRAVALENT ACTINIDE NITRATES

Fig n° 16

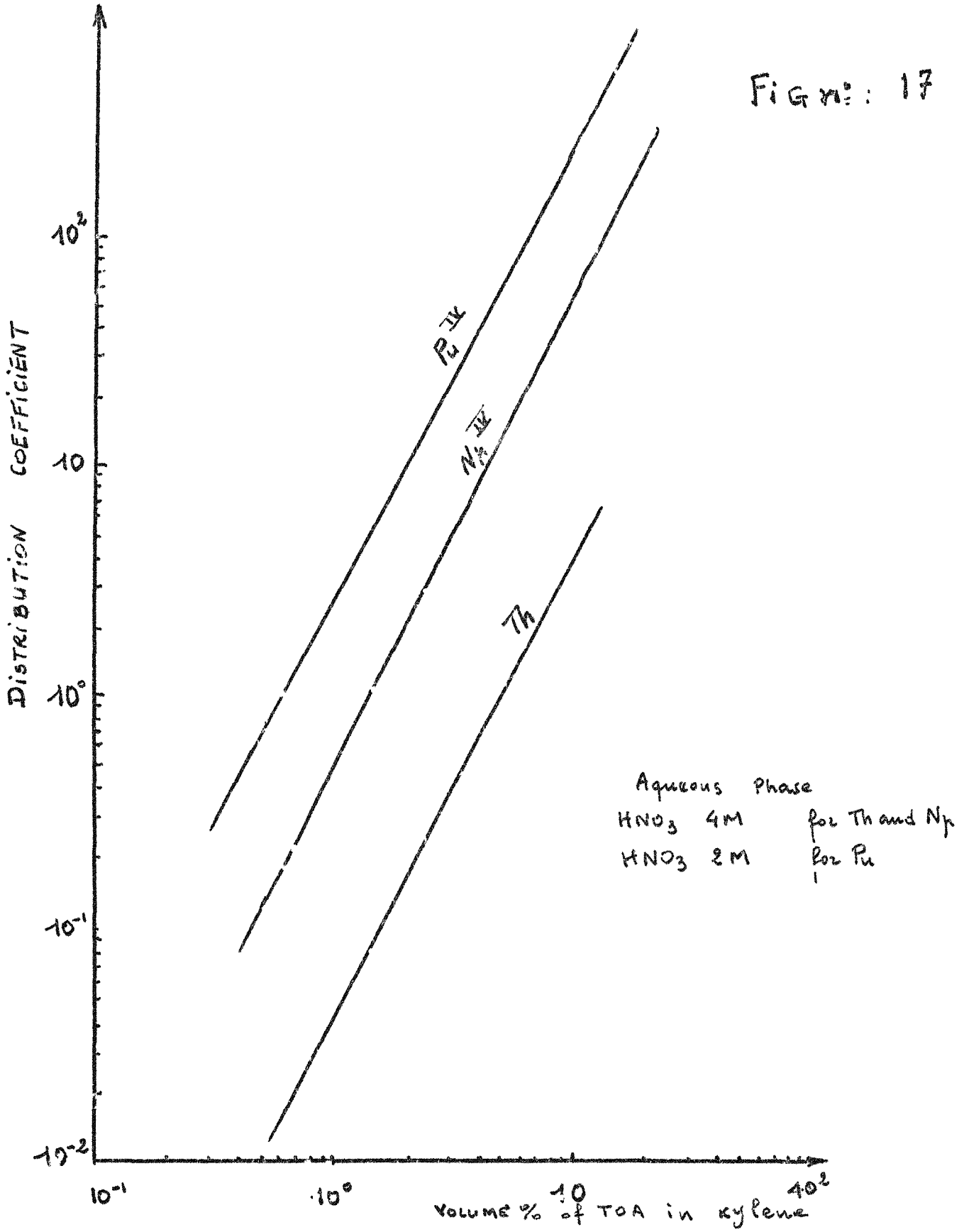


Solvent : TOA 10% in xylène

FROM : W.E. KEDER et al.

EFFECT OF Amine CONCENTRATION

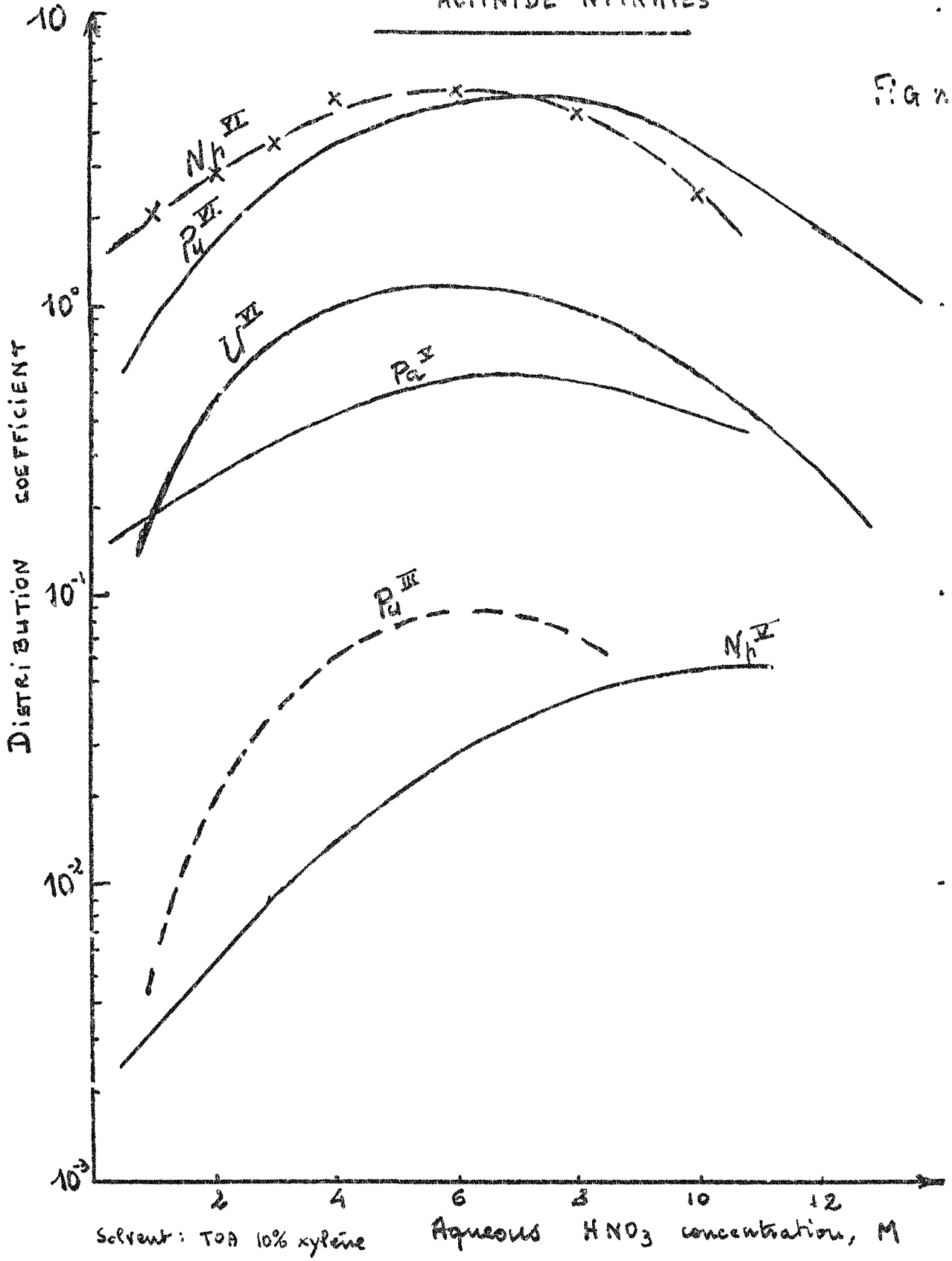
FIGURE : 17



FROM: W.E. KEDER et al.

The Extraction of Hexa-, Penta-, and Tri-valent Actinide Nitrates

Fig n° 18



From : W.E. Keder et al.

SEPARATION COEFFICIENTS BETWEEN Pu^{IV} AND SOME ACTINIDES AND FISSION PRODUCTS

FIG n° 19

ELEMENTS	$\alpha = \frac{\text{Dist. Coef. } Pu^{4+}}{\text{Dist. Coef. element}}$
Th	100
Pa	500
U^{VI}	600
Np^{IV}	4
Np^{V}	$> 2 \times 10^4$
Np^{VI}	90
Pu^{III}	10^5
Am^{III}	10^5
Ce^{III}	10^5
Zr	10^4
Ru	$\sim 5 \times 10^3$

Aqueous Phase : HNO_3 2M

Solvent : TLA nitrate 0,17 M in Dodecane

FROM : DE TRENTINIAN and A. CHESNÉ

Plutonium Extraction by several tertiary amines

Fig n° 20

Tertiary amines	Distribution coefficient
Tri - n hexyl	85
Tri - n - heptyl	92
Tri - n - octyl	250
Tri iso octyl	300
Tri décyl	115
Tri lauryl	140
Tri - nonyl *	4.7

Solvent : Amine 10% in xylène
aqueous : HNO_3 2N - $NaNO_2$ 0.03 M - Fe in traces

FROM : A.S. WILSON

* TNA 0.17 M in xylène
2M HNO_3 in aqueous.

FROM : J. BERTOZZI

EFFECT OF URANIUM AND NITRIC ACID ON THE EXTRACTION OF PLUTONIUM

FIG n° : 21

	Pu^{IV} DISTRIBUTION COEFFICIENT					
M U aq.	1.26	0.84	0.42	0.126	0.042	0.00
M HNO_3 aq.						
1	9	10	20	31	59	65
2	7	10	18	67	105	140
4	6	8	20	47	90	170

SOLVENT : TRI-LAURYL AMINE 0.15 M
in AMSCO - 2% octyl alcohol

FROM : A.S. WILSON

EFFECT OF THE DILUENT ON THE LOADING OF PLUTONIUM WITHOUT THIRD PHASE *

Fig n°: 22

Diluent	Limit of Plutonium concentration
CCl_4	0.1 g/ℓ
$CHCl_3$	8.3 g/ℓ
$CHBr_2$	12 g/ℓ
$2\,CCl_4 + C_2Br_4$	7.6 g/ℓ.
Nitromethane	26 g/ℓ

EFFECT OF ALCOHOL * *

% alcohol	Plutonium conc.
2	0.5 g/ℓ
10	> 5.2 g/ℓ

* Tri.n.octylamine 0.22 M

* * TRI Laurylamine 0.15 M in Amsco

FROM: A. S. Wilson

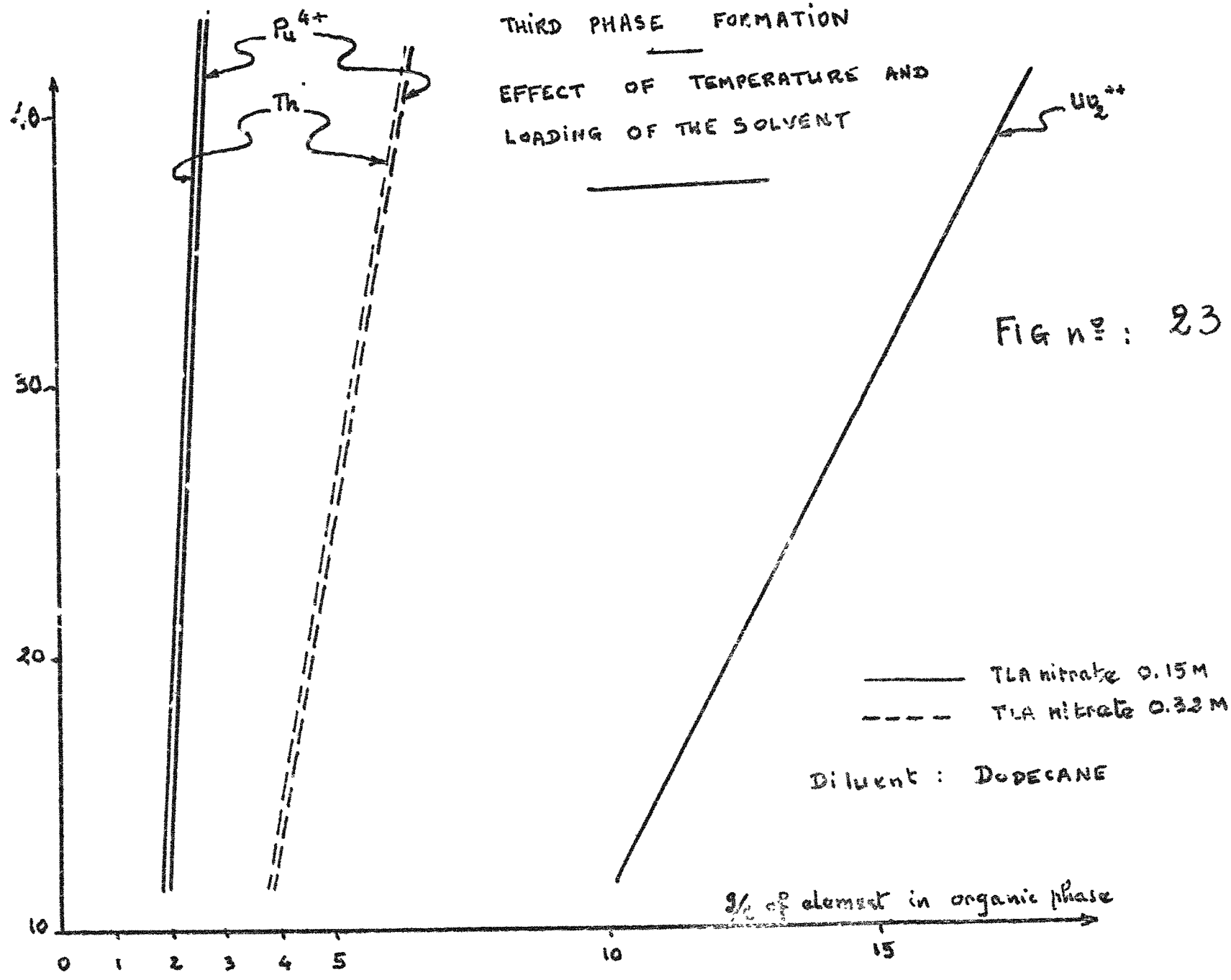
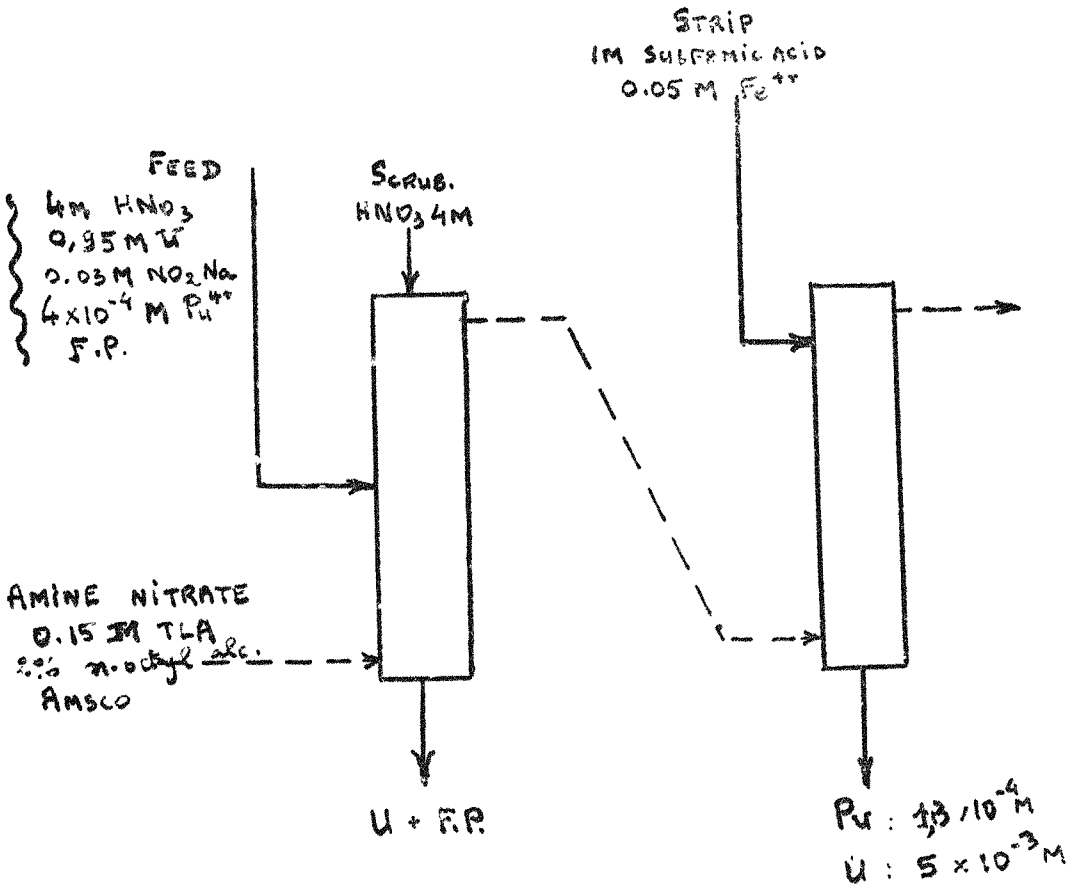


FIG n° : 23

FROM: DE TRENTINIAN and A. CHESNÉ

SEPARATION OF PLUTONIUM FROM NITRIC ACID SOLUTIONS OF IRRADIATED URANIUM

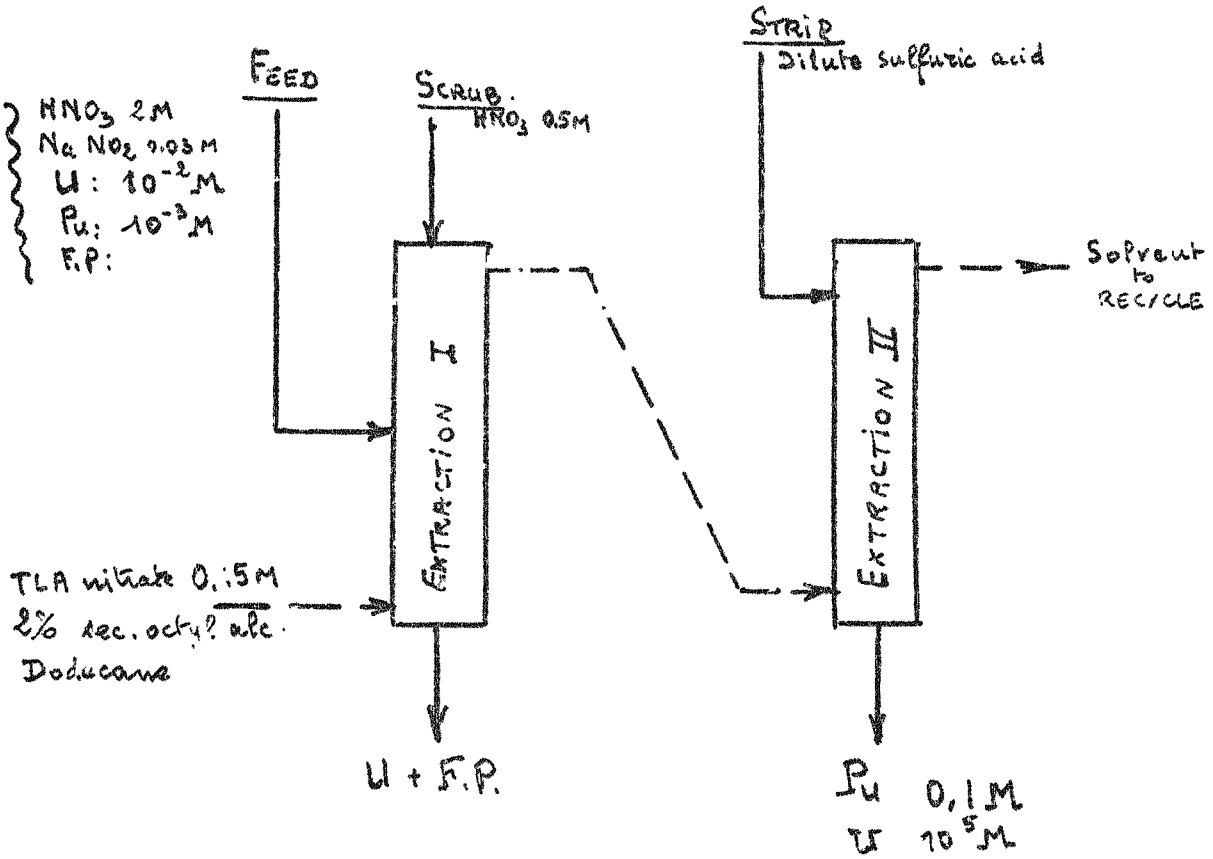
FIG n°: 24



DEDUCED FROM : A.S. WILSON

CONCENTRATION AND PURIFICATION OF PLUTONIUM NITRATE SOLUTIONS

FIG n°: 25



FROM : A. CHESNÉ

THE ADVANCED SUMMER INSTITUTE AT KJELLER

Section III

TAIL-END TREATMENT FOR ISOLATION OF PU

A. Chesné
Centre d'Etude Nucléaires
Fontenay-aux-Roses, France.

S O M M A I R E

TAIL-END TREATMENT FOR ISOLATION OF PU

by

A. CHESNE

I. INTRODUCTION

Dans le cours du traitement chimique des combustibles irradiés, les cycles d'extraction par solvant permettent de séparer les éléments Uranium et Plutonium d'un grand nombre d'impuretés: les produits de fission. Le degré de séparation, appelé facteur de décontamination doit être très élevé et dépend en particulier de la nature du solvant utilisé et du nombre de cycles d'extraction effectués. Selon les conditions, ces facteurs de décontamination se répartissent dans une zone allant de 10^5 à 10^8.

Bien que ces facteurs soient très élevés, les solutions d'uranium et de plutonium résultant du cycle de partition de ces deux éléments, contiennent encore quelques produits de fission et certaines impuretés pondérales qui sont les produits de corrosion.

Le but des procédés de purification ultime, appliqués aux solutions d'uranium, comme aux solutions de plutonium sera donc de parfaire le travail de décontamination effectué dans la première partie du traitement chimique et aussi d'amener les éléments uranium et plutonium sous forme de composés solides aptes à fournir du métal par réduction.

Dans le premier stade du tail-end: élimination des impuretés, différentes méthodes de purification seront évoquées plus loin. Elles peuvent être identiques à celles utilisées dans la séparation primaire ou bien faire appel à d'autres propriétés des éléments à purifier. Dans ce dernier cas, nous les appellerons complémentaires. Ce sont ces méthodes complémentaires qui donnent aux procédés de purification ultime une grande importance sur le plan technique comme sur le plan économique.

Sur le plan technique on peut ainsi obtenir des facteurs de décontamination supplémentaires et sur le plan économique ceux-ci peuvent permettre de réduire le nombre de cycles d'extraction dans la séparation primaire. La nature et le degré d'irradiation du combustible à une importance déterminant sur le nombre de ces cycles. On doit par exemple effectuer trois cycles d'extraction à l'hexone lors du traitement d'élément U - Al du M.T.R., pour obtenir un produit manipulable sans protection. La figure I montre d'ailleurs les facteurs de décontamination obtenus pour divers procédés: 25 - Redox-Purex.

En résumé, les trois objectifs principaux que tend à réaliser le traitement chimique final sont:
- concentration du plutonium et de l'uranium
- purification de ces éléments
- transformation des solutions purifiées en un composé insoluble apte à fournir l'oxyde ou par une réaction de réduction, le métal.

Les procédés de traitement que nous allons décrire ci-dessous font appel à des techniques diverses, mises en application à l'échelle pilote ou dans les usines de retraitement.

D'autres techniques pourront être utilisées dans l'avenir, au fur et à mesure que ces procédés se développeront. Aussi, pour ménager les possibilités futures nous classerons arbitrairement les procédés en fonction des opérations effectuées sur le corps à purifier.

Nous distinguerons ainsi les méthodes directes où l'on agit sur l'élément à purifier soit en le séparant de la solution sous forme solide: par exemple précipitation, fixation sur résine échangeuses d'ions,
- soit sous une forme liquide par exemple: extraction par solvant.

Les méthodes indirectes consistent essentiellement à agir non pas sur l'élément, mais tout ce qui n'est pas l'élément: impuretés, solution.

On y trouve donc les techniques d'évaporation en ce qui concerne l'action sur la solution et les séparations des impuretés sous forme solide, exemple: fixation sur colonne de silica gel ou sous forme liquide.

Pour des raisons de simplicité, nous examinerons à part le traitement des solutions d'uranium et celui des solutions de plutonium, ces deux sortes de solutions venant de la séparation primaire. Deux chapitres seront abordés: a) concentration et purification - Ces deux objectifs étant souvent réalisés de pair. b) Transformation en composés solides.

II. TRAITEMENT FINAL DE L'URANIUM

Les solutions aqueuses d'uranium provenant de la réextraction à l'acide dilué d'un solvant ayant subi un ou plusieurs cycles de purification et un cycle de partition U - Pu, sont relativement diluées. Dans le cas d'un solvant à 40% de TBP, la solution aqueuse résultante a une composition voisine de:

- U (sous forme de nitrate d'uranyle) 0,235 M
- HNO_3 0,7 M
- Produits de fission: principalement Zr-Nb - Ru

Dans le cas d'un traitement au 3β : dibutoxy-dibutyl-ether (Butex) on obtient:

- U environ 0,5 M
- HNO_3 0,7 M
- Produits de fission: principalement Ru-Zr-Nb

A. METHODES DE CONCENTRATION ET DE PURIFICATION

1. Evaporation

La concentration par évaporation du nitrate d'uranyle ainsi obtenu ne présente pas de difficultés spéciales. Cependant il est souhaitable d'éviter l'entraînement dans l'évaporateur de traces de solvant qui créent des risques d'explosion. Ceci est réalisé par lavage de la solution aqueuse nitrique par un diluant inerte (kérosène) et ou par entraînement à la vapeur (steam-stripping). Une bonne régulation de l'évaporateur est souhaitable également pour éviter des surchauffes.

Cette opération de concentration conduit à des solutions finales de concentration voisine de 2 M en nitrate d'uranyle. A signaler qu'elle n'amène aucune décontamination de la solution en

émetteurs γ et que par contre une légère corrosion de l'évaporateur à pour conséquence d'introduire en solution des cations tels: Fe et des particules solides.

2. Emploi des collones de gel de silice

On à trouvé que l'activité γ dûe au couple Zr^{95}-Nb^{95} pouvait être enlevée d'une solution de nitrate d'uranyle par passage de celle-ci sur du gel de silice. A côté de l'état physiocochimique des ces deux éléments dans la solution, l'effet d'un certain nombre de variables sur l'absorption a été étudiée. Nous passerons en revue les facteurs suivants:

- dimension des particules. L'absorption du Zr-Nb étant un phénomène de surface, l'augmentation de celle-ci par diminution du diamètre des particules est favorable à la fixation de ces deux éléments.
- acidité de la phase aqueuse: entre 0,3 et 0,9 N en acide nitrique, aucun effet de l'acidité n'a été observé. Au-delà de 0,9 N, l'efficacité de l'absorption du Zr-Nb décroit quand l'acidité croit.
- caractéristique des colonnes de silica-gel. Pour une hauteur de colonne fixée l'augmentation du débit diminue l'efficacité de la fixation et donc le facteur de décontamination de l'uranium en Zr-Nb.

A débit donné ce facteur de décontamination augmente avec la hauteur de colonne. Le résumé de ces remarques est indiqué sur la figure 2.

Sur la figure 3 est indiqué un schéma de traitement d'une solution d'uranium partiellement décontaminée. Les conditions en sont les suivantes:

- Gel de silice: Réfrigération grade silica (12-42 mesh)
- conditionnement: lavage du gel par trois fois son volume d'eau bouillante puis par 3 fois son volume de HNO_3, 1 N.
- purification: la solution de nitrate d'uranyle amenée à $UO_2(NO_3)_2$ 1,7 M HNO_3 0,75 M est passée sur le gel. Un volume allant jusqu'à 200 fois le volume du gel est admissible.
- lavage: 3 fois le volume du gel par NO_3H, 1 N.
- régénération: $C_2O_4H_2$ 0,4 M à 80-90°C 6 volumes
  puis: H_2O 30°C 4 volumes du gel

Le résultat que ce traitement permet d'obtenir est une décontamination appréciable de l'uranium en Zr-Nb. La fixation de ces éléments sur le silica gel est en partie mécanique, le gel jouant le rôle de filtre. Le facteur de décontamination, voisin de 7, dépend de l'activité initiale en Zr-Nb.

3. Emploi de nouveaux cycles d'extraction

L'efficacité du silica-gel est limitée au couple Zr-Nb.

Dans le cas où la contamination de la solution de nitrate d'uranyle est trop importante, ou lorsque cette contamination est dûe aux traces de plutonium ou au ruthenium, il est préférable d'effectuer à nouveau un cycle d'extraction. On a réalisé ceci dans de nombreuses installations généralement en utilisant dans ce nouveau cycle le même solvant que dans le cycle primaire.

La figure 4 représente un traitement de purification de l'uranium du procédé au butex. Après réextraction à l'acide nitrique dilué de l'uranium contenu dans le solvant, la solution aqueuse résultante, concentrée, reconditionnée est à nouveau introduite dans un cycle Butex (c'est-à-dire Extraction-Réextraction). Le conditionnement a permis par action d'hydrazine et de sulfamate ferreux de fixer la valence du plutonium à +3 et de modifier l'état du ruthenium.

Les résultats finaux sont: facteurs de décontamination de 200, 200 et 40 respectivement pour Ru, Zr-Nb, Pu.

L'extraction par solvant sera la méthode de choix lorsque la contamination en plutonium dépassera le niveau tolérable.

B. TRANSFORMATION DE L'URANIUM EN COMPOSES INSOLUBLES

A côté des solutions classiques de transformation du nitrate d'uranyle en sels aptes à être réduit à l'état métallique, deux nouvelles méthodes ont été préconisées. Il s'agit des procédés Excer et Flurex. Dans ces deux procédés, le produit final obtenu est le fluorure uraneux, matière de base permettant de réaliser la calcio-ou la ragnésio-thermie.

Dans la transformation que nous appelerons classique le nitrate était transformé en oxyde UO_3 (avec ou sans l'étape intermédiaire du peroxyde UO_4) puis cet oxyde réduit en oxyde uraneux UO_2 (réducteur gaz-ammoniac craqué). La fluoration de cet oxyde à l'acide fluorhydrique fournit le fluorure UF_4.

Le principe du procédé Excer est la réduction électrolytique de UO_2^{++} en U^{4+} et la précipitation de ce dernier cation par HF en milieu aqueux donnant UF_4 - 0,75 H_2O. Ce fluorure hydraté est séché à 400°C en présence d'azote et donne UF_4 anhydre.

Les facteurs de décontamination obtenus sont compris entre 10^3 et 10^4 pour Fe, Cr, Ni, Mn, V, Mo - compris entre 10 et 100 pour Zr-Nb Ru compris entre 1 et 5 pour Cs, Sr, Terres Rares.

Le flow-sheet du procédé est indiqué sur la figure 5. Signalons que l'utilisation d'un cycle supplémentaire sur colonne anion en milieu chlorhydrique donne des facteurs de décontamination de 68 pour Zr, 1480 pour Nb, 525 pour Sr, 7600 pour Cs, 275 pour Ru. Des élutions de la colonne cations à HF ont donné des résultats intéressants en ce qui concerne la décontamination.

Dans le procédé Flurex la séparation de l'uranium UO_2^{++} des ions NO_3^- et sa réduction à l'état tetravalent sont effectués dans une cellule d'électrolyse comportant 3 compartiments séparés par une membrane de résine échangeuse de cations et une membrane de résine échangeuse d'anions. Comme on le voit sur la figure 6, l'uranium diffuse dans le compartiment cathodique tandis que les ions NO_3^- diffusent dans le compartiment anodique. Une solution fluorhydrique (HF + NH_4F) est admise en continu dans le compartiment cathodique dont l'électrode est une cathode de mercure. L'uranium réduit est précipité à l'état de sel double puis prélevé, filtré, séché et converti en UF_4 par chauffage à 400°C-500°C.

Les densités de courant utilisées sont de 2 ampères/inch^2 à la cathode et 1 ampère/inch^2 sur les membranes avec des efficacités d'utilisation du courant de 85 à 90%. Les facteurs de décontamination obtenus ne sont malheureusement pas encore publiés en détail mais les premières indications semblent satisfaisantes.

III. TRAITEMENT ULTIME DU PLUTONIUM

Etant donné la faible teneur en Pu du combustible irradié les solutions obtenues après un traitement Purex par exemple sont très diluées. Le plutonium s'y trouve à l'état de valence +3 en présence d'acide nitrique dilué, d'acide sulfamique, de quantités plus ou moins importantes d'uranium non séparé et également en présence de cations ayant servi à la réextraction; généralement: Fe^{++}/Fe^{+++} quelquefois U^{4+}/UO_2^{++}.

Une telle solution est encore contaminée par des produits de fission ayant suivi le plutonium dans les cycles d'extraction. L'activité de ces produits de fission est en général dûe au couple Zr^{95}-Nb^{99} à $Ru^{103-106}$ et à Ce^{144}.

A. PROCEDES DE CONCENTRATION ET DE DECONTAMINATION

Ils sont variés. Abordons d'abord deux procédés de concentration qui n'amènent aucune purification.

1. Evaporation

Afin de pouvoir effectuer les opérations de purification ultérieures sur les solutions plus concentrées, l'évaporation de la solution résiduelle de plutonium est effectuée jusqu'à obtenir des teneurs voisines de 1M en nitrate de plutonium. Cette méthode est simple mais elle a le désavantage d'introduire dans la solution des produits de corrosion. Cette opération est effectuée dans des récipients en acier inoxydable et comme dans le cas de l'uranium, on doit éviter au maximum l'entraînement de solvant organique dans l'évaporateur.

2. Précipitation

Cette méthode de concentration a été employée dans certains traitements. La forme sous laquelle le plutonium est coprécipité est l'hydroxyde, l'entraîneur étant l'hydroxyde d'uranium. Cette concentration du Plutonium n'entraîne aucune purification du produit. Le précipité est ensuite redissout dans l'acide nitrique. Il est signalé comme résultat de cette opération dans des conditions bien

déterminées (U 0,5 g/l - Pu de 0 à 0,1 g/l), un facteur de concentration de 40 et une perte dans l'eau mère de précipitation de 0,5%.

Cette perte, ainsi que l'importance de l'équipment utilisé constitue un gros handicap pour ce procédé comparé à d'autres que nous allons voir maintenant.

3. Extraction par solvant

a) Une méthode de reflux a été proposée dans la purification et la concentration de solutions de plutonium pouvant être issues de divers traitements. Le solvant utilisé est du TBP dilué dans un solvant organique tel CCl_4 ou kérosène.

La composition de la phase aqueuse à extraire varie avec l'origine du plutonium; cependant, la présence de relargant 0,7 à 1M en $(NO_3)_3$ Al et 2,5 M NO_3H est nécessaire pour permettre une bonne extraction du plutonium. Le principe de cette extraction en reflux est le suivant: un premier extracteur met en contact le solvant TBP avec la solution de plutonium à extraire. Dans cet extracteur un lavage de la phase organique chargée est effectué. Un deuxième extracteur est utilisé pour la réextraction du plutonium en phase aqueuse par de l'acide nitrique très dilué 0,01 M. La majeure partie de ce plutonium réextrait constitue après réacidification la solution de lavage du premier extracteur.

La figure 7 représénte le schéma d'un cycle d'extraction de plutonium en reflux.

Ce flowsheet nous montre que le facteur de concentration obtenu entre la solution aqueuse finale et la solution aqueuse de départ est très élevé. Des chiffres supérieurs à 100 g/l dans la solution finale ont déjà été obtenus. Cette solution a une acidité libre relativement peu élevée. Ceci représente un avantage pour effectuer les opérations suivantes (précipitations d'oxalate, de peroxyde, etc.). Deuxième avantage de l'opération en reflux: la haute concentration en plutonium dans le premier extracteur permet d'atteindre des facteurs de décontamination très élevés.

Enfin le réglage des conditions de reflux permet d'obtenir une phase aqueuse finale de composition constante, quelle que soit la concentration du produit initial. Cette opération de reflux permet une grande souplesse de marche.

Cependant, on doit soulever quelques objections en ce qui concerne principalement l'importante quantité de plutonium recyclée. Une grande quantité de matière fissile est accumulée. Il en résulte que la conception des appareillages doit être conçue spécialement en vue d'éviter des possibilités de conditions sur-critique. Une autre conséquence de cette grande concentration en plutonium concerne la dégradation du solvant. On risque ainsi d'accroître les pertes dans le solvant sortant du 2ème extracteur. Enfin, une troisième conséquence est la nécessité d'avoir un premier extracteur possédant un nombre élevé de plateaux théoriques pour éviter des pertes substantielles dans les résidus aqueux.

b) Une méthode d'extraction par solvants composée de deux cycles effectués avec des solvants différents a été utilisée. Ces deux cycles successifs sont représentés sur les figures 8 et 9. Ils suivent une première séparation U-Pu-P.F. au solvant Butex. Le premier cycle utilise le solvant Butex, deux extracteurs et un évaporateur.

Le plutonium issu de la séparation primaire est oxydé ainsi que le sulfamate ferreux en excès par du bichromate de sodium qui fait passer le plutonium à l'état hexavalent. Cet élément est extrait en phase organique et réextrait par de l'acide nitrique diluée (0,05 N). Cette solution aqueuse est concentrée et contient environ 2 à 3 g/l de Pu et une concentration équivalente d'U. Les facteurs de décontamination obtenus sont respectivement 15 - 30 - 130 et 10 pour Ru-Zr-Nb-Ce.

Cette solution est ensuite traitée dans le deuxième cycle par un solvant TBP 20% dans le kérosène. Cependant, le plutonium de l'état hexavalent doit être ramené à l'état tétravalent. Ceci est réalisé par addition d'hydrazine à la solution amenée à 8,5 NO_3H libre et chauffée 1/2 H. à 90°C environ. Après refroidissement à 20°C, du NO_2Na est ajouté afin de détruire l'excès d'hydrazine et de stabiliser le Pu à la valence 4.

Lors de l'extraction au TBP, l'uranium et le Pu sont décontaminés en Ru et Zr par des facteurs de 2000 et 10. De ce premier extracteur, la solution organique arrive à un second extracteur qui

réalise la partition U-Pu basée sur la différence des coefficients de partage de ces deux éléments à basse acidité.

Le Plutonium recueilli en phase aqueuse à la sortie de cet extracteur est en solution nitrique 0,5 à 0,6 N. Le facteur de décontamination en U est de 1000. Cette solution de Plutonium est évaporée jusqu'à 250 g/l, puis traitée pour la préparation du métal.

c) La possibilité d'utilisation d'autres solvants tels les amines bien qu'encore peu développée à ces fins est également intéressante. Comme nous l'avons signalé, les coefficients de distribution du Plutonium dans ces solvants sont extrêmement élevés, permettent de résoudre le problème de la concentration et d'autre part, les coefficients de séparation Pu/P.F. et Pu/U laissent présager une décontamination très bonne.

4. Exchange d'ions

L'utilisation des résones échangeuses d'ions réalise les deux buts que nous nous sommes proposés: concentration et purification.

Comparés à l'évaporation, les échangeurs d'ions présentent un avantage marqué en ce que cette méthode n'introduit dans l'élément concentré aucun produit de corrosion.

a) Utilisation des échangeurs de cations

Les résines échangeuses de cations sont principalement utilisées à des fins de concentration dans le cas de solutions déjà fortement décontaminées. En particulier les solutions aqueuses provenant de cycles Purex ou Redox furent ainsi traitées à l'échelle pilote et fabrication. La décontamination $\beta - \gamma$ obtenu bien que de 3 à 5 seulement est intéressante du fait que pour Zr et Nb les facteurs de décontamination sont respectivement de 37 et 21. Le produit récupéré étant à la concentration de 50 g/l environ, le principe de cette opération est de laisser au cours du cycle le Plutonium à la valence 3.

Si le Plutonium était tetravalent, on pourrait craindre des polymérisations et l'élution se ferait de telle façon que la séparation U-Pu serait mauvaise. Des résines telles la Dowex 50 x 12 sont utilisées. Elles permettent des charges de 100 g. de Pu par litre de résine.

Le flowsheet des opérations effectuées dans l'usine pilote d'O.R.N.L. est indiqué sur la figure 10.

La possibilité de séparation U-Pu est basée sur le fait que des complexes sulfuriques de l'uranium sont formés lors du lavage de la colonne de résine, complexes neutres et négatifs qui permettent une élution de l'uranium alors que le plutonium trivalent reste fixé.

La figure 11 indique les facteurs de décontamination obtenus pour certains P.F.

b) Utilisation des résines échangeuses d'anions

L'utilisation des réactions de fixation d'anions ou de complexes anioniques a été développée très largement car elles permettent à priori une plus grande souplesse par leur utilisation dans différents milieux. Le milieu nitrique a été particulièrement étudié et un procédé canadien d'extraction du plutonium a été basé sur la propriété de cet élément de donner en milieu fortement nitrique des complexes anioniques susceptibles d'être fixé sur les résines par échange d'anions.

De nombreuses impuretés (Fe, Terres Rares, etc...) ne donnant pas de complexes négatifs une purification intéressante du plutonium est possible.

Cette méthode a été utilisée dans le traitement direct des combustibles à l'uranium. Nous allons voir que par un choix convenable des conditions opératoires, les résultats obtenus dans le traitement de purification ultime peuvent être très intéressants.

A côté de décontaminations élevées et d'une récupération excellente du plutonium, on doit également avoir des vitesses d'absorption et d'élution aussi grandes que possible pour assurer un débit convenable de solution à purifier.

Les courbes de la figure 12 indiquent l'influence de la température et de l'acide NO_3H sur les coefficients de distribution du plutonium tetravalent. Bien que les coefficients de distribution en milieu NO_3H soient plus faibles qu'un milieu salin, la capacité de la résine est plus forte dans le cas des solutions acides. Or, ce facteur capacité est très important pour réaliser une concentration. De même, la température joue défavorablement sur les coefficients de distribution, mais comme le montrent les figures 13 et 14, les vitesses d'échanges sont plus grandes à haute température et pour

des conditions opératoires données la fixation à température élevée est plus intéressante.

Enfin, l'influence de la nature de la résine et de son cross-linking est indiqué sur la figure 15. On peut y voir l'influence de la porosité et de la granulométrie sur la vitesse d'élution d'une résine chargée en Pu.

Cette influence du degré de pontage est mise en évidence sur la figure 16 où l'on voit que le facteur de concentration que l'on peut obtenir varie considérablement d'une résine pontée à 4% à une résine pontée à 8%.

En résumé, le flowsheet d'utilisation de ce procédé comprendra:

1°) Une étape de fixation après ajustement de l'acidité à 7,5 M NO_3H. La colonne de résine fonctionne à 55°C et est constituée de Dowex I X-4 (100-200 mesh). Vitesse de fixation: $<$ 80 mg Pu cm^2/min.

2°) Lavage de la colonne de résine avec NO_3H 7,5 M. Le volume de cette solution dépendant de la décontamination que l'on cherche et des éléments contaminants. Vitesse de lavage: $<$ 20 cm^3/cm^2/min.

3°) Elution du plutonium par de l'acide NO_3H 0,35 M Vitesse $<$ 1,5 cm^3/cm^2/min.

Un exemple de tail-end est donné sur la figure 17 où sont représentées une extraction par solvant 1 cycle et une purification par échange d'anion (1 cycle).

c) Utilisation d'échangeurs de cations et d'échangeurs d'anions

Dans certains cas il peut être intéressant d'utiliser en série deux types différents d'échangeurs d'ions.

L'échangeur de cations a pour fin:

a) de concentrer le plutonium

b) de permettre un changement de milieu

La figure 18 représente un flowsheet spécialement adapté à des solutions de plutonium ayant subi deux cycles d'extraction et contenant comme impuretés principales: U, Fe, Ce, Zr-Nb, Th.

La solution initiale contient 0,6 à 0,7 N d'acidité libre Pu 2 à 10 g/l, U - 0,5 à 1 g/l, Fe, Th, P.F.

Cette solution passe d'abord sur la colonne d'échangeur cationique où 90% du Zr sont séparés des autres cations fixés.

Après lavage l'élution est effectuée en milieu HCl6N contenant Fe^{+++} Pu^{+++} UO_2^{++}, Th^{4+}, Ce^{+++}. Un passage sur une première colonne de résine anions enlève le Fe et l'uranium.

La solution effluente contient donc Pu^{+++}, le Ce, le Th.

Après oxydation au nitrite de sodium, cette solution passe sur une deuxième colonne de résine anion où le plutonium seul est fixé à l'état de complexe chloré du plutonium tetravalent.

Après lavage par HCl 8 N qui enlève les dernières traces de Ce et Th, le plutonium est élué en HCl 0,5 N et est dirigé vers les opérations de transformation en métal.

Le facteur de décontamination γ obtenu peut être supérieur à 100 et le plutonium résultant est suffisamment purifié en Fe et U < 500 ppm.

B. TRANSFORMATION FINALE EN SELS.

Le but de cette opération est de fournir un composé de plutonium apte à être recyclé aisément après une opération simple telle la réduction à l'état métallique ou la décomposition thermique permettant d'obtenir l'oxyde PuO_2.

A la sortie des stades de purification finale le plutonium se trouve en solution nitrique en général, chlorhydrique quelquefois et toujours sous concentration élevée.

Nous allons examiner les étapes possibles qui permettant d'aboutir soit au métal, soit à l'oxyde. Certaines conditions de précipitation ou choix de composés insolubles devront être fait pour permettre·

- une récupération aussi quantitative que possible du plutonium
- une granulométrie correcte permettant une filtration aisée du précipité.

Les anions liés au Pu dans le précipité devront etre facilement éliminés lors de la formation du métal du de l'oxyde.

La figure 19 donne quelques chiffres concernant la solubilité de certains sels de plutonium et la possibilité de leur emploi selon la valence du plutonium dans les solutions à précipiter.

1. Formation du peroxyde

La valence du plutonium dans la solution aqueuse de départ peut être 3, 4 ou 6. Dans tous les cas, le produit final est le même.

L'obtention de peroxyde est dûe à la réaction de l'eau oxygénée sur l'ion plutonium tetravalent. La solution de nitrate d'origine peut contenir de 10 à 100 g/l Pu et une acidité libre de 1,5 à 6 M, NO_3H.

De nombreuses impuretées peuvent ainsi être séparées lors de cette précipitation.

La composition du précipité varie avec les conditions. Il contient en général 3 oxygènes de peroxyde, des anions, NO_3^-, SO_4^{--}, hydroxyde, oxyde et H_2O.

Le présence de sulfate dans la solution est souhaitable pour donner la forme cristalline convenable.

Pour obtenir un précipité aisément filtrable, certaines conditions doivent être respectées: excés de 8 à 12% de H_2O_2, - addition lente de cette eau oxygénée (30 à 50%) - température supérieure à 30°C, acidité finale 2,5 M ou plus.

Parmi les corps gênants lors de la précipitation de ce peroxyde, on doit citer:
- les éléments catalysant la décomposition de H_2O_2
- les éléments complexant fortement le plutonium tels PO_4^{3-}, F^-, $C_2O_4^{--}$, qui accroissent la solubilité du précipité.

Un flowsheet de la précipitation du peroxyde est indiqué sur la figure 20.

2. Oxalate

Le plutonium peut être précipité soit à l'état trivalent, soit tetravalent. Pour ce dernier une addition de H_2O_2 permet l'ajustement

à cette valence. Afin d'obtenir une bonne séparation des impuretés, la liqueur finale doit titrer entre 1,5 N et 4,5 M en NO_3H. Au-dessus de 4,5 M, la solubilité de l'oxalate devient gênante et le précipité est thixotropique.

L'excès d'acide oxalique doit être de 0,05 à 0,15 M tandis que la température de précipitation recommandée est voisine de 50°C.

Les facteurs de décontamination obtenus sont: 3 à 6 pour ZrNb - 12 pour Ru.

Un schéma type est donné sur la figure 21. Le Pu trivalent peut être précipité à température ordinaire dans des solutions d'acidité inférieurs à 4 M. Les agents réducteurs utilisés peuvent être IH ou NH_2OH. Il est facilement filtrable.

3. Fluorure

La précipitation du fluorure de plutonium trivalent peut s'effectuer dans de bonnes conditions et présente deux avantages -
solubilité très faible.
- le fluorure trivalent est plus cristallin et moins hygroscopique que le tetravalent.

L'acidité fluorhydrique lors de la précipitation doit être 4 N après agitation et digestion de quelques heures. Le F_3Pu est filtré, lavé à FH 5% et à l'alcool. Le séchage peut s'effectuer à 200°C sous atmosphère d'helium pendant plusieurs heures.

L'oxalate, comme le peroxyde peuvent être transformés par calcination en oxyde PuO_2. Cet oxyde peut être utilisé sous cette forme ou transformé en fluorure par action de HF + H_2 à 450°C pour donner le fluorure trivalent, à 600°C en présence de HF + O_2 pour donner le fluorure tetravalent. Ces deux fluorures conviennent l'un et l'autre pour la fabrication du métal.

BIBLIOGRAPHIE A CONSULTER

F.R. BRUCE: T.I.D. 7534 Book I	p. 277 ... 285
	p. 303 ... 332
V.R. COOPER M.T. WALLING, Jr.	Sec. Gen. Conf p/2409
P. FAUGERAS A. BRUT R. HELOU	Rapport CEA n° 1363
K.M. HARMON - W.H. REAS Book I	p. 332 348
G.R. HOWELS T.G. HUGHES	Sec. Gen. Conf p/307
D.R. MACKEY K. SADDINGTON	
B.F. JUDSON: T.I.D. 7534 Book I	p. 296 302
I. PREVOT J. CORPEL P. REGNAUT	Sec. Gen. Conf p/1171
M. ZIFFERERO Eurochemic - Technical Report n°4	

St.nr. 3776

DECONTAMINATION FACTORS

Fig n° 1

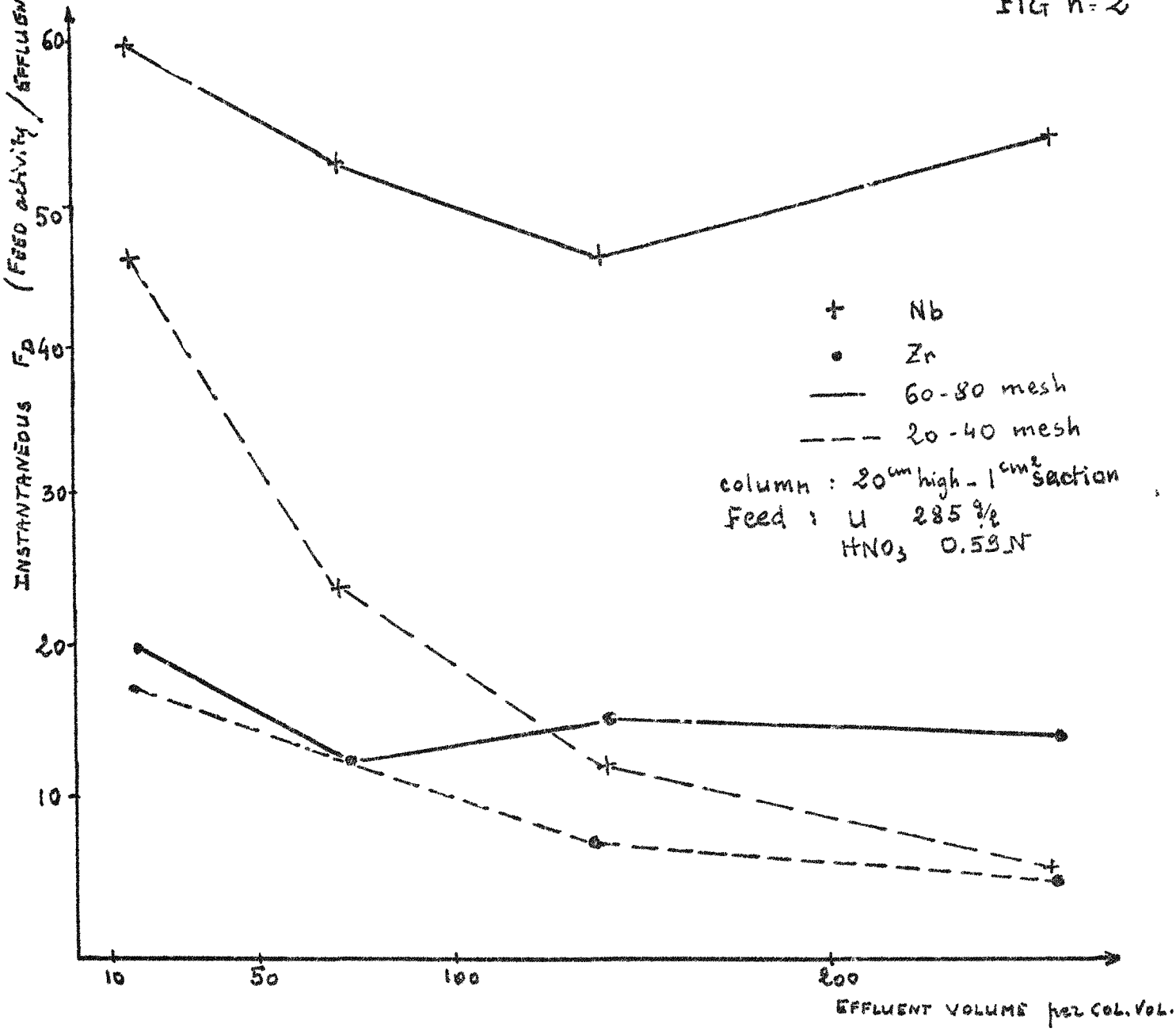
PROCESS	NUMBER OF CYCLES	ELEMENT	LOG. OF DECONTAMINATION FACTOR	
			Gross β	Gross γ
REDOX	2	U	6	6,5
		Pu	7,6	7,7
PUREX	2	U	6,8	6,4
		Pu	6,9	6,3
25 - hexone	2	U	6,45	6,2
25 - TBP	2	U	8	6,5

FROM : F.L. CULLER

SILICA-GEL ABSORPTION

INFLUENCE OF PARTICLE SIZE AND EFFLUENT VOLUME ON THE DECONTAMINATION FACTOR

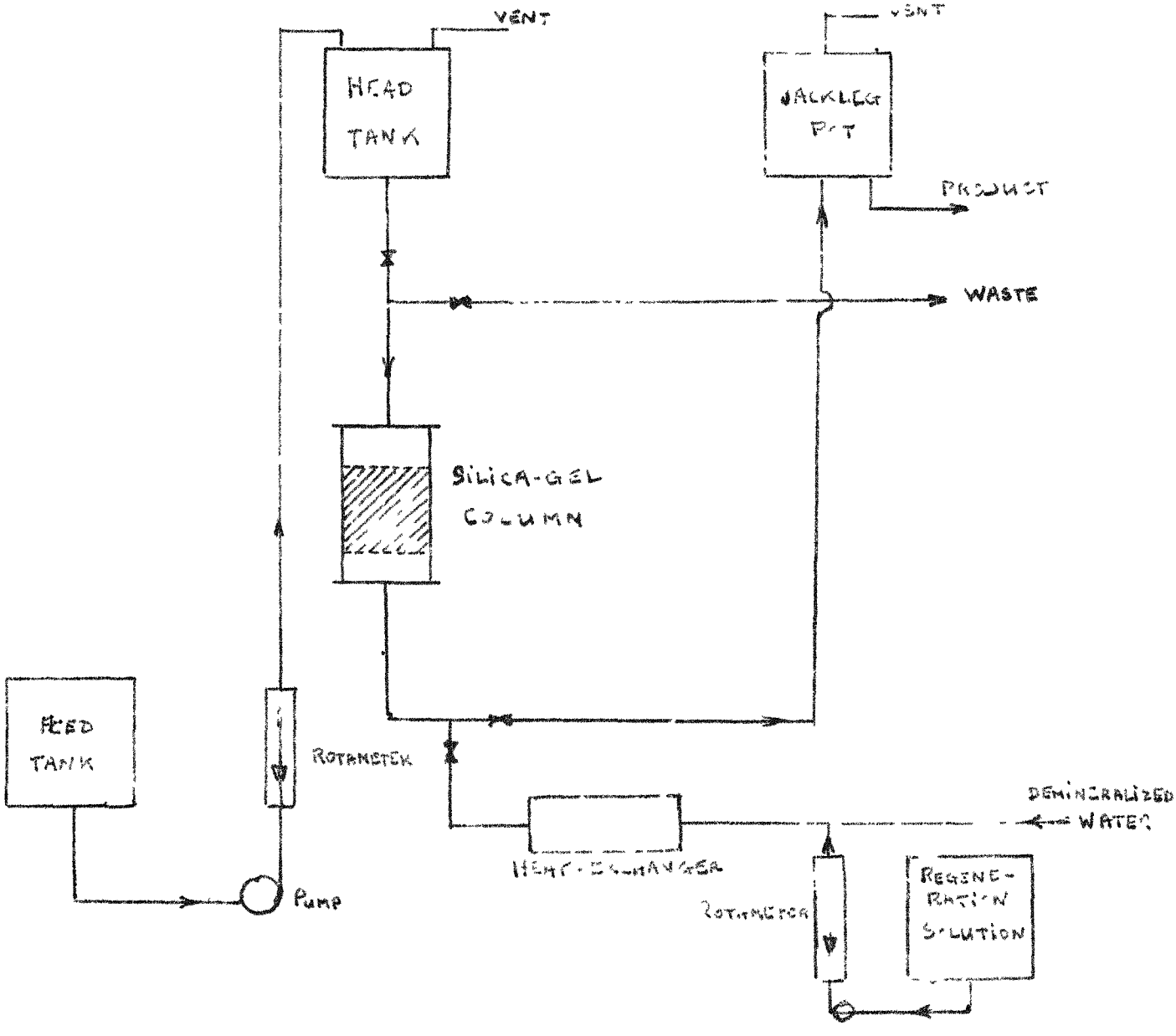
Fig n° 2



FROM: M. ZIFFERERO

SILICA GEL ABSORPTION SYSTEM

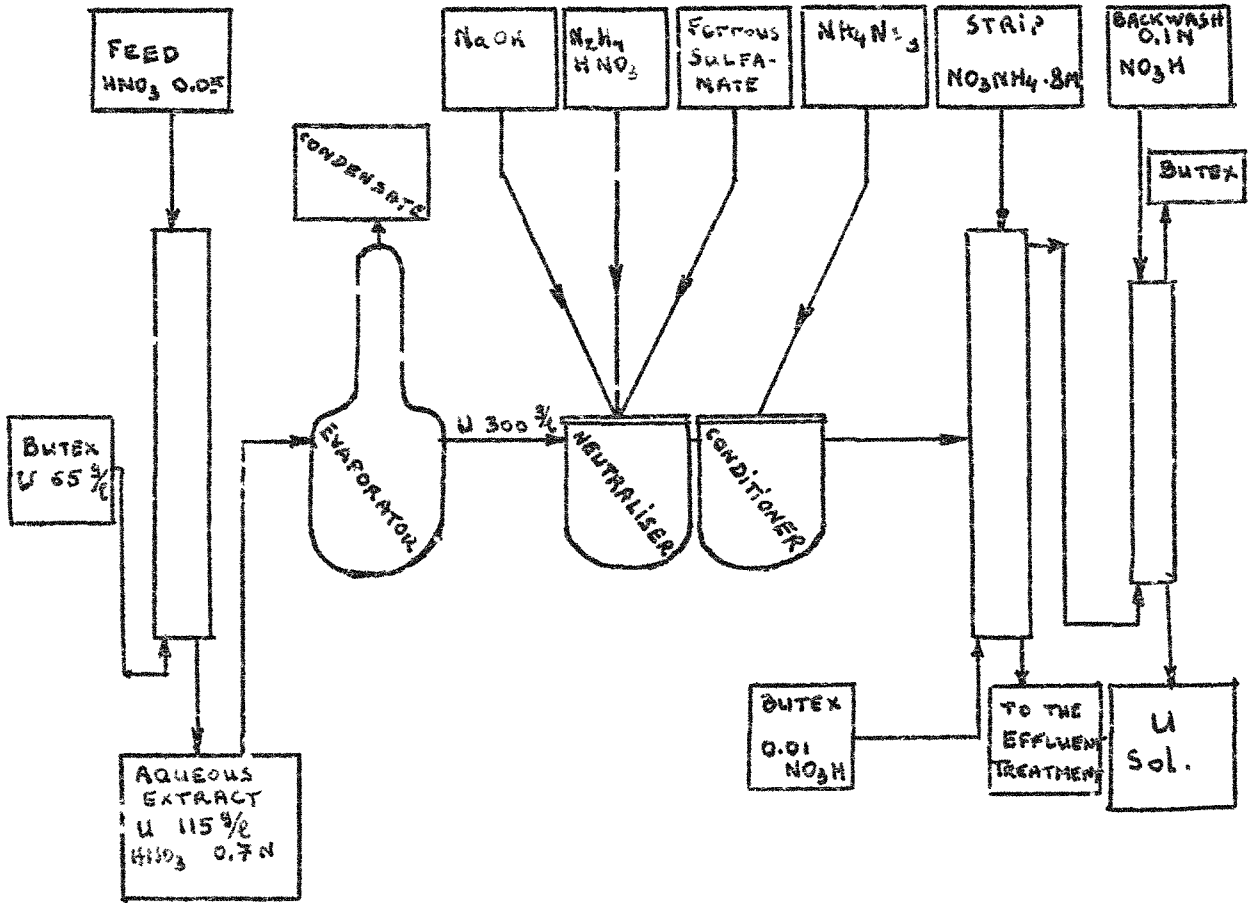
FIG N°: 3



FROM: F.R. BRUCE

URANIUM PURIFICATION

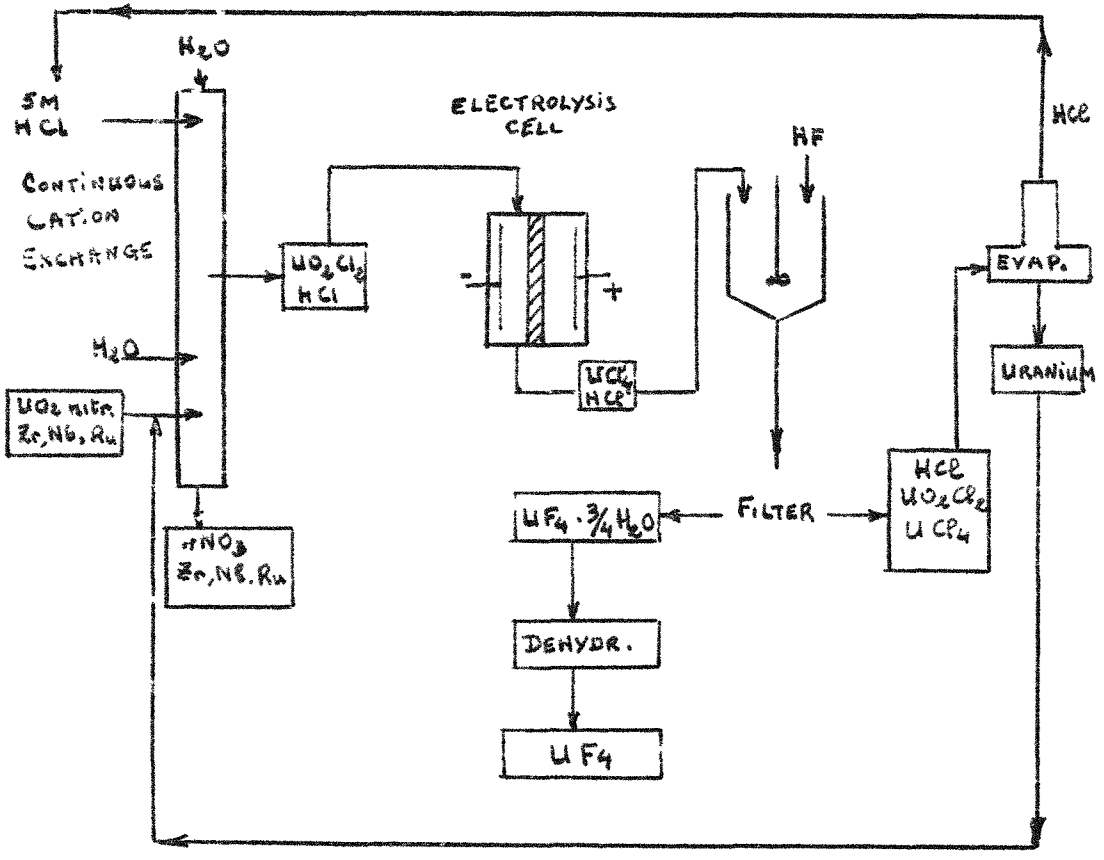
FIG n° 4



FROM G.R. HOWELLS et al.

EXCER PROCESS

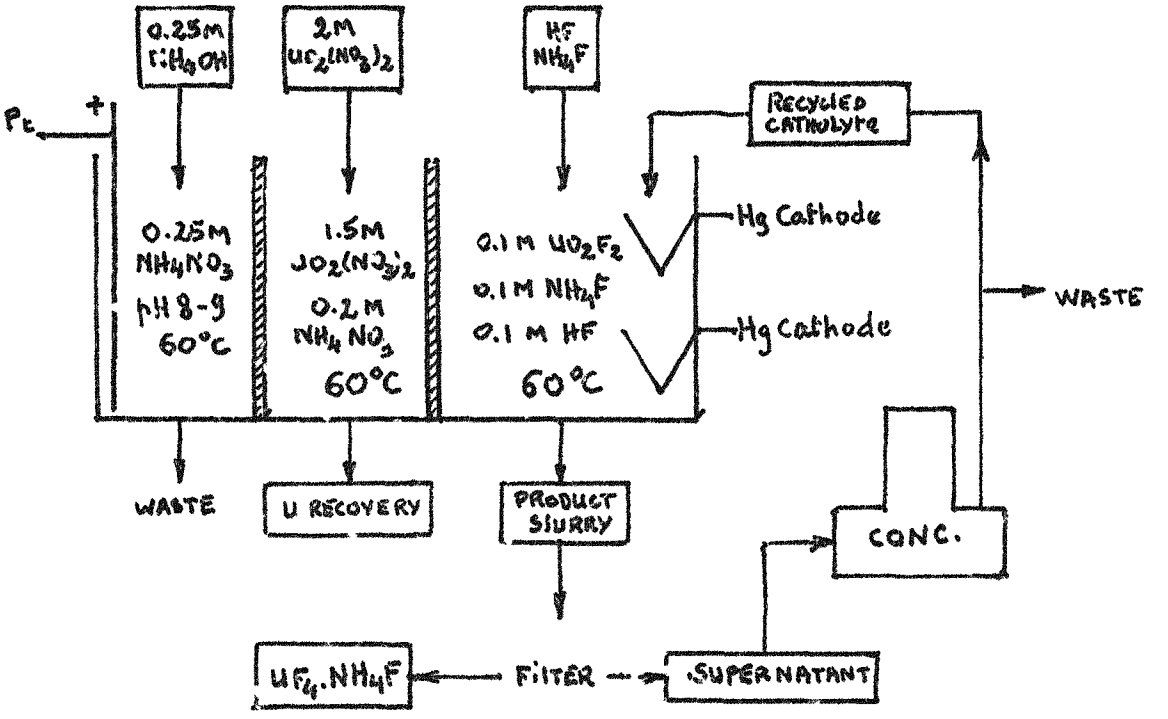
FIG n° 5



FROM V.R. COOPER & M.T. WALLING Jr.

FLUREX PROCESS

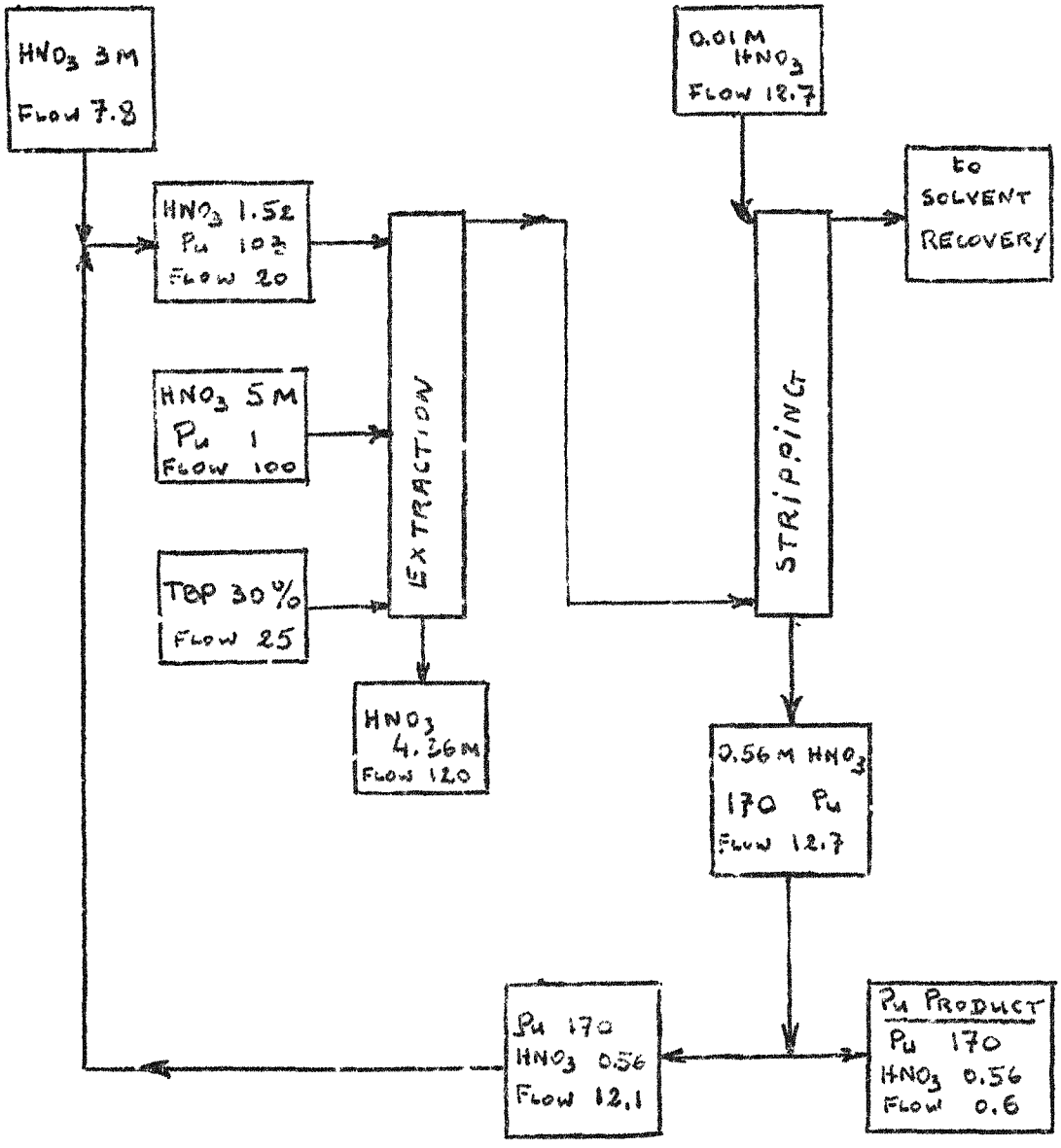
Fig n°: 6



FROM V.R. COOPER and M.T. WALLING Jr.

REFLUX PLUTONIUM CYCLE

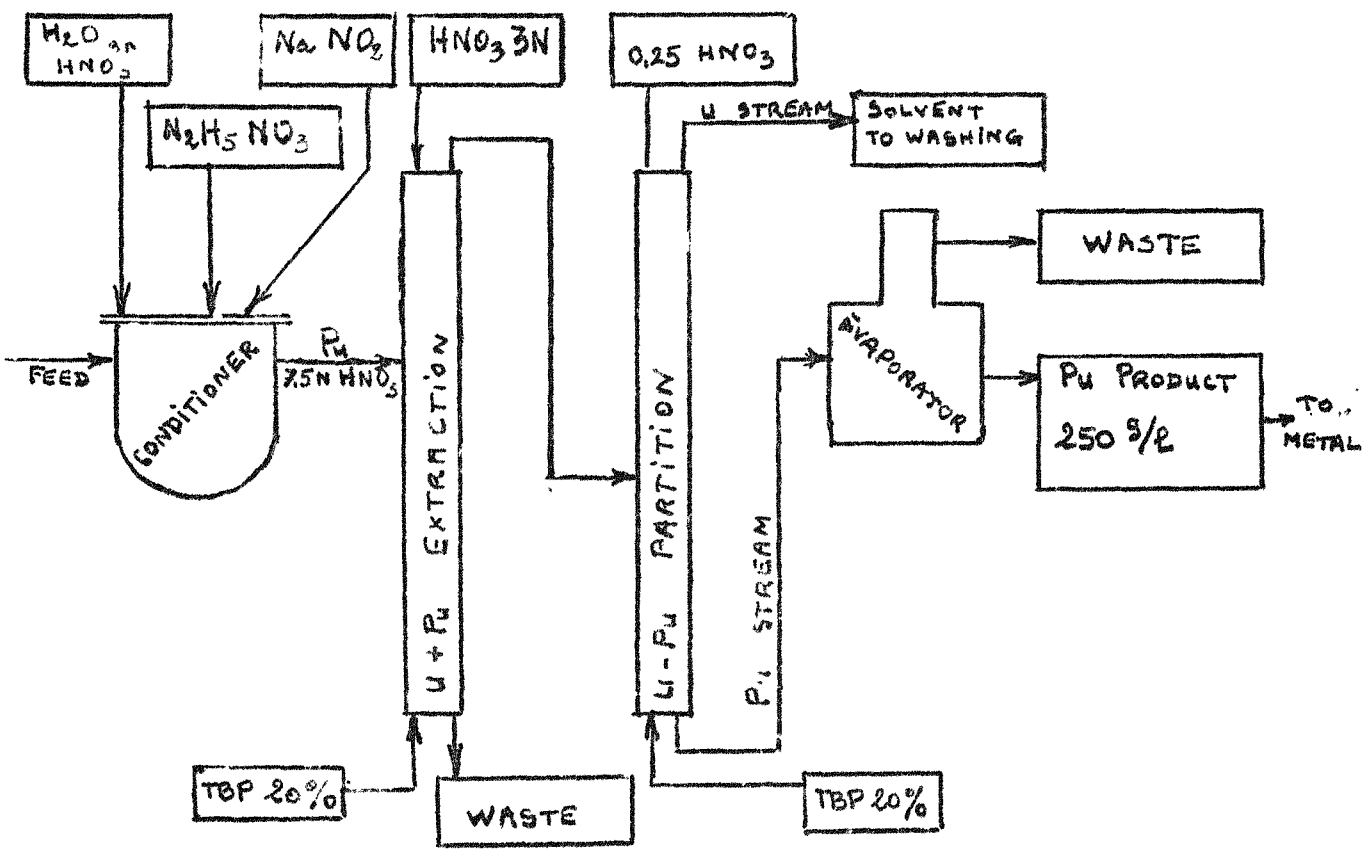
FIG n° 7



FROM : V.R. COOPER and M.T. WALLING Jr.

SECOND CYCLE PLUTONIUM PURIFICATION

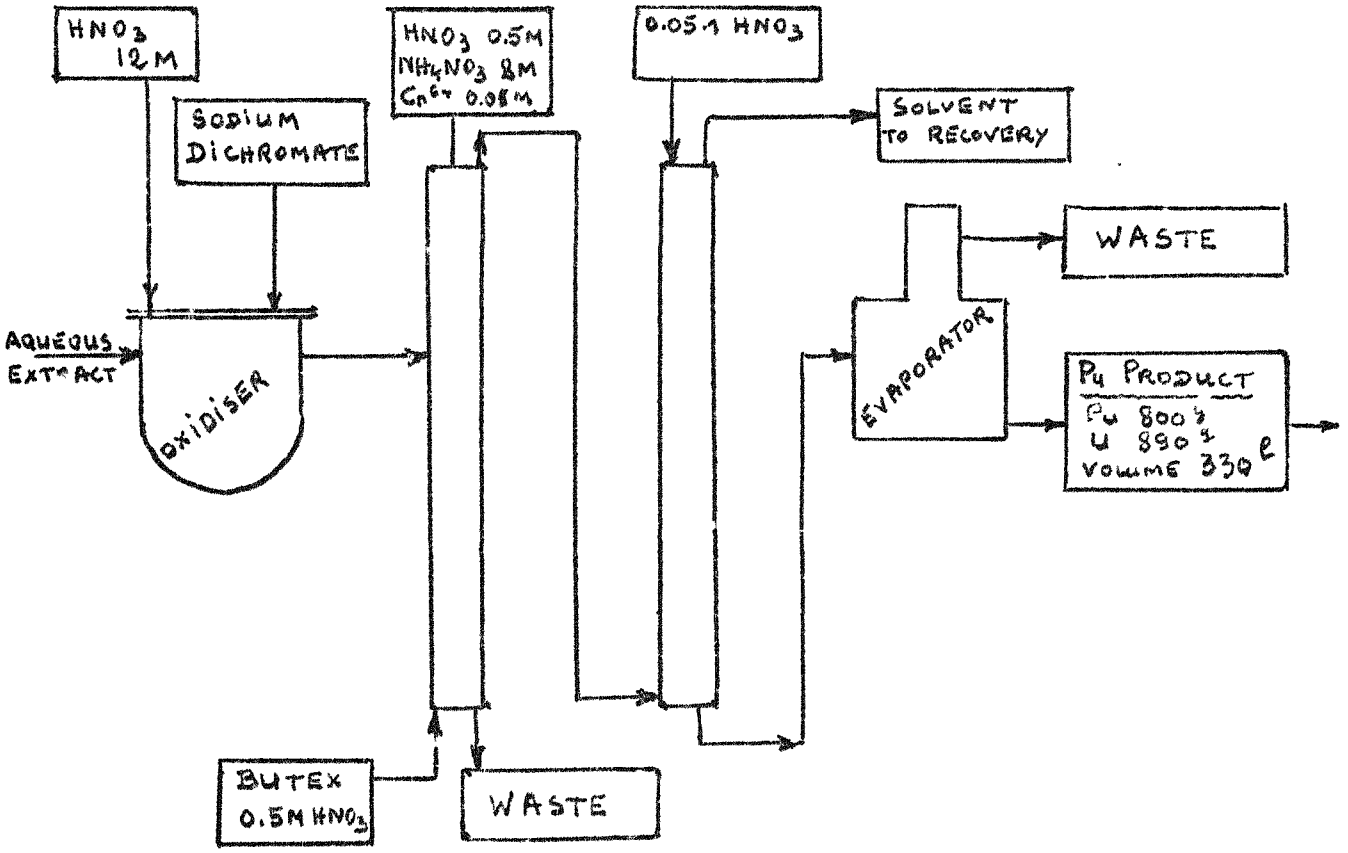
FIG n° 8



FROM : G.R. HOWELLS et al.

FIRST CYCLE PLUTONIUM PURIFICATION

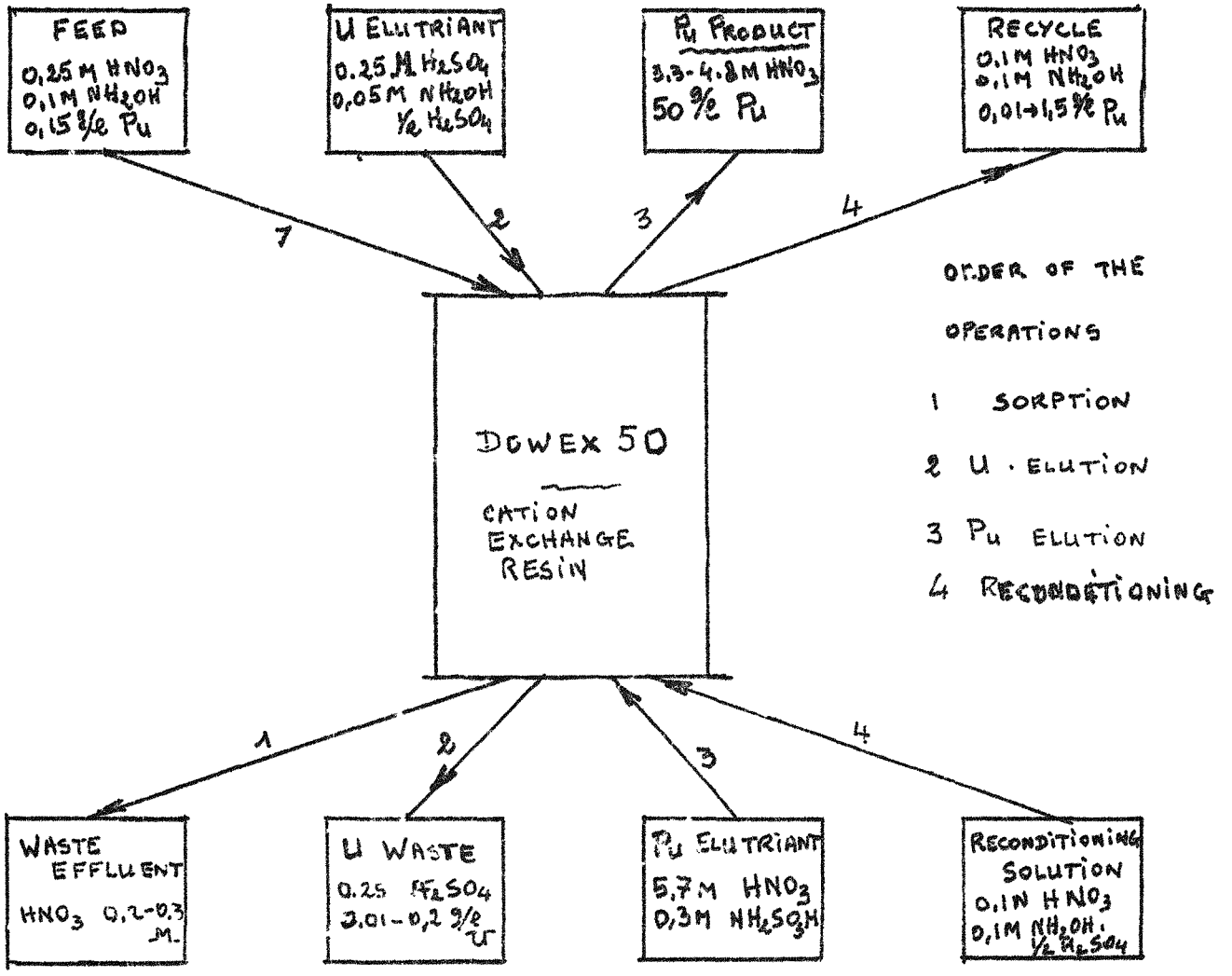
Fig n° 9



FROM: G.R. HOWELLS et al.

PLUTONIUM RECOVERY BY CATION EXCHANGE

FIG n° 10



FROM: F.R. BRUCE

DECONTAMINATION ACHIEVED IN

Pu PURIFICATION BY CATION EXCHANGE

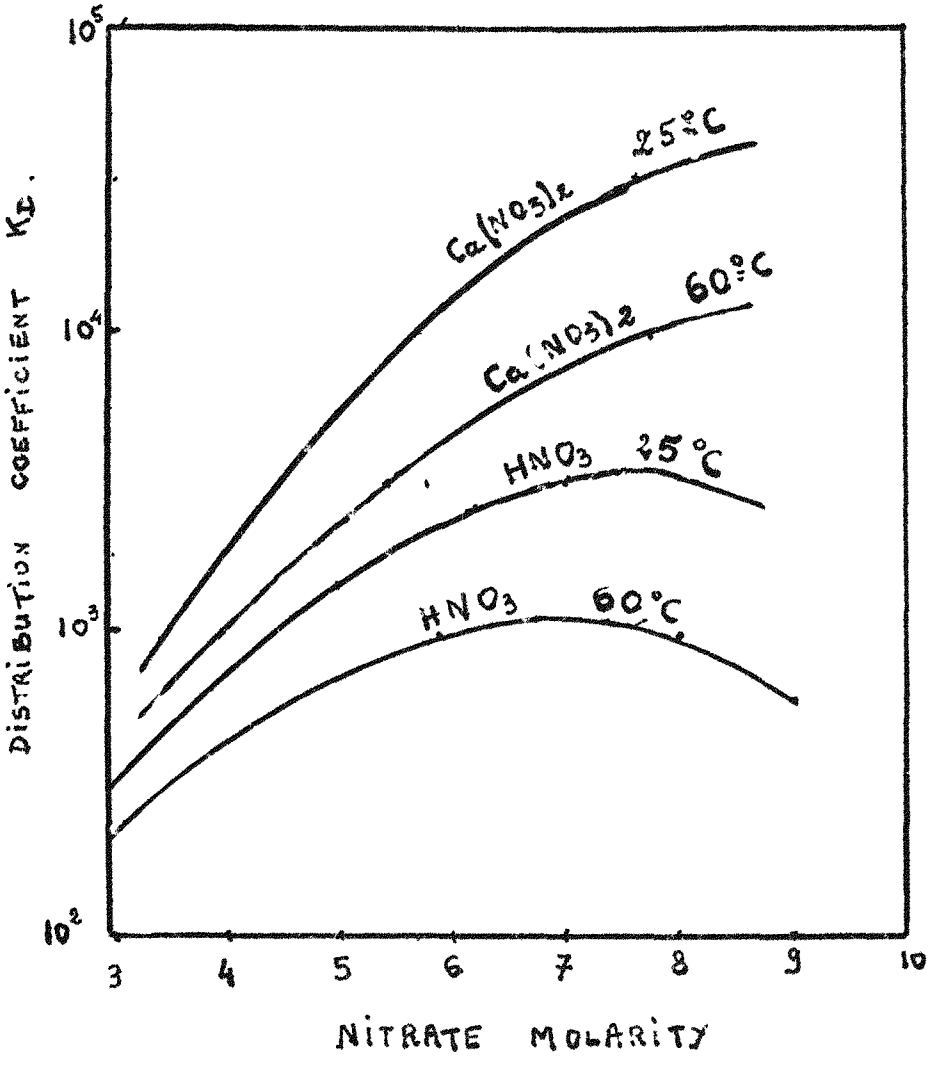
Fig n: 11

CONTAMINANT	DECONTAMINATION FACTOR
Ru	2.4
Zr	37
Nb	21
Total R.E.	6.6
$UX_1 + UX_2$	6,5
Gross β	3.2
Gross γ	5,1
Al	3.4
Cr	8,5
Fe	5.4
Ni	3.5

FROM : F.R. BRUCE

DISTRIBUTION OF Pu BETWEEN ANION-EXCHANGE RESIN AND AQUEOUS NITRATE SOLUTIONS

Figure 12



FROM: J.L. RYAN and E.J. WHEELWRIGHT

PLUTONIUM LOADING RATES

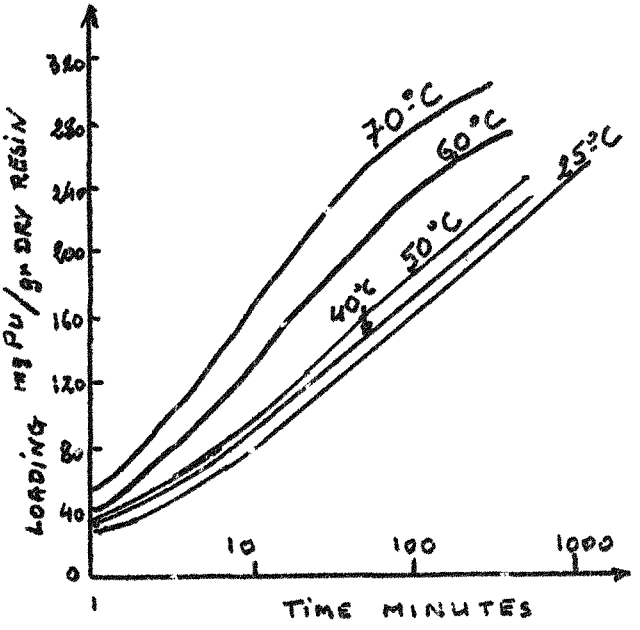


FIG n° 13

Feed : HNO_3 7.2 M
Pu 1 g/l

Resin : DOWEX I X 4
50 - 100 mesh

BREAKTHROUGH CURVES AT VARIOUS TEMPERATURES

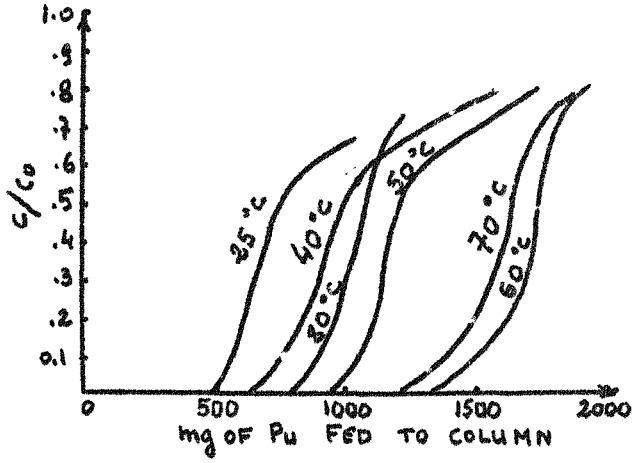


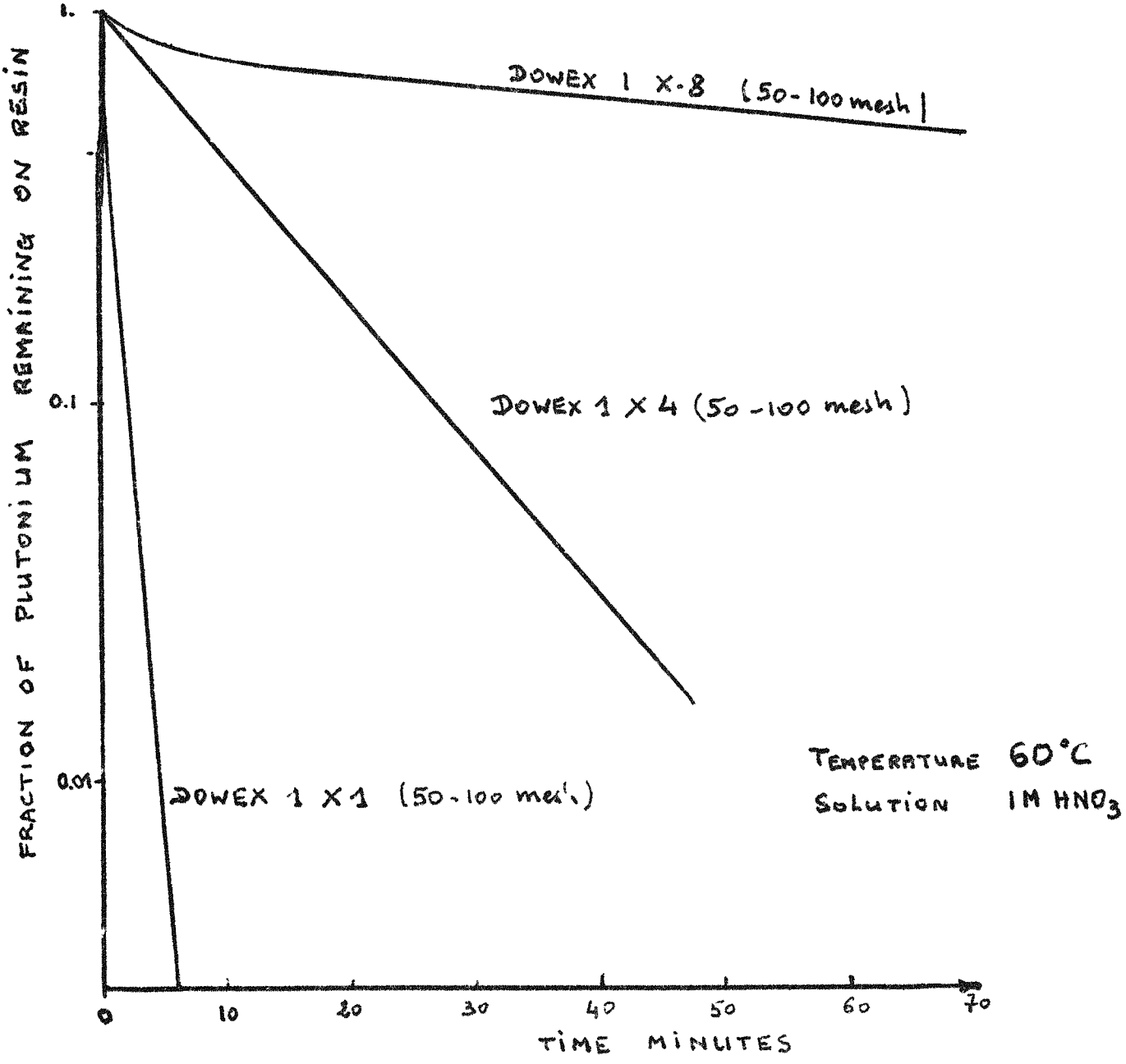
FIG n° 14

Feed : HNO_3 7.2M
Pu 0.55 g/l.
Column : 45 cm x 0.28 cm^2
resin : Dow. I X 4 (50-100 mesh)
Flow-rate : 20 - 25 ml/min./cm^2

FROM: J.L. RYAN and E.J. WHEELWRIGHT

DESORPTION OF PLUTONIUM

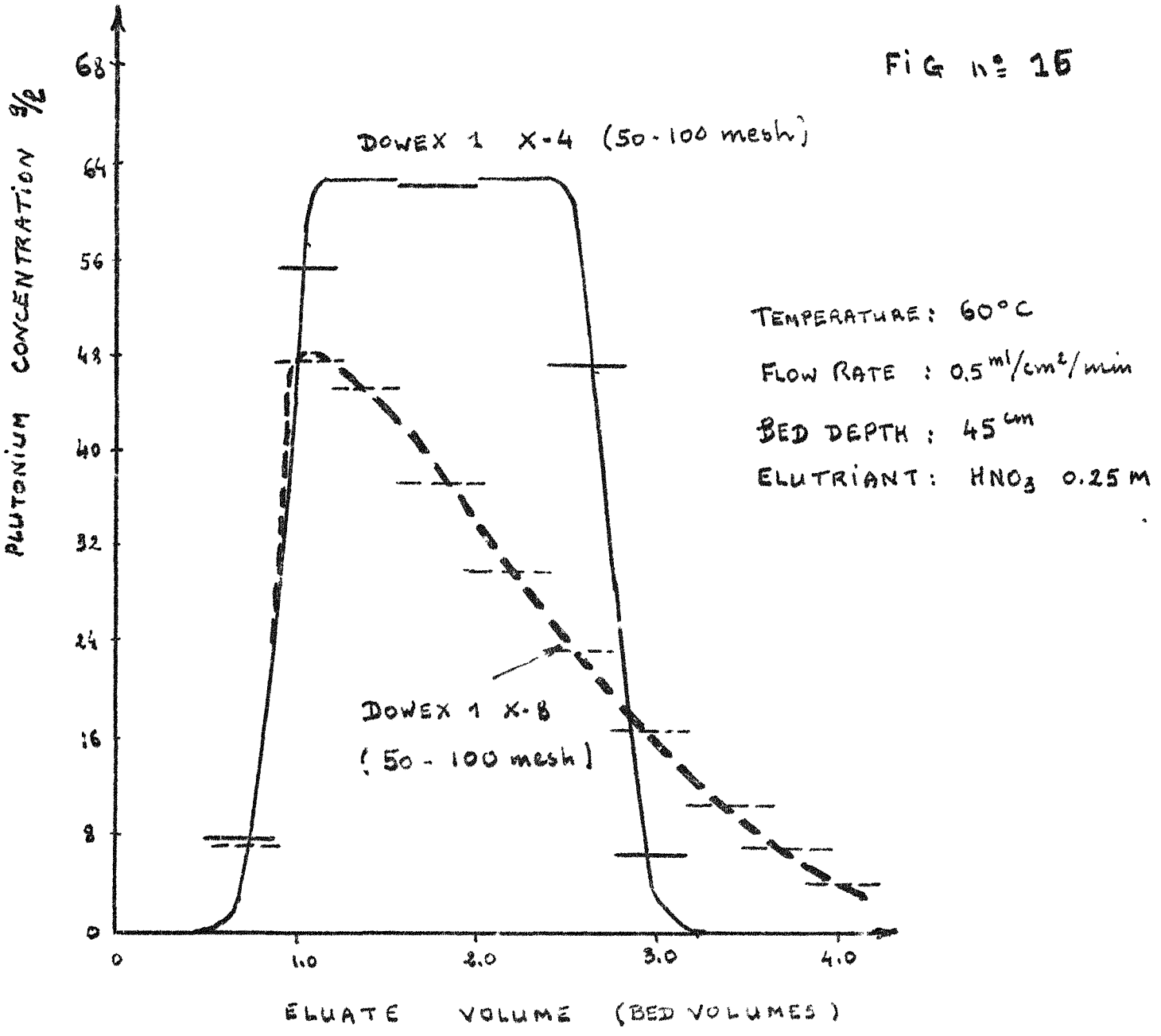
Fig 15



FROM: J.L. RYAN and E.J. WHEELWRIGHT

ELUTION OF PLUTONIUM

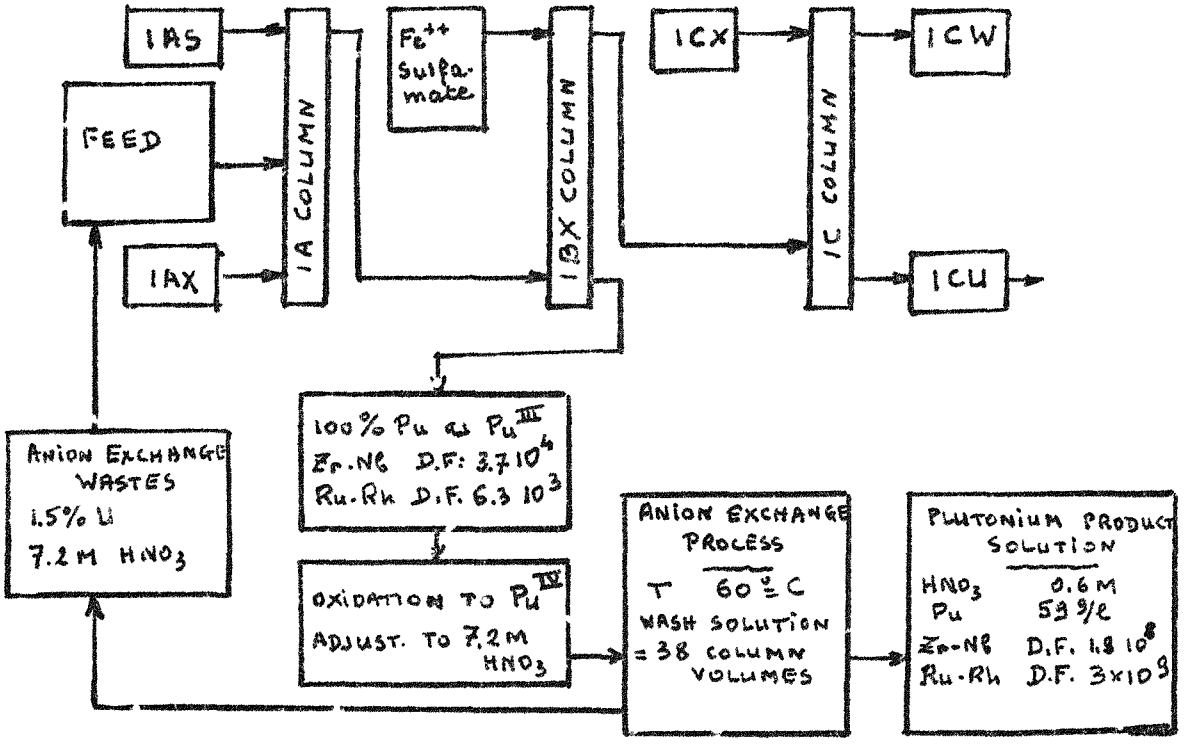
FIG n° 16



FROM : J.L. RYAN and E.J. WHEELWRIGHT

COMBINED SOLVENT EXTRACTION / ANION EXCHANGE FLOWSHEET FOR PLUTONIUM DECONTAMINATION

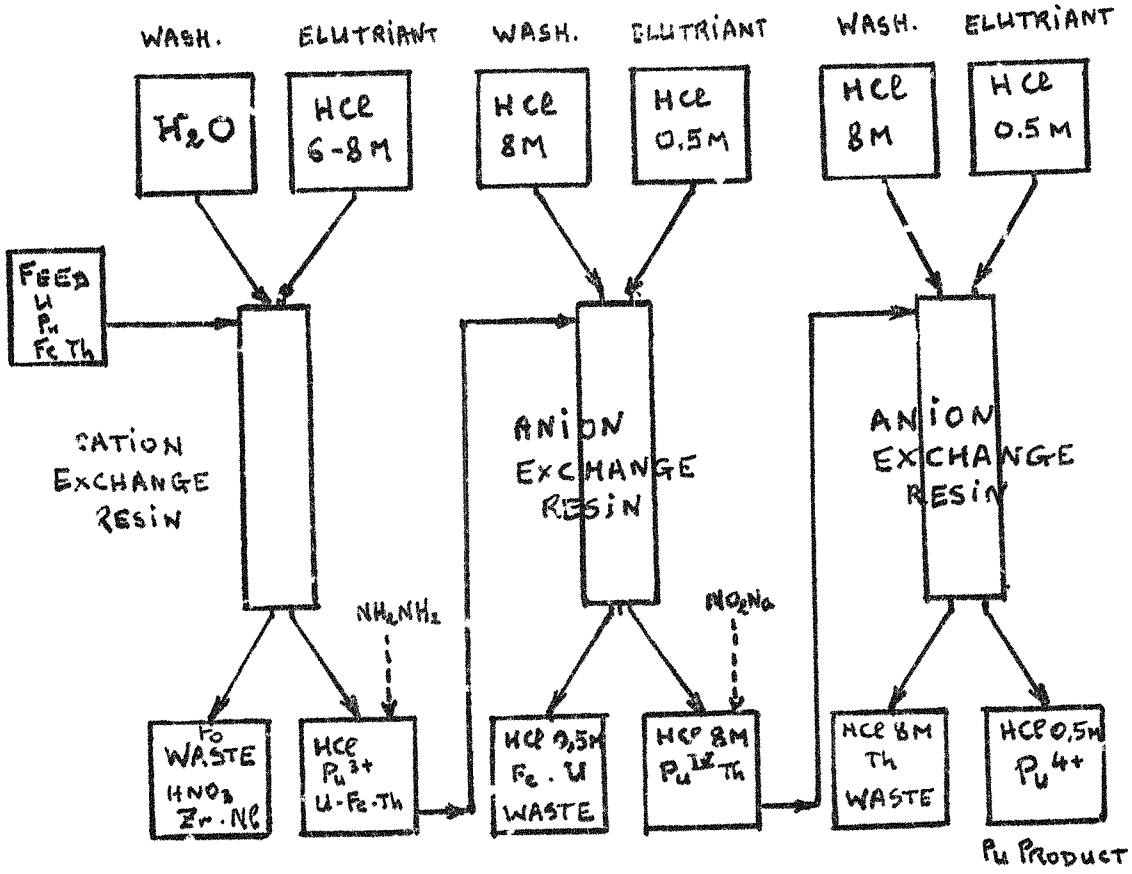
Fig n° 17



FROM: J.L. RYAN and E.J. WHEELWRIGHT

CATION - ANION EXCHANGE CYCLE

FIG n° 18



FROM: I. PRÉVOT et al.

SOLUBILITY OF Pu COMPOUNDS

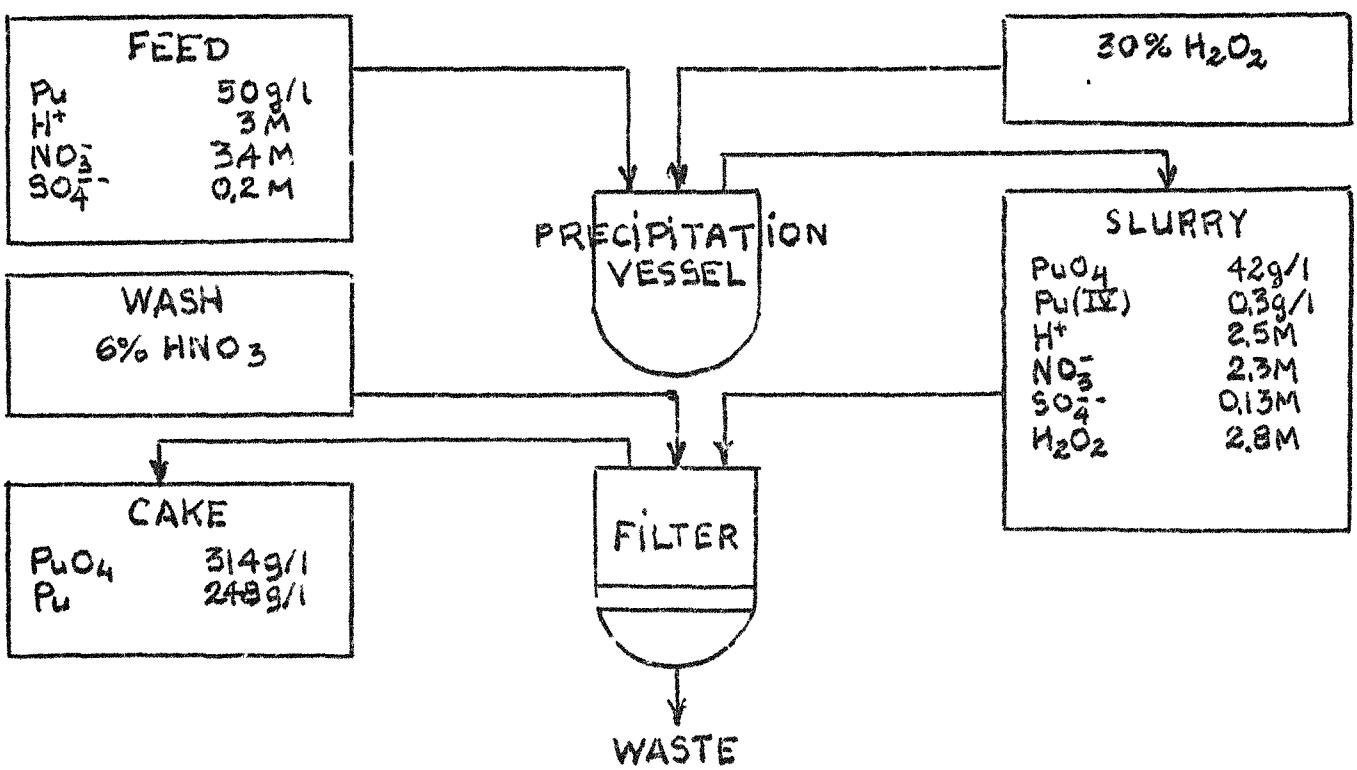
Fig n° 19

COMPOUND	MEDIUM	Pu g/l
Pu^{III} oxalate	0,5M $C_2O_4H_2$ - 3M HNO_3	0,01
Pu^{IV} oxalate	0.1M $C_2O_4H_2$ - 4M HNO_3	0,003
Pu^{IV} peroxyde	3M H_2O_2 - 1M HNO_3	0,10
Pu^{III} fluoride	1M HF - 1M HCl	0.037
$CaPu^{IV}$ fluoride	2M HF - 4M HNO_3	0.06
Pu^{IV} fluoride	2M HF - 2M HNO_3	0,70
Pu^{IV} oxyde		

FROM : F.R. BRUCE

FLOWSHEET FOR PuO_4 PRECIPITATION

Figure 20



FROM: F. R. BRUCE

THE ADVANCED SUMMER INSTITUTE AT KJELLER

Section IV

CURRENT DEVELOPMENTS IN TBP PROCESSES FOR IRRADIATED FUELS

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CURRENT DEVELOPMENTS IN TBP PROCESSES FOR IRRADIATED FUELS

by

J. M. Fletcher

1. As a solvent system for the processing of irradiated fuels, tributyl phpsphate has been in use for less than ten years and therefore such TBP processing is, relatively, in its infancy: substantial developments and improvements are to be expected. Table 1 shows the location and function of plants which are already using TBP cycle.

TABLE 1.

PROCESSING PLANTS FOR IRRADIATED FUELS WHICH USE TBP.

			Commenced	Ref.
U.K.	Windscale	Adjunct to Butex Process for Plutonium Purification	1952	1
		Uranium Purification	1959	
	Dounreay	U-Al Fuel (MTR type) Reprocessing	1958	2
U.S.A.	Savannah River	Purex Plant		
	Hanford	Purex Plant	1956	3
	Idaho Falls	Enriched U Plant		4
	O.R.N.L.	Recovery Plant		5
France	Marcoule	Reprocessing Plant	1958	6

2. There are incentives to improve TBP processes on economic grounds: firstly to lower the cost of nuclear power from a particular type of reactor and secondly, since finality on the best type of reactor is far from being reached yet, to enable a particular plant to deal with different types of fuels. Some of the targets are set out in Table 2. This lecture covers various developments (recorded in papers and reports issued in the U.S.A., in the U.K. and elsewhere) in aid of improved operating flowsheets: it does not include engineering improvements directed towards equipment and maintenance.

TABLE 2

SOME TARGETS FOR THE IMPROVEMENT OF TBP PROCCESES

		Target
A.	Flowsheet	
		1. Reduction in Shielding Requirements
		2. Reduction in Wastes (for Storage or Disposal)
		3. Reduction in Radioactive Colloids and Particulates
		4. Reduction in Cooling Time for Fuel
B.	General	
		5. Improved flexibility, to permit same plant to be used for several fuels
C.	Equipment	
		6. Better Performance of contactors, evaporators
		7. Instrumentation

3. The "conventional" TBP process for a natural or near-natural uranium fuel has been given by Flanary[7]; that for uranium (enriched) - aluminium fuels by Culler[8] and that for a uranium-zirconium fuel by Stevenson.[4] For the first category of fuels, TBP has already replaced hexone since it uses nitric acid, i.e. an evaporable salting-out agent, instead of aluminium nitrate: the proposed use of TBP for the second Windscale Plant in place of butex (used in the Primary Separation Cycle for the first Windscale Plant) is not for this reason since both solvents can use nitric acid: instead it is mainly based on the different behaviour of TBP as a solvent, which avoids the low decontamination factor (about 10) from ruthenium in the first extractor[1] of the Butex process.

4. The need for improvements in TBP processes arise

(a) from the physical and chemical limitations of TBP as a solvent;

(b) from the waste disposal problem which is posed when alloyed or other fuels introduce unevaporable effluents.

Some of the limitations of TBP as a solvent are listed in Table 3.

TABLE 3.

LIMITATIONS OF TBP AS A SOLVENT

Property	Consequence
1. Uranium Partition Coefficient is High.	Needs dilution. Hence:- (a) Low Solvent Loading. (b) High volume of aqueous backwash stream. (c) Diluent problems. (d) Phase separation difficulties.
2. Products formed by Thermal and Radiolytic attack are strong extraction agents[9] and emulsifiers.	(a) Solvent has to be washed each cycle. (b) Elevated temperatures in cycles must be used cautiously. (c) Problems arise in effluent streams. (d) Phase separation difficulties.
3. G values for Radiolytic attack relatively high[9].	

TBP errs on the side of being too STRONG an extraction agent for use with unenriched uranium in continuous counter-current extraction: it is diluted (usually to 20 - 35%), not merely to reduce its viscosity and density, but also to reduce the uranium partition coefficient and thereby allow the uranium to be stripped from the organic to a smaller volume of an aqueous phase. With 30% TBP (which permits a max. loading of about 100 g U/l) and a backwash contactor at 50°C, the uranium, after a TBP cycle, still, however, emerges[9] in a volume which exceeds that of the feed by a factor of 5 to 6: for the "weaker" solvent, Butex, (for which the partition coefficients for uranium are comparable to those with 2 - 10% TBP) the uranium after a solvent cycle at ambient temperature can be obtained[1] in a volume 2.7 times that of the feed. The curves in Fig. 1 illustrate the difference between even 20% TBP and Butex. Substitution of phenyl for the butyl groups in TBP reduces[10] the extraction power of the phosphate in the desired manner:

	K_U
Tributyl phosphate	2230
Dibutyl phenyl phosphate	214
Butyl diphenyl phosphate	11
Triphenyl phosphate	~ 1
cf. Butex	1.5

Values of K_U are expressed in terms of the thermodynamic constant, K, defined as m_{org}/m^3 ^{3} i.e. as (UN molality)$_{org}$/ $\sum$(UN molality)$^3_{aq}$ x (UN activity coeff.)$^3_{aq}$.

As the extraction power of the organic phosphate decreases, the mechanism of complex formation is believed to change from direct attachment to the metal, as in $\sum UO_2(NO_3)_2(TBP)_2$, to attachment by hydrogen bonding to aquo groups, e.g. as $\sum UO_2(NO_3)_2(S\text{-}H.OH)_x$, such as occurs for butex and hexone.

5. The main items of research to meet the targets to which reference has already been drawn (Table 2) are listed in Table 4. Several of these items must be considered together, e.g. elevated temperatures, residence times and nitrous acid in conjunction with solvent degradation.

TABLE 4.

ITEMS OF RESEARCH FOR TBP FLOWSHEETS

	Examples
1. Kinetics of Slow Reactions	Reactions of Ru complexes. Polymerisation of Pu, Zr. Influence of Residence Times.
2. Inorganic Side Reactions	Role of Nitrous Acid. Oxidation by Air of RuNO complexes. Complexing by Phosphoric Acid.
3. Organic Side Reactions	TBP decomposition to DBP, MBP, H_3PO_4. Diluent degradation.
4. Inorganic-Organic Side Reactions	Complexing of Metals by Organic Acids.
5. Temperature Effects	On Distribution Coefficients of Nitrates. On HNO_2 concentrations. On Solvent Degradation.

6.	Formation and Removal of Radiocolloids and Particulates	In Solvent Washing.
7.	Reagents	U IV for Fe II Sulphamate. Improved Diluent for TBP. Nitric Acid Economy.
8.	Conditioning Procedures	To improve U-Ru Separation. Addition of Inactive Isotopes of Fission Product Metals.

6. Kinetics of Slow Reactions

The nitrosylruthenium complexes present in feed solutions differ from the complexes of uranium, plutonium and most of the fission products in undergoing slow reactions in phases containing nitric acid. Conventional processing equipment is based on achieving an adequate performance for uranium and plutonium and therefore ruthenium often distributes itself disadvantageously. Contactors are often selected with little attention to the influence of residence times in Extractor I on the chemistry of reactions which affect decontamination factors: thus, it is usual to make the residence time per stage the same both in the extraction and scrub stages of this extractor. A number of undesirable reactions, viz.

(i) Radiolytic Attack of Solvent,

(ii) Slow formation of complexes in which TBP is attached directly to RuNO (Table 5),

are dependant on the residence time of stages in the extraction section, which should therefore be low (this also reduces the volume of equipment in which there is very high activity). On the other hand, as many of the RuNO nitrato complexes that pass into the solvent phase are only scrubbed out by slow reactions (Table 5), there is a benefit if the scrubbing stages have a relatively long residence time with an elevated temperature for preference. As there can be extensive recycling[12] of ruthenium between the feed-plate and the uranium-free stages, the actual residence time of ruthenium in the extraction section is not merely a function of design and the flow-rates used but also of reagent concentrations which determine both the degree of recycling and the proportions (Fig. 2) of the various ruthenium complexes.

TABLE 5

INFLUENCE OF TIME ETC. ON ....
RuNO NITRATO COMPLEXES IN TBP. (Ref 11)

I. Formation of Complexes Resistant to Scrubbing

(a) Variable Ageing Time in TBP: RuNO Nitrato Complexes (10^{-5}M Ru). 20% TBP/OK, 0.6M HNO_3. Temp. 20°

Time	.02	.25	.85	2.5	4.5	66 hours
% Ru Retained in Solvent after 3M HNO_3 elution.	6	10	13.5	14	16	16

(b) Variable Nitric Acid Concentration in TBP. See Fig. 2.

TBP phases aged to equilibrium (24 hours)

Test Conditions: (i) 3M HNO_3 elution;
(ii) Na_2CO_3 scrub.

II. Effect of Time of Scrub. See Fig. 3.

Solutions: RuNO Nitrato Complexes (10^{-5}M Ru) aged in 20% TBP with 55 g U/l and with two different concentrations of HNO_3.

Scrub Conditions: One-fifth volume of 2.4M HNO_3 at 60°.

7. Inorganic Side Reactions

(a) Nitrous Acid

Nitrous acid is formed in nitric acid systems by radiation and thermal effects: it is extracted by TBP phases with a high distribution coefficient: from TBP phases it is volatilised and also probably oxidised by air. It influences

(i) Pu valency;

(ii) Ru behaviour due to the formation of RuNO Nitro complexes (Fig. 4);

(iii) Diluent degradation;

(iv) The Consumption of Ferrous (and hence its required concentration) in U-Pu separation.

In the future, TBP processes may be able to use high and low concentrations of this acid to the maximum advantage (Table 6).

TABLE 6.

DESIRABLE LEVELS OF NITROUS ACID CONCENTRATION

In conditioning between Dissolver and feed (at 50 - 80°)	High to form Pu IV and RuNO complexes (Fig. 4*)
Cold scrub stages of Extractor I	-
Hot scrub stages of Extractor I	Low to prevent diluent degradation (reduce by air oxidation or by addition of urea or sulphamic acid)
Solvent Product from Extractor I	Low to prevent consumption of reducing agent used to separate U-Pu

* Conditions for results in Fig. 4: RuNO Nitrato Complexes (10^{-2}M Ru) in 3M HNO_3, 2.5M $NaNO_3$ saturated with Nitrous Fumes for 2 hours at different temperatures and then extracted with an equal volume of conditioned 30% TBP (Ref. 11 and Patent Application C3397/1956).

(b) Oxidation by Air of RuNO Complexes

Spectrophotometric observations on aqueous solutions of nitrato complexes of RuNO by Woodhead[13] have shown that there is slow oxidation in the presence of air to RuIV polymer. The significance of the occurrence of this oxidation in TBP phases has been overlooked until recently: as the distribution coefficients of these RuIV polymers in DBP/kerosene - nitric acid systems is low, it was believed that they would not lead to any retention of ruthenium even in degraded TBP. However, the ruthenium concentration after an initial decontamination factor of about 1000 in the first extractor is about 10^{-7}M and at this low concentration the second stage of the sequence:-

$$\text{(RuNO) Complexes} \xrightarrow{\text{oxidation}} \underset{\text{mononuclear}}{\text{Ru IV}} \qquad \underset{\text{polymer}}{\text{Ru IV}}$$

probably only occurs to a small extent. Recent results[11], such as those given below, indicate that RuNO complexes in TBP phases can be oxidised by air (as well as by a reagent such as permanganate sometimes used in solvent washing) and that after such oxidation, ruthenium is tenaciously retained in the organic phase when chelating agents are present. Results such as these draw attention to the importance of the actual concentrations of fission products present at various stages of a TBP process and suggest that the decontamination factors for ruthenium could be improved by the addition of inactive rutherium.

RuNO Complexes Aged in a Closed Vessel at 20°C in 20% TBP, 0.1M HNO_3.

Ru		Complexing Agent	Residual Ruthenium in Organic Phase after washing with Na_2CO_3.	Also Mixed, after ageing, with air at 50°
10^{-3}M	5 x 10^{-5}M DBP‡	. .	1%	1%
	" "	+ 1% D2EHP	1%	15 - 25%
10^{-7}M	" "	.	17%	-
	" "	+ 1% D2EHP	6%	29%

* Spectrophotometry indicates presence of Ru IV

‡ Formed In Situ from TBP

8. Organic and Inorganic-Organic Side Reactions

(a) TBP Decomposition Products

Many details of the formation of DBP and MBP, which add substantially to the cost of TBP systems, have been published [14, 15, 16]. Measurements of their partition coefficients [17, 18], in 2-phase systems enable the recycling and fate of these two acids in TBP processes to be calculated [19], but no comprehensive results of their concentrations and fate in an actual process have been published. The formation constants, the distribution coefficients under various extractor conditions, and solubilities of the complexes that they form with U VI, Pu IV, Zr IV, Na are of importance. Uranium, when present as the predominant metal in the organic phase, "blocks" DBP [15, 16] but not MBP [15] from being complexed by Pu IV (and by any Zr IV and mononuclear Ru IV present). On account of the formation of DBP and MBP it is necessary to wash the solvent, prior to reuse, with an alkaline solution e.g. of sodium carbonate. This converts DBP and MBP to their sodium salts which pass to the aqueous phase. However the formation of these alkyl phosphoric acids and the alkaline wash to remove them is objectionable since

(i) Plutonium complexed by MBP may appear in the aqueous wastes from solvent washing. Its recovery therefrom may be difficult.

(ii) Due to the use of sodium compounds in the solvent washing system, the aqueous wastes cannot be evaporated by a high factor.

(iii) Phase separation is impeded by the presence of DBP and MBP: this is particularly noticeable during alkaline washes of the solvent.

(iv) Fission Products (Zirconium and Ru IV) are converted when released by the alkaline wash, to radiocolloids which present a separation problem. Unless collected, e.g. by the manganese dioxide formed when permanganate[3] is included in the alkaline wash, or removed at suitable interfaces, e.g. in a pulsed column with bottom interface or in a series of mixer-settlers, these radiocolloids may persist in the organic phase and be plated out. A wide range of fission product decontamination factors have been reported[20] for solvent washing: the lack of consistency is a reflection on the use of various types of equipment and variables such as reagent concentrations, temperature and residence times, in the washing conditions.

The formation of DBP and MBP in a TBP process may therefore well be considered as a serious handicap. While extractor conditions may be adjusted to minimise the formation of DBP and MBP by thermal degradation, their presence in a highly active solvent cycle puts a limit on the decontamination factors and recoveries that can be achieved at the very part of the process where it is most desirable. So far no outstanding success has been reported for preferentially complexing the butyl phosphoric acids by the addition of an inactive metal but some work[11] along these lines has been undertaken with zirconium.

(b) Degradation Products from Diluent

The commercial grades of kerosene frequently used as diluents for TBP are attacked[21] in TBP phases by nitrous acid with the formation of yellow compounds such as nitrolic acids (-C N.OH group). More than 10% of the hydrocarbons in kerosene have been attacked over a period of days at elevated temperatures[11] but most of the products are innocuous and are removed by contact with the aqueous phases which they meet in the solvent cycle. However, the degradation products formed from a small fraction of the hydrocarbons (probably certain naphthenes)[11] are recycled with the solvent with detriment to the process since:-

(i) They chelate with Pu IV, Zr IV, and Ru IV to form strong metal complexes:

(ii) These metal complexes are only partly converted to the sodium salts by washing the solvent with Na_2CO_3.

(iii) The distribution coefficients of the sodium salts formed are such that they are largely retained in the solvent phase.

As a result of this behaviour, decontamination factors for Pu, Zr, Ru in solvent washing are lowered and there may also be a mass transfer of sodium from the solvent wash to Extractor I. A slow build-up of activity in the solvent may be noticed.

TABLE 7.

DILUENTS FOR T.B.P.

Diluent	Composition	Boiling Range	Z or H Value ±
Odourless Kerosene	Includes 20% naphthenes and 1 - 2% aromatics	195-262°C	5,500
n-dodecane	Straight chain $C_{12}H_{26}$	214	390
Dodecane (by hydro-generation of propylene tetramer) ex France	Branched chain	160-220	1,220
Shellsol T (from iso-octane residues)	C_{11} - C_{13} Isoparaffins	185-210	410
Mepasin (ex Germany)	Hydrogenated fraction from Fischer-Tropsch synthesis	220-230	2,070

± This value[11] is the concentration of diluent degradation products in units of 4×10^{-9}M left in the solvent after a standard accelerated ageing test (in the presence of TBP) and after washing. The concentration is determined using Zr (Z value) or Hf (H value).

Attention has therefore been paid [21, 11] to diluents superior to kerosene (Table 7). At Marcoule, a dodecane[6] is used. The use of a good diluent is foreseen for future TBP processes since it will permit beneficial modifications of the conventional process, e.g. the use of heated scrubs, which otherwise are a potential source of diluent degradation: at the same time it will lessen the need for making solvent washing an elaborate process, e.g. by the introduction of permanganate.

9. Temperature

Temperatures, higher than ambient, can be used to advantage in TBP processes, e.g.

(i) In stripping uranium from solvent phases[3, 9] into a relatively small volume of an aqueous phase (the uranium partition coefficients fall with a rise in temperature).

(ii) To improve phase separation in contactors.

(iii) To increase the rate of slow reactions, e.g. in a heated scrub and in solvent washing.

(iv) To improve decontamination factors.[19, 21].

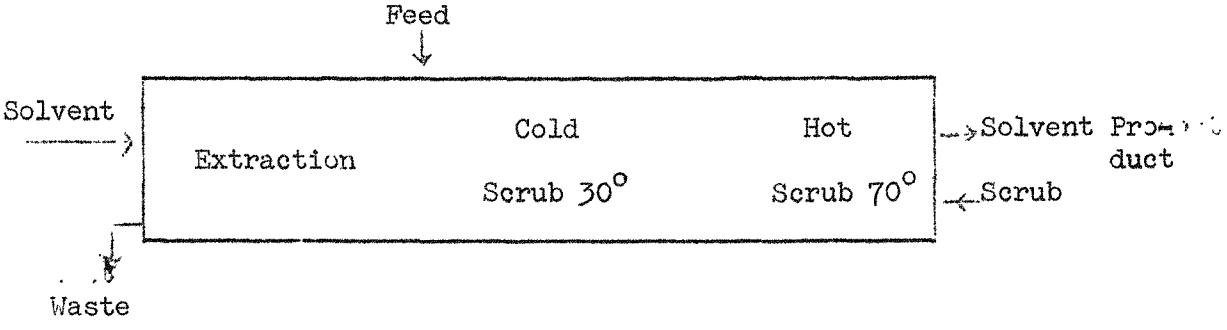
While elevated temperatures can produce these benefits, they have the disadvantages of

(i) Increasing the volatility (and fire hazard) of the diluent:

(ii) Increasing the formation of nitrous acid:

(iii) Increasing the tendency of Pu IV to polymer formation.

An interesting example of the use of elevated temperatures is the work of Karraker[22] at Savannah River. When the extractor which separates Pu from U is run warm (70°) the fission products mainly follow the plutonium stream: this stream always requires further decontamination and can therefore probably carry the extra load. A dual scrub, firstly of cold stages at 30° (which removes zirconium[19] without increasing DBP formation) and secondly of stages at 70° is also proposed.



This duality is desirable since the temperature coefficients of the distribution coefficients of certain fission products such as zirconium are positive (Table 8); of others negative. At A.E.R.E., we have examined[11] a heated scrub with synthetic U-Ru solutions and have concluded that a single stage with a residence time of 5-10mins.

at 50° - 60° will increase DF_{Ru} by a factor of about 3-5. Very much longer times, which could lead to marked degradation of TBP and the diluent, are necessary to achieve any further significant improvement (fig. 3): this is the case because the reaction rates of the ruthenium complexes which remain in the organic phase are very low: the complexes remain tenaciously in the solvent phase in Extractors II and III and even in solvent washing, and seem likely to contain TBP bonded directly to ruthenium as in $[Ru\ NO(NO_3)_3 (TBP)_2]$. It is to be expected that an alkaline wash will be as ineffective on them as a water wash.

TABLE 8.

TEMPERATURE DEPENDANCE OF DISTRIBUTION COEFFICIENTS OF NITRATES WITH T.B.P.

Nitrate	Aqueous Phase (M HNO_3)	Org.Phase	Temp.Coeff.	$D_{50°}/D_{25°}$
HNO_3 *	0.5	40% TBP	- ve	0.77
	3	"	"	0.93
Uranyl*	0.07	"	"	0.7
(.21M)	1.7	"	"	0.83
Pu IV*	0.5	20	"	0.45
	1.7	"	Variable‡‡	0.7
RuNO III	0.85*	50	- ve	0.5
	1‡	100	") only	~1
	6‡	"	") below 25°	~1
	12‡	"	+ ve	1.8
Zr IV	0.5*	35	+ ve) above	3.0
	3*	"	") 25°	2.0
	3.2‡	20	"	1.7
Nb	3 + .85M UN	30	"	3.7

* Schevchenko and Fedorov, Radiokhimiya, 2, 6, 1960.

‡ For short stirring times (ref. 11)

‡‡ This temperature coefficient changes from being negative above 20° to 40° to being positive at lower temperatures.

So far, little attention has been given to the use of temperatures below ambient: there is scope for such a condition in extraction sections, e.g. of Extractor I, to give a greater degree of separation from fission products and to decrease undesirable reactions such as TBP degradation and slow ruthenium reactions.

10. Reagents

The objection to the use of reagents such as ferrous sulphamate and sodium carbonate lies not so much in their cost as in the limitation they place on the evaporation factors that can be reasonably achieved on radioactive aqueous raffinates that have to be stored. Their effect is similar whether backcycling (Ref. 3 or Fig. 2 of Ref. 9) of evaporated aqueous wastes is employed or not employed: their presence is likely to cause a substantial reduction from the evaporation factor of 100 - 150 achieved in the salt-free raffinates from a butex or TBP process.

For the reduction of plutonium to Pu III (for its separation from uranium in Extractor II), uranous sulphamate[23] appears suitable for replacing ferrous sulphamate as a kinetically fast reducing agent: its preparation (by electrolytic reduction of the purified uranium stream) is readily integrated into the plant: the increased contamination of the plutonium stream of uranium which occurs as a result of using U IV presents no major problems since the plutonium purification process, whether by TBP or amine extraction or by ion exchange, can remove the additional uranium. Ferrous sulphamate is also used to reduce and hence remove traces of plutonium in the feed to uranium purification: here, a pretreatment with a reducing agent such as hydrazine[11] is not only beneficial to ruthenium decontamination but also reduces plutonium to Pu III and so can eliminate ferrous sulphamate.

The main reagent used in TBP processes is nitric acid but this is very largely recycled by employing waste evaporators. With the improvements over earlier TBP flowsheets already proposed, e.g. in the Two-Cycle Purex Process employing Backcycle of Aqueous Wastes given in Fig. 2 of Ref. 9, the flowsheet use of nitric acid is reduced to only 2.5 moles per mole of uranium: at least 2 of these 2.5 moles would probably be recovered by evaporation for reuse.

11. Flexibility and the Future

The requirements of many of the plants of which descriptions have been published concern the processing of a steady supply of irradiated natural or near-natural uranium fuels with a view to the isolation of plutonium and the reuse of uranium. The cost of processing falls substantially with the throughput of such a plant if the plant can be operated for long periods with a fuel of constant quality. However, with fuels which come exclusively from power reactors it seems likely to be several years before there will be forthcoming from nuclear power plants a fixed fuel supply adequate in quantity to require large capacity plants.

Factors which will influence future processing trends are:-

(a) If different fuels are processed in the same plant, there is a loss of operating time in wash-cuts which could offset the benefits of a large plant.

(b) The activity associated with some of the isotopes of uranium and plutonium which are present after high burn-up makes it less important to achieve very low levels of fission products in the fissile product.

(c) Reactor schemes may not always require the conventional separation of plutonium from uranium, but accept, if it is cheaper to do so, a decontaminated uranium-plutonium product which can be reused after suitable adjustment.

Ir the U.S.A., proposals[24] have already been made for using large existing plants for processing spent fuels from Demonstration Power Reactors. When new processing plants expressly designed for power reactor fuels are built, it is suggested that the most economic unit will be a single cycle solvent extraction unit capable of being used, via appropriate head-end treatments, by various fuels: some desirable features of this common unit would be:-

(a) A high throughput (achieved by columns) particularly in the extraction section;

(b) Ability to be run down quickly and washed out easily, to enable campaigns on different fuels to be employed: for this requirement, columns may be preferable to mixer-settlers.

(c) A high decontamination factor for fission products in the first extractor.

(d) A minimum of recycling apart from from nitric acid.

(e) A solvent sufficiently stable to thermal degradation (as well as to radiation) to permit the use of elevated temperatures and to reduce solvent washing to a simple process.

Although developments in TBP may go a long way to meet these requirements it seems possible that a solvent, such as another phosphate or phosphonate or butex, of greater stability and of lower (or more selective) extraction power may eventually be more suitable for this common unit, which would require, after the primary separation step, one or more purification procedures.

Finally, it is pertinent to consider the future of active pilot plant studies of TBP processes: the cost of testing various flowsheets in their entirety is high, even on the miniature scale and it is difficult to duplicate exactly all the features of a plant. As the background chemistry becomes increasingly better known, it is foreseen that design will be able to proceed with confidence on information available and that development work will be limited to the testing of items of equipment and instrumentation together with such few chemical items as leave cause for doubt. When this philosophy is accepted, the plant experience already gained in solvent extraction by TBP and allied solvents together with research results will be helping to provide nuclear power (which must eventually pay for research and development costs) at an economic price.

REFERENCES

1. Howells, Hughes and Saddington, Geneva Conference 1958, Paper 307.
2. Buck, Howells, Parry, Warner and Williams, Geneva Conference 1958, Paper 82.
3. Irish, Hanford Report, HW-60116 (1959).
4. Reid, Stevenson, Lemon and Rigley, Geneva Conference 1958, Paper 526.
5. Culler, Geneva Conference 1955, Paper 822: also Process Chemistry, Vol. I, p. 185.
6. Galley, Énergie Nucléaire, 2, 2 (1958), and Trans. Instn. Chem. Engrs., 36, 400 (1958).
7. Flanary, Geneva Conference 1955, Paper 539: also Process Chemistry, Vol. I, p. 195.
8. Culler, Geneva Conference 1955, Paper 541: also Process Chemistry, Vol. I, p. 201.
9. Cooper and Walling, Geneva Conference 1958, Paper 2409.
10. Healy, U.K.A.E.A. Document, AERE C/R1772 (1956).
11. Unpublished Results, AERE.
12. Ashworth, Brown, Fletcher and Wain, U.K.A.E.A. Document, AERE C/R2319 (1957).
13. Fletcher, Brown, Gardner, Hardy, Wain and Woodhead, J.I.N.C., 12, 154 (1959).
14. Burger, Process Chemistry, Vol. II. p. 307 (1958).
15. Rigg and Wild, Process Chemistry, Vol. II. p. 320 (1958).
16. Dukes, Savannah River Report, DP-250 (1957).
17. Burger, Results given in Fig. 14 of Ref. 9.
18. Hardy and Scargill, J.I.N.C., 11, 128 (1959).
19. Siddall, Geneva Conference 1958, Paper 521.
20. Davis, Oak Ridge N.L. Report, ORNL - 2848 (1960).
21. Pollock, Savannah River Report, DP-294 (1958): also Ref. 9.
22. Karracher, Geneva Conference 1958, Paper 519: also Ref. 9.
23. Jenkins and Streeton, U.K.A.E.A. Document, AERE-R3158 (1959).
24. Symposium on the Reprocessing of Nuclear Fuels, Richland, Washington, U.S.A., 1959, Document TID 7583.

FIG. 1.

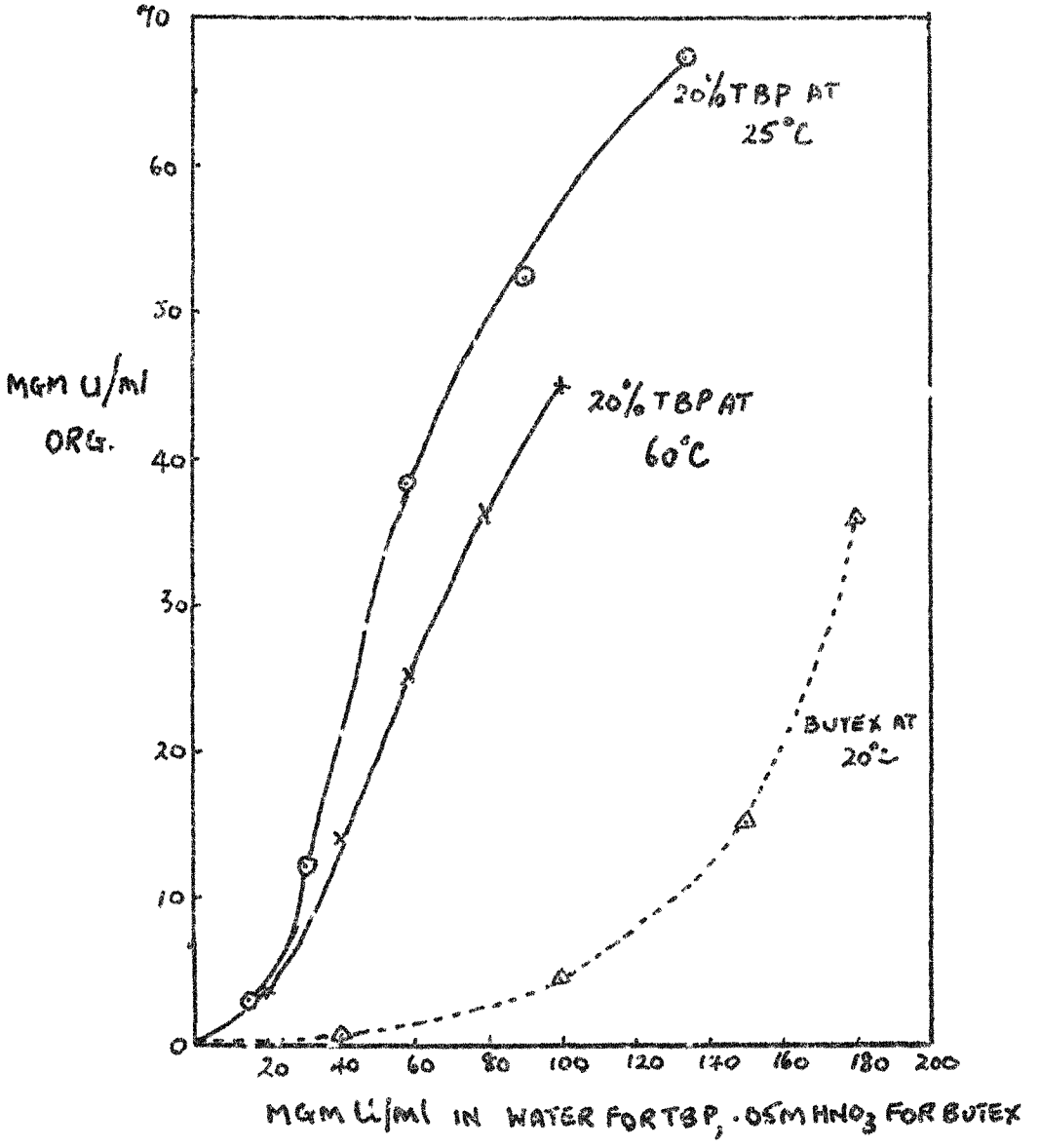

70
60
50
40
30
20
10
0
MGM U/ml ORG.
20% TBP AT 25°C
20% TBP AT 60°C
BUTEX AT 20°C
20
40
60
80
100
120
140
160
180
200
MGM U/ml IN WATER FOR TBP, .05M HNO3 FOR BUTEX

FIG. 2.

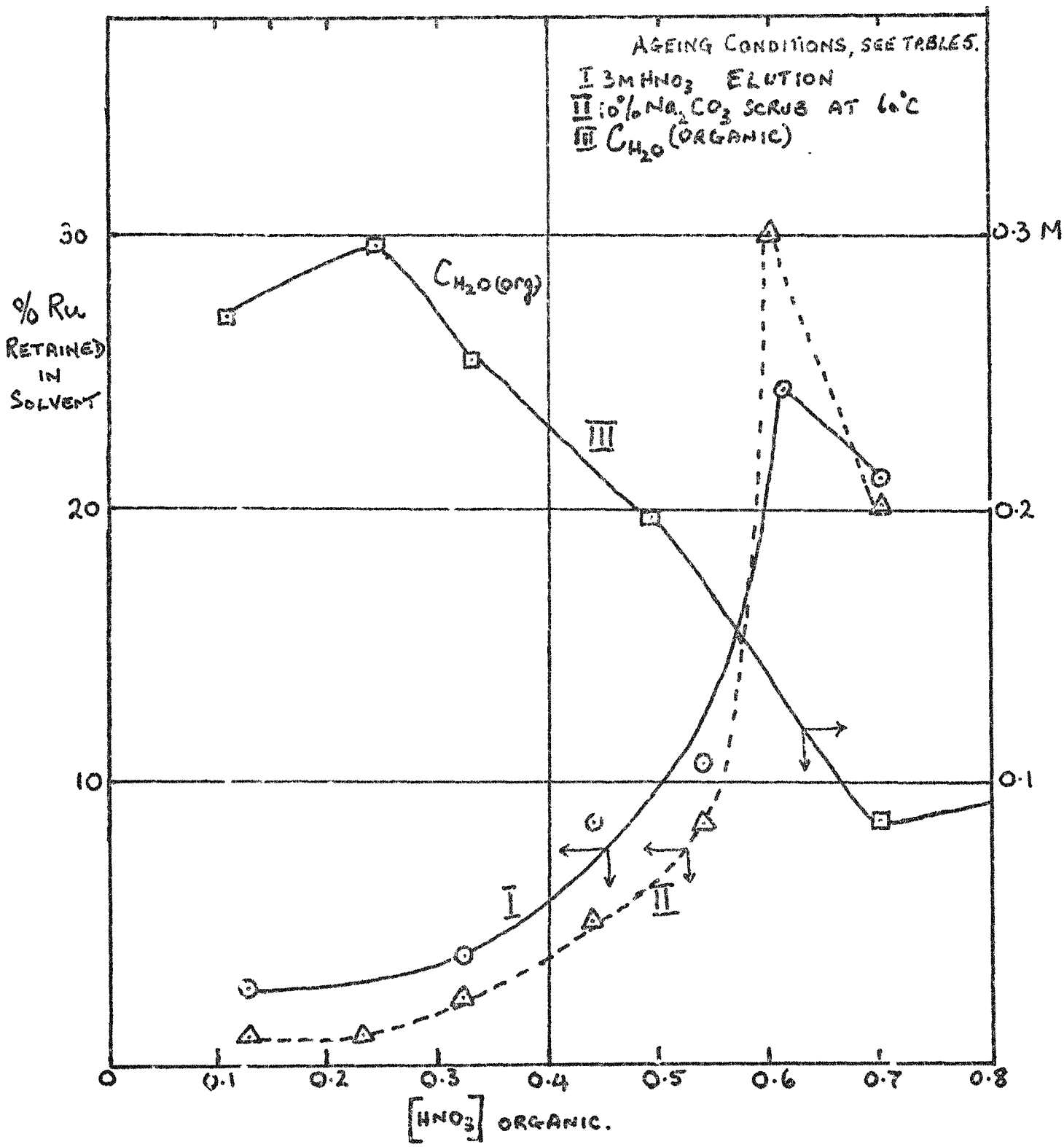

AGEING CONDITIONS, SEE TABLES.
I 3M HNO3 ELUTION
II 10% Na2CO3 SCRUB AT 60°C
III CH2O (ORGANIC)
% Ru RETAINED IN SOLVENT
30
20
10
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.3 M
0.2
0.1
CH2O (org)
III
I
II
[HNO3] ORGANIC.

FIG. 3.

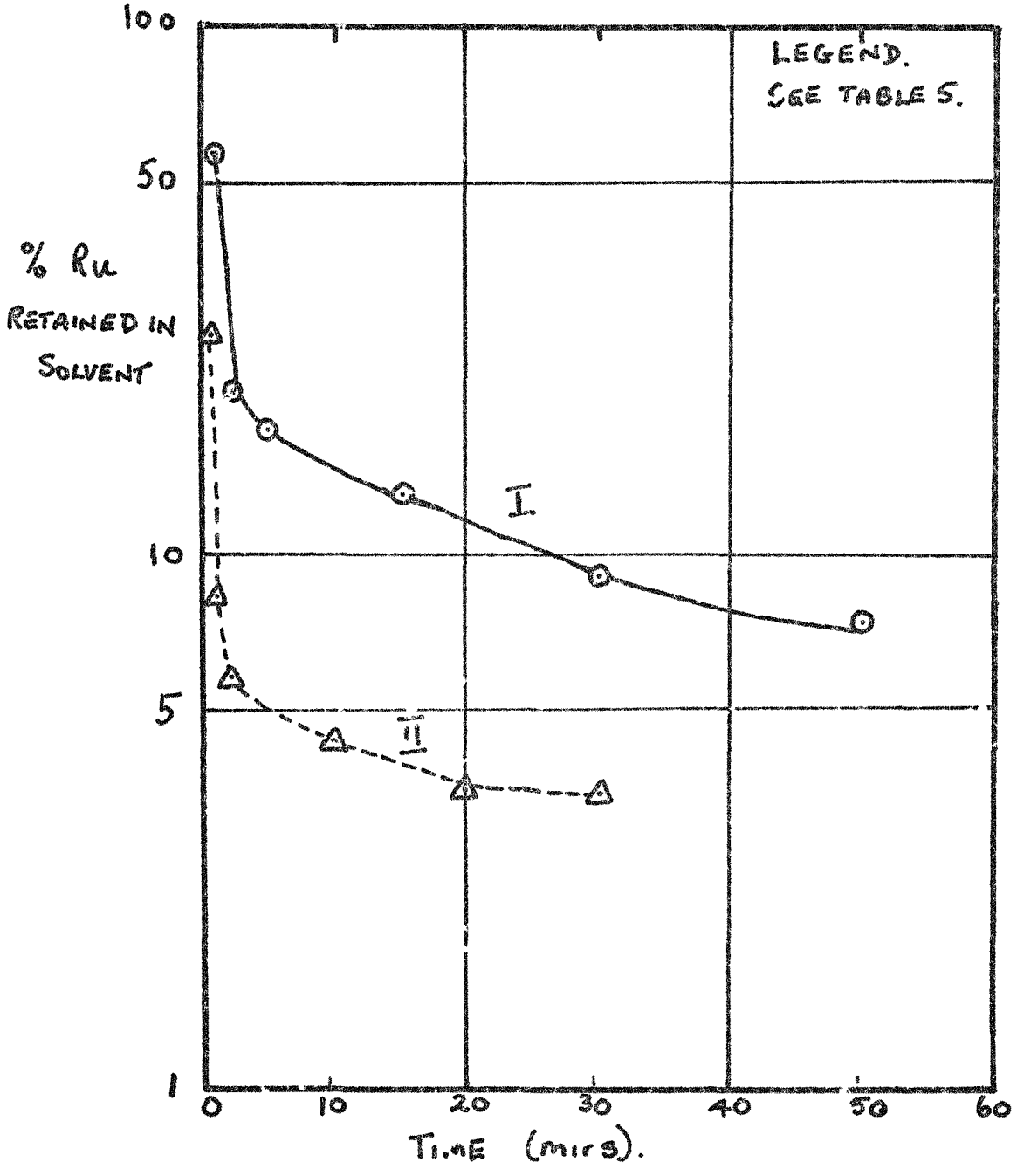
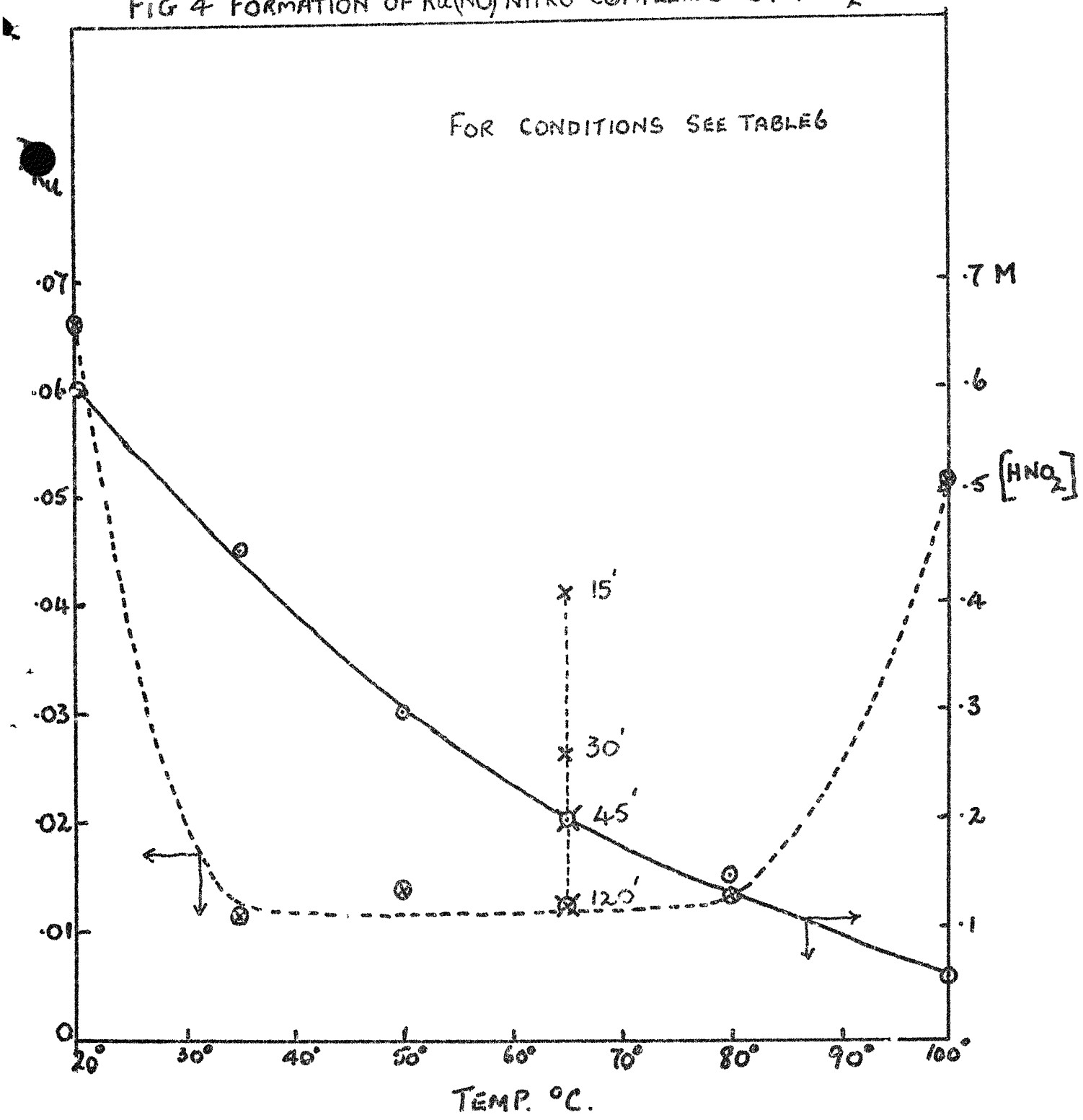

100
50
10
5
1
% Ru
RETAINED IN
SOLVENT
LEGEND.
SEE TABLE 5.
I
II
0
10
20
30
40
50
60
TIME (mins).

FIG 4 FORMATION OF Ru(NO) NITRO COMPLEXES BY HNO_2



THE ADVANCED SUMMER INSTITUTE AT KJELLER

Section V

AQUEOUS REPROCESSING OF THORIUM AND ISOLATION OF U^{233}

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AQUEOUS REPROCESSING OF THORIUM AND ISOLATION OF U^{233}

by

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1. Experience on the aqueous reprocessing of irradiated thorium has been reported from A.E.R.E., Harwell and from O.R.N.L., Oak Ridge. The experimental plant[1] erected at Harwell recovered kilogram quantities of U^{233} from irradiated thorium metal which had been allowed to cool sufficiently long for protactinium to have decayed almost completely: the object was primarily to recover U^{233} and the process chosen left a mixture of thorium and fission products for treatment at a later date. At O.R.N.L. an interim process[2] of a similar nature was used but replaced by the Thorex process[3,4] in which thorium and U^{233} are recovered simultaneously. Both the Harwell and Thorex processes used TBP as the solvent and were based on the usual type of laboratory data for a solvent extraction system.

2. In this lecture, firstly the two types of processes that have been used will be reviewed (paras 3 and 5): and secondly, the peculiar problem presented by the half-life (27.4 days) of protactinium-233 will be discussed in relation to future schemes.

3. The Harwell System: Separate U^{233} and Thorium Cycles

3.1 The main differences between the U - Pu and Th-U^{233} systems for aqueous reprocessing are due to:

(i) The presence in the Th - U^{233} system of fluoride (at about 0.05M) which is used to increase the dissolving rate of thorium metal[1,3] or of thoria.

(ii) The relatively low value of the partition coefficient of thorium compared to uranium (fig. 1) which permits separation without any change of valency (as used for plutonium).

3.2 The Harwell system[1] used the second of these features in the manner shown in figure 2. The choice of solvent[5] for the uranium cycle lay

between Butex and well-diluted TBP. The partition data (Table 1) indicated that the best separation of uranium from thorium and from $\beta\gamma$ fission product activity would be achieved from an acid-deficient system with Butex. The superiority of these conditions (which Spence et al. had noticed as early as 1948 for the U-Pu system) was sacrificed, for the plant, in favour of 5% TBP with acid conditions, since the latter were somewhat more flexible and TBP seemed desirable for the thorium cycle.

3.3 The flowsheet[1] for uranium separation, is shown in figure 3. Interesting features of the operation[1], which used pulsed columns of 2" diameter, were:

(i) Flow-rates were maintained accurately to $\pm \frac{1}{2}$ % with KONTAK metering pumps.

(ii) The scrub solution consisted of slightly acidulated 1M sodium nitrate rather than nitric acid: this reduces the acidity of the solvent product and enables the uranium to be recovered by a backwash at ambient temperature, more readily.

(iii) It was unnecessary to wash the solvent before it was reused. It was calculated that it could have been used without appreciably affecting the performance for 1000 days.

(iv) The recovery of uranium in the solvent cycle was 99.9%; the decontamination factor from thorium was 10^5 and from fission product activity $> 10^5$.

3.4 The flowsheet[1] subsequently used for thorium recovery in the same columns but with 40% TBP is shown in figure 4. In this case the solvent was washed with an alkaline solution before reuse. Operating conditions were chosen to avoid third phase formation, which have previously been studied in detail[6]. The fluoride present in the feed to this cycle was complexed by aluminium to permit a high recovery of thorium: an incidental effect of the presence of fluoride, even in the presence of aluminium nitrate, is the improvement in DF_{Zr} to which it leads[5]. Observed values for K_{Zr} were in the region of .04 to .08 instead of 0.25 to 0.9 for comparable conditions in the absence of fluoride. Even so, the thorium product was slightly contaminated with zirconium as well as with Pa^{233}; both were removed by a silica gel column.

4. Thorex Processes

4.1 These have been operated[4] in 5" diameter pulsed columns in the Thorex Plant at Oak Ridge both with high levels of U^{233} (up to 3000g U^{233} per ton of Th) and also with short decay times. From the activity in the feed there has been as much as 20 watts per litre. The results[4] are of very considerable interest because they indicate the limits beyond which an acid-deficient TBP process (with $\sim$ 40% TBP) cannot be taken without a severe breakdown in performance.

4.2 The One-Cycle TBP process[3], like the Harwell process, operated satisfactorily for well cooled ($>$ 180 days) fuel of moderate irradiation (up to 1500g U^{233} per ton of thorium): the γ decontamination factor (3×10^4 for continuous operation) for uranium was rather lower than at Harwell: this suggests that the benefit of an acid-deficient system was more than outweighed by the higher percentage of TBP (43.5 versus 5%) which must be used to extract thorium as well as uranium. The process incorporated two unusual features, viz:

(a) The dissolver solution (containing aluminium from chemical dejacketting) was evaporated to an acid-deficient condition: this also renders silaceous material insoluble. After further digestion, water was added to provide the feed conditions.

(b) The scrub contains phosphate and ferrous sulphate: decontamination from zirconium and protactinium are enhanced by the former and from chromium by the latter reagent.

4.3 When, however, material cooled for only 30 days was processed, values of DF_{Ru} and hence of DF_{γ} for the thorium product fell sensationally and even a Two-Cycle Thorex Process, in which a Codecortamination Cycle and Evaporator precede the Second Cycle (figs. 5 and 6), is only believed to be capable of handling material cooled for 90 days or longer. The poor decontamination from ruthenium has been traced[4] to the presence of nitrous acid (formed by radiation in the feed): as little as 10^{-3}M of this acid influenced DF_{Ru} adversely: the experience gained on the Thorex Plant is consistent with laboratory determinations of partition coefficients (Table 2) made by Brown[7] for RuNO nitro complexes, i.e. those formed in the presence of nitrous acid. These and results by Brown[7] with other solvents indicate quite clearly where trouble from

ruthenium will be experienced if nitrous acid is allowed to form these complexes. Thus acid-deficient conditions with ketones such as Hexone will also give low values of DF_{Ru} if such complexes persist. The role of nitrous acid on DF_{Ru} therefore changes with acidity, since for acid flowsheets it is beneficial[8]. The overall performance to be expected in various systems is summarised in Table 3.

5. The U^{233} product, from the TBP processes that have been used, has had the following composition:

Uranyl nitrate, 0.1 to 1 g U/litre
Nitric acid, 0.01 to 0.02M
Ratio Th : U, 0.01 to 0.1
Fission Products; Traces of Zr, Nb, Ru
TBP, Traces by dissolution and entrainment.

The main requirement is concentration of the uranium by a factor of up to 100: evaporation has not been used to do this as it also concentrates the impurities and in addition leaves phosphate (from TBP) in the product. Instead, ion exchange processes have been examined and successfully used (Table 4) both at ORNL and at Harwell. At ORNL[9], the uranium stream was purified by passage through a silica gel column prior to concentration by cation exchange (two columns in series; the first takes out thorium preferentially). At Harwell[1] an anion exchange process[10] was used: the presence of sulphate in the concentrate could be a disadvantage if a peroxide precipitation is required as the next step. In practice[11], $U^{233}O_2$ of high purity has been made from such a concentrate by ADU precipitation (to reduce the sulphate content), followed by a peroxide precipitation to remove traces of unwanted metals.

6. <u>The Protactinium and Thorium Problems</u>

The presence of Pa^{233} presents the crucial problem in the Th-U^{233} system. The three conditions given in Table 5 may be considered. It is suggested that the best compromise for thorium fuels will be with about 100 days cooling. If this (or a longer time) is accepted, the next main consideration concerns thorium recovery. Plant and laboratory experience suggests that no simple TBP process will give a good separation of both uranium and thorium from fission products in one

cycle: the thorium is of minor value compared to U^{233} and it is even doubtful if its rapid recovery will be economically necessary. Processing costs can therefore be kept down by using (fig. 7) a 5% TBP cycle to extract the U^{233} with a flowsheet which could be

(i) The acid system used in the Harwell plant (para. 3), or

(ii) An acid-deficient feed and extraction system modified to extract uranium; considerable work[12] has been done on these conditions for enriched U-Al fuels from MTR reactors and it is of interest to note that the presence of thorium has been found to improve the decontamination factor for cerium which is abnormally high compared to its value in acid flowsheets.

The actual plants used for processing enriched U-Al fuels could very probably be used for this type of recovery of U^{233}.

7. Subsequent recovery (Stage 2 of fig. 7) of U^{233} grown from Pa^{233} would be undertaken from the Extractor I raffinate after a further 100 - 200 days if the initial cooling period is only of the order of 100 days. Also

(a) If thorium recovery is not worthwhile, the raffinate from Stage 2 would be evaporated and reduced to a minimum bulk. This might be achieved by conversion to a glass; or

(b) If thorium recovery is required, it could be removed after the small amount of U^{233} (at Stage 2), i.e. when the activity is relatively low due to the disappearance of Pa^{233} etc. Solvents such as di-n-amyl n-amylphosphonate (DAAP) have been suggested[13] as being better than TBP for thorium recovery, in so far as they permit a higher solvent loading without third phase formation.

REFERENCES

1. Wells and Nicholls, Process Chemistry, Vol. I, p.221 (1956).

2. Culler, " " " p.189 (1956).

3. Gresky, " " " p.212 (1956).

4. Bruce, Brussels Symposium (1957), TID 7534, p.180.

5. McKay and Fletcher, Process Chemistry. Vol. I, p.145 (1956).

6. McKay, Naish and Scargill, AERE Document C/R 1168 (1953).

7. Brown, J. Inorg. Nuclear Chem., 13, 73 (1960); also in Process Chemistry, Vol. I, p.113 (1956).

8. Fletcher, Current Developments in TBP Processes for Irradiated Fuels, Lecture notes for the Advanced Course on Fuel Elements for Water Cooled Power Reactors, organized by the Netherlands'-Norwegian Reactor School, Kjeller, Norway, 1960.

9 Bruce, Brussels Symposium (1957), TID 2534, p.303.

10. Jenkins and Richardson, AERE Document C/R 1217 (1953).

11. Airey, Wain, Lister and Gillies, AERE Unpublished Information.

12. Buck, Howells, Parry, Warner and Williams, Geneva Conference 1958, Paper 82.

13. Siddell, Geneva Conference 1958, Paper 521.

Table 1. Partition Coefficients relating to U^{233} Extraction (I)

Initial uranium concentration: ca. 1 g U/l (as uranyl nitrate)
Equal volumes of phases

Expt. No.	(Initial) Aqueous phase concentrations					Partition coefficients (Organic/aqueous)			
	Th	HNO_3	NH_3	$NaNO_3$	NaF	K_U	K_{Th}	$K_{\beta\gamma}$	K_U/K_{Th}
	g/l	*M*	*M*	*M*	*M*				
First Series (Solvent: DBC)									
1	100	4	—	—	—	1·9	0·15	0·012	13
2*	100	1	—	3	—	4·1	0·04	0·011	102
3	100	—	0·2	4	—	1·65	<0·001	0·0002	>1000
4	100	—	0·8	4	—	1·57	<0·001	0·0001	>1000
5	250	0·5	—	3	—	26	0·05	—	520
Second Series (Solvent: 10% TBP/kerosene)									
6	100	4	—	—	—	6·1	0·11	0·001	55
7	100	1	—	3	—	7·2	0·135	0·001	53
7_A	100	1	—	3	0·05	8·2	0·121	0·0007	68
8	100	0·5	—	3	—	—	0·14	0·0008	—
9	100	—	0·2	4	—	14·1	0·135	0·004	104
10	100	—	0·8	4	—	33	0·154	0·008	210
Third Series (Solvent: 10% TBP/dibutyl ether)									
11	100	4	—	—	—	4·8	0·048	0·001	100
12	100	1	—	3	—	9·5	0·12	0·001	79

* DBC conditioned with nitric acid.

TABLE 2

PARTITION COEFFICIENTS RELEVANT TO THE SEPARATION OF RUTHENIUM FROM THORIUM

Aqueous Phase Nitrate		For 30% TBP		D_{Ru}		D_{Th}
Total	As HNO_3	RuNO Nitro (ref.7)		RuNO Nitrato*		for tracer Th (ref.6)
		Forward	Scrub	Forward	Scrub	
4 to 5M (as $NaNO_3$)	pH ~ 2	2.2	-	0.5	3	4
5.5	3M	0.21	0.21	-	-	3
3	3	0.51	0.51	0.082	1.7	3

* Results by A.G. Wain, A.E.R.E.

TABLE 3

THE RELATION OF RUTHENIUM BEHAVIOUR TO NITROUS ACID FOR VARIOUS TBP SYSTEMS

TBP Conc.	HNO_3 Conc.	D.F.$_{Ru}$ in Extractor I for		Overall Performance for Ruthenium
		RuNO Nitrato	Nitro Complexes	
High (20-40%)	2-3M	Limited to about 10^3 by kinetics	V. High if scrubbing good	Reasonably good
	Negative	v. high	v. low	Bad if radiation causes HNO_3 to persist
Low (5%)	2-3M	v. high(~10^4?)	v. high	Very good
	Negative	v. high	high (?)	Probably good

TABLE 4

CONCENTRATION AND PURIFICATION OF U^{233} BY ION EXCHANGE

Type of Resin	U Solution Applied	U Solution Eluted By	U Solution Eluted g U/l	DF_γ	DF_{Th}
Anion Exchange (Deacidite FF)	As Sulphate	1M HNO_3, but H_2SO_4 present	~10	Not tested	5 - 10
Cation Exchange (Dowex 50)	Direct	Ammonium citrate-acetate	~10	5	~10

TABLE 5

Pa^{233} AND COOLING TIMES

Cooling time	Short ~ 30 days	Moderate ~100 days	Long ~200 days
U^{233} Recoverable at once (at 10^{14} - 10^{15} flux)	~ 50%	~ 95%	> 99%
Advantages	Low U^{233} inventory for this 50%	Good recovery of U^{233} with moderate inventory	No secondary recovery of U^{233} necessary
Disadvantages	(a) High activity and iodine problems in solvent extraction system	Recovery of remaining 5% U^{233} desirable	High U^{233} inventory
	(b) Need to recover remaining 50% U^{233} after further 150 days		

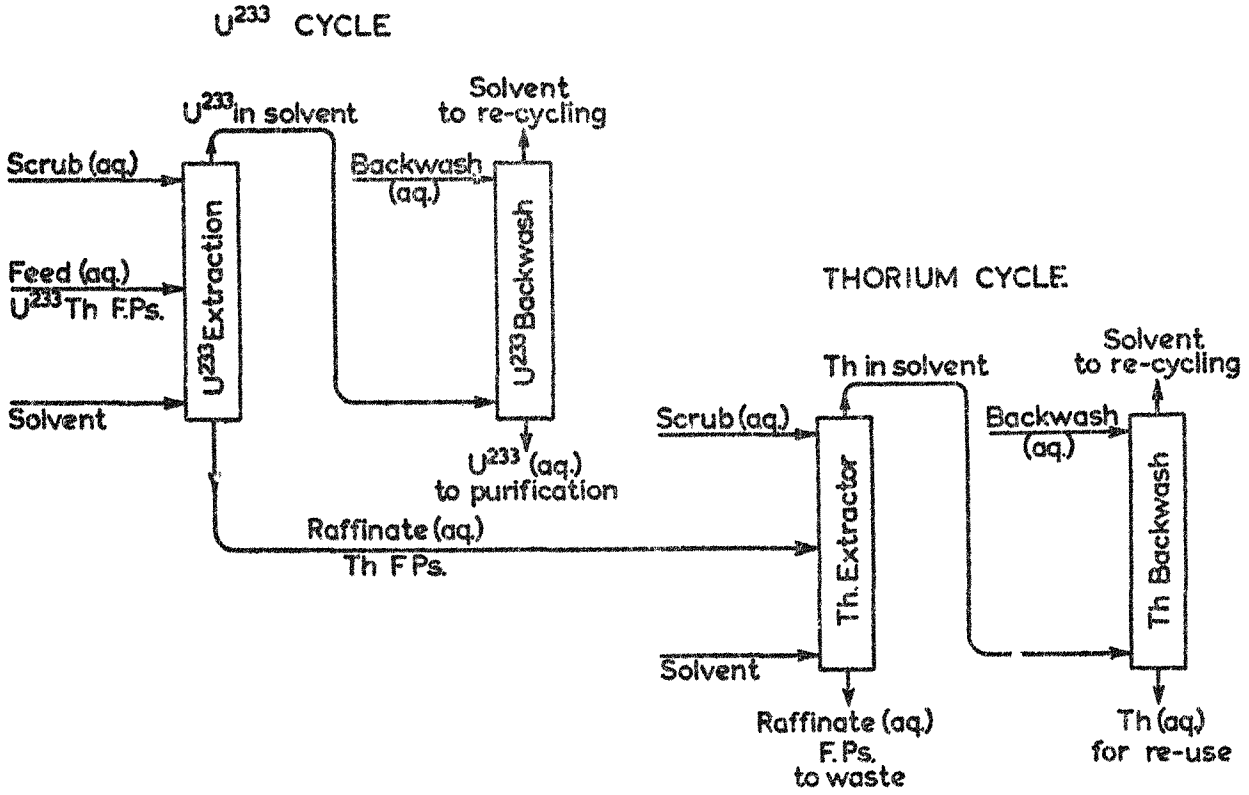


FIG. 1.—Outline of proposed process for U^{233} separation and thorium recovery.

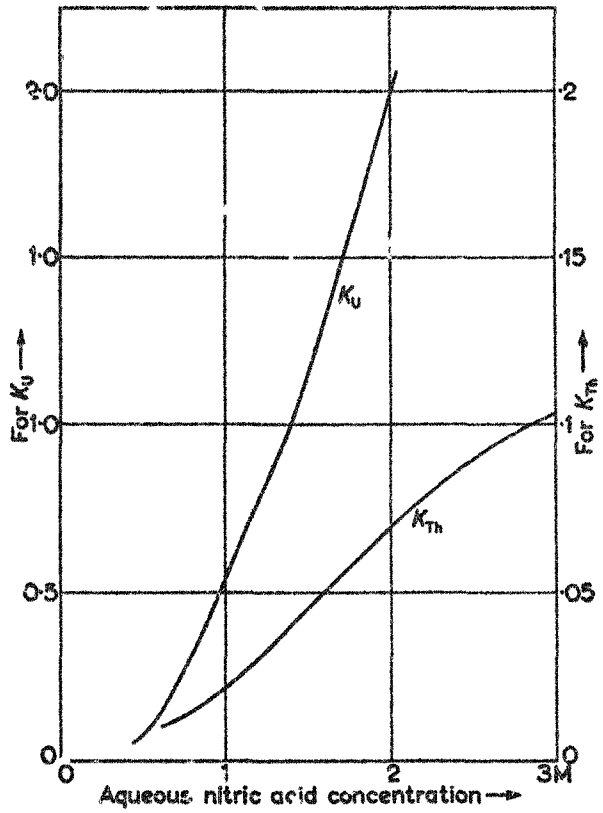


Fig 2.—K_U and K_{Th} for 4·7% TBP/kerosene as a function of $[HNO_3]_{aqueous}$

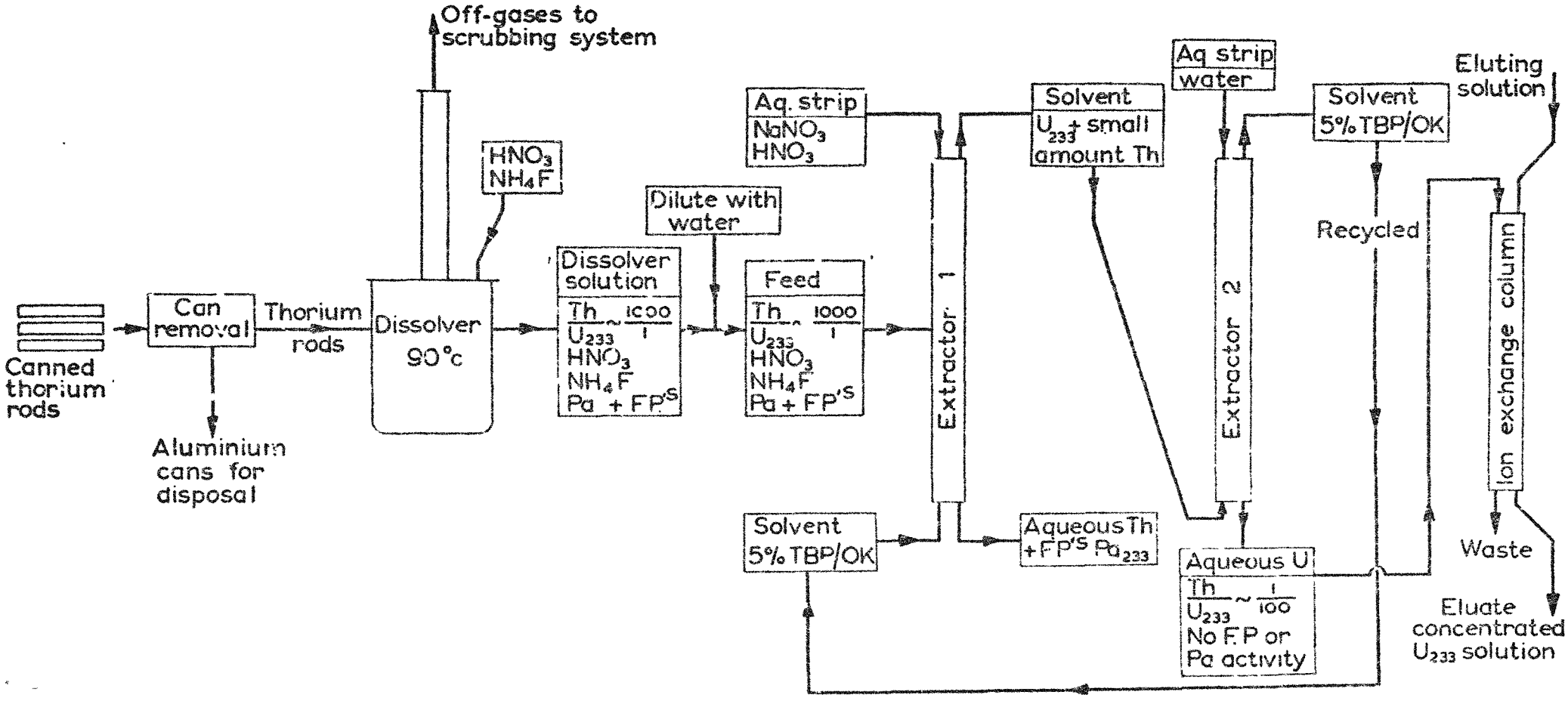


FIG. 3.—Flowsheet for decanning, dissolving and separation of uranium 233 from thorium and fission products.

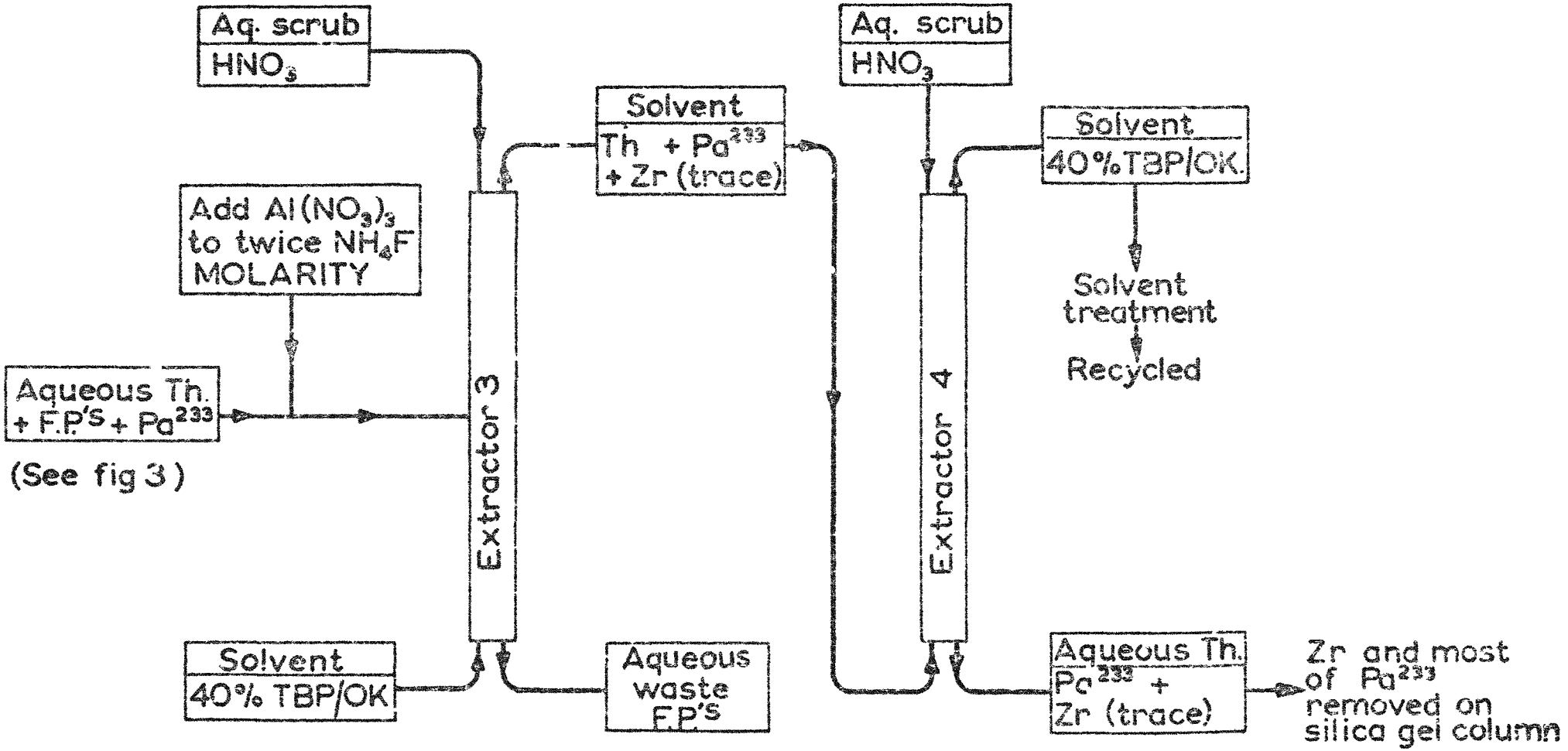


FIG. 4.—Flowsheet for thorium recovery process.

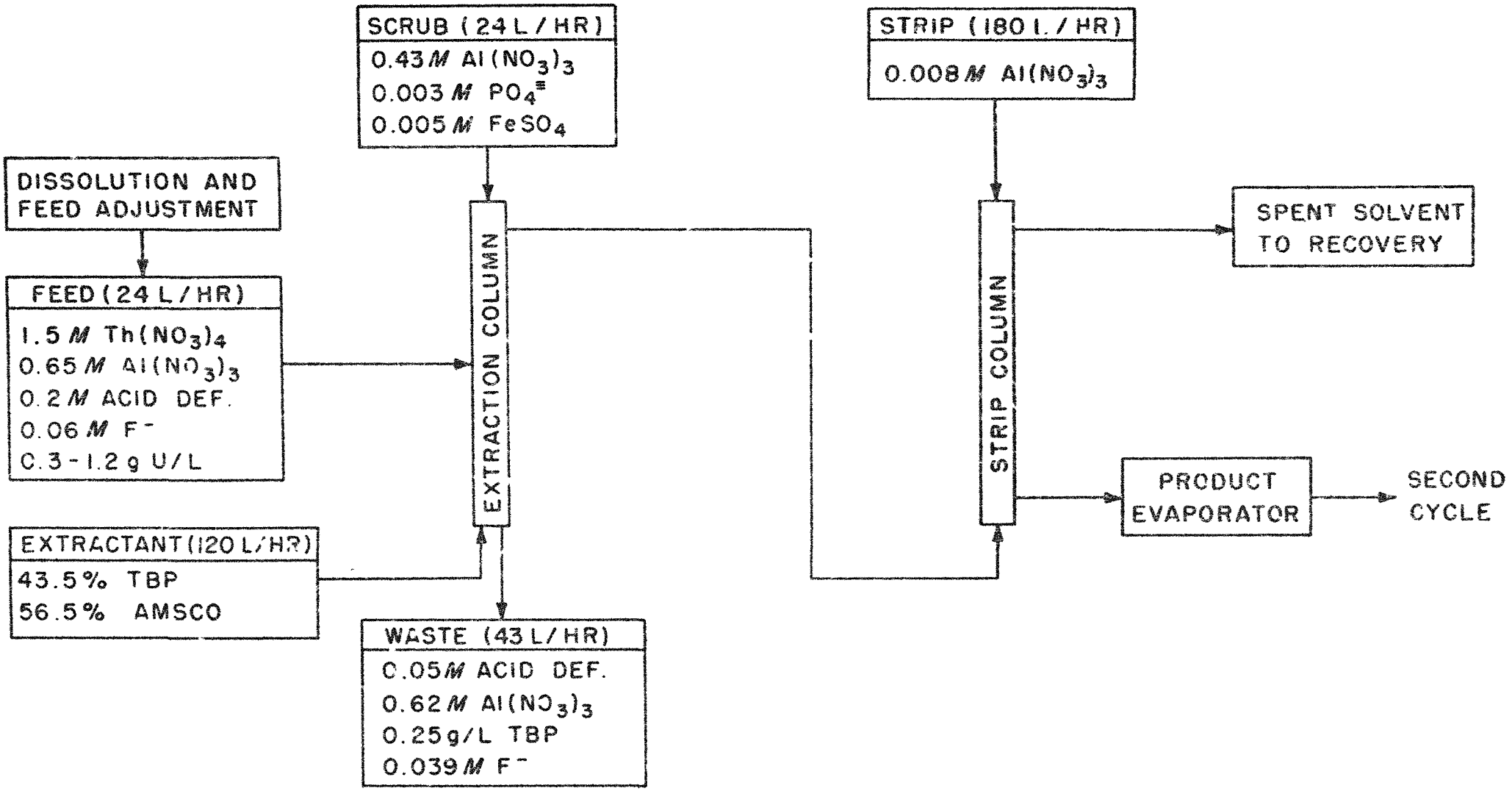
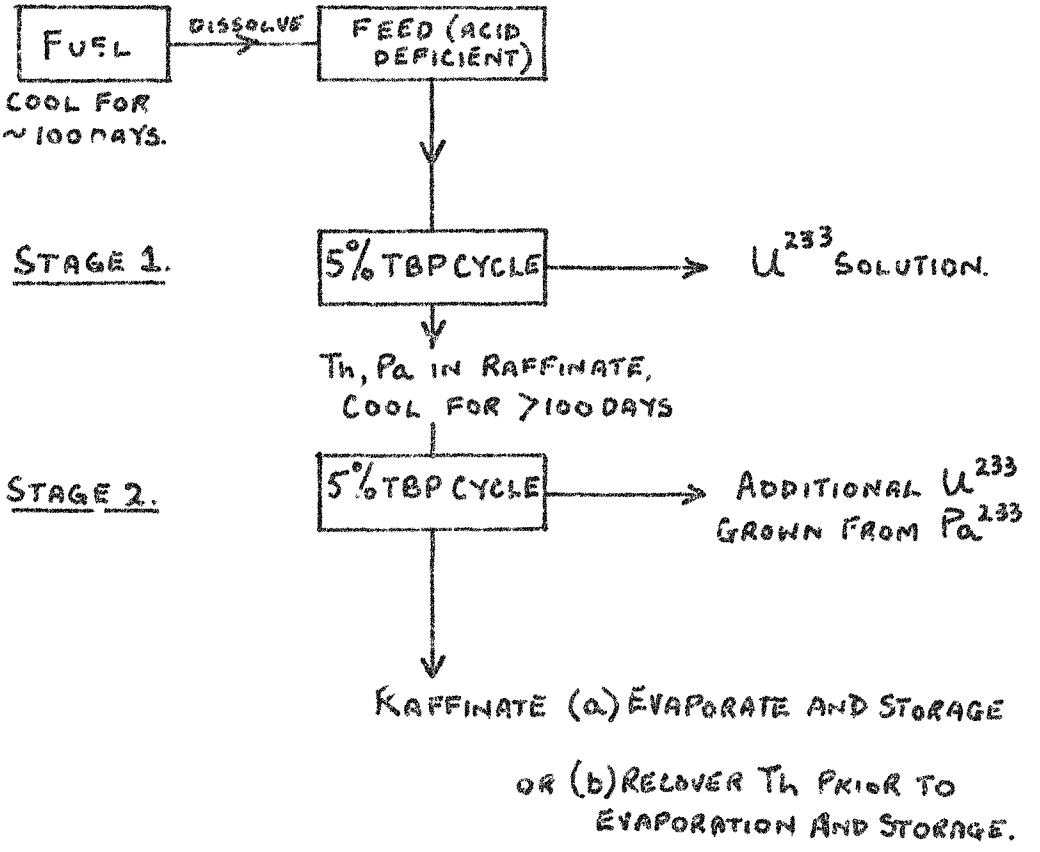


Fig. 5 - First cycle Thorex flowsheet (basis: 200 kg of thorium per day).

FIG. 7. PROPOSED SCHEME FOR U^{233} – Th PROCESSING



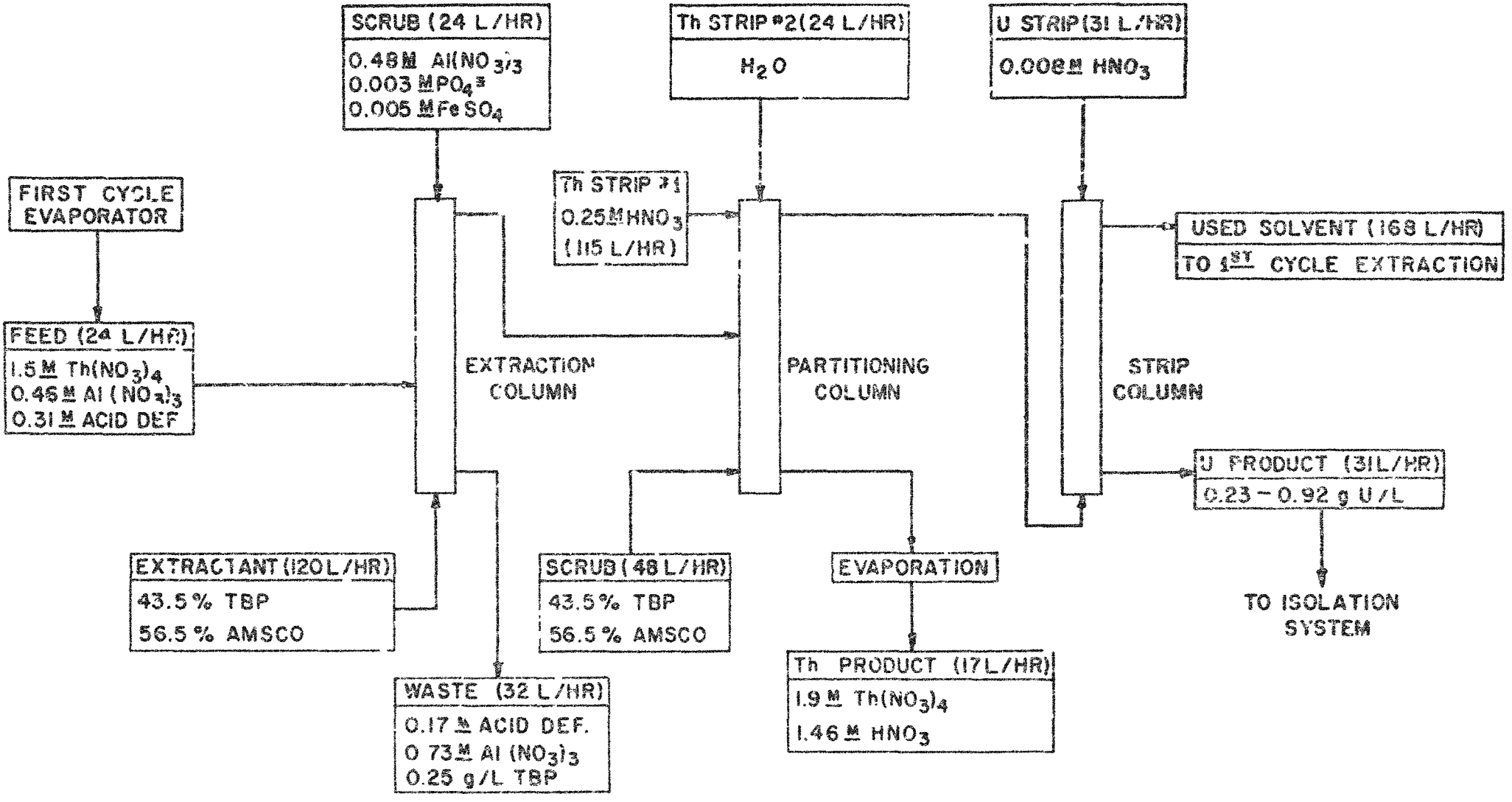


Fig. 6 - Second cycle Thorex flowsheet (basis: 200 kg of thorium per day).

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Section VI

REPROCESSING COSTS

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REPROCESSING COSTS

by

T. J. Barendregt

1. INTRODUCTION

An important step in the recycle of irradiated fuel is the radiochemical reprocessing of this material. The numerous reactor designs proposed, under construction or in operation and the variety of fuel elements and assemblies, containing natural or enriched uranium, in metallic or oxide form, clad in different materials like stainless steel, zircaloy or aluminium achieving different burn-up of fissionable material during the irradiation cycle make the analysis of recycle cost rather difficult.

Starting from the basic fuel, uranium 235 for nuclear reactors, any atomic energy power program can in principle be based on two different fuel cycles, either the irradiated material is reprocessed and the recovered fissile material is refabricated into new fuel elements or the fuel, after discharge from the reactor might be stored or buried rather than reprocessed. The decision for one of these cycles will entirely depend on the economical result which can be achieved.

It is generally accepted that the investment costs of a nuclear power plant are higher than those of power plants using fossil fuels. The successful competition of nuclear power with conventional power can thus only be achieved in case the fuel bill for nuclear power is substantially lower. In Western Europe, power made using fossil fuels costs at present 6.3 mills/kwh for oil fired units and 7.6 mills/kwh for coal fired power stations with a capacity of 150 MW electricity and a production of 10^9 kwh/year.

The nuclear power stations which have been offered so far ask already for an investment which corresponds to 6.1 - 6.2 mills/kwh. Consequently, the first aim for the nuclear industry will have to be an appreciable decrease in investment costs, before one even can think of an acceptable fuel cycle. Although the investment costs of nuclear stations do not belong to our present discussions, it is obvious that we have to start with a reasonable estimate to be able to arrive at an allowable figure for fuel cycle costs.

To this extent a break-down of the cost figure for conventional stations is given below:

TABLE 1.

150 MW capacity	Coal fired station	Oil fired station	Nuclear station	
10^9 kwh/y production	Western Europe,	1960		
Capital costs	2.1 mills/kwh	2.1	(6.2)	(3.2)
Operation and maintenance	0.3 " "	0.3	1.0	
Fuel	5.2 " "	3.9	?	

It does not seem too optimistic (1,2) to assume for the next generation of reactors a decrease in investments to somewhat over half the present costs, still some 50% more than for conventional stations. Due to safety regulations, it cannot be expected that the item operation and maintenance will decrease appreciably in the near future. Under these assumptions approximately 2 mills/kwh are left for total recycle cost to be competitive with nuclear power. The total recycle can be divided in burn-up costs. radiochemical separation, refabrication of fuel and waste disposal. To make a choice between the two principle alternatives, throw-away cycle or reprocessing, the 2 mills/kwh for the entire fuel bill have to be considered somewhat closer.

2. BURN-UP COSTS

To be able to make a better estimate for allowable reprocessing costs, we have to separate from the total fuel costs first of all the burn-up costs. As the price, according to the U.S.A.E.C. price scale, is for uranium 235 ranging from 5.62 dollars/gram in natural uranium to 17.07 dollars/gram in 90% enriched uranium, the burn-up costs will vary with enrichment.

The net burn-up costs are calculated according to the loss of uranium 235, either by fission or capture. For the case of natural uranium, assuming an initial uranium 238 resonance escape probability of 0,8 and a net thermal efficiency of 25% we arrive at 0,6 mills/kwh increasing to as high as 3,5 mills/kwh for highly enriched material.

The remaining fissile material after irradiation has to be recovered or stored. In the latter case, the net burn-up costs will be as large as the cost of the fissile material originally present in the fuel element. On the other hand, the net burn-up costs will be decreased in case not only the remaining fissile material (U235) is recovered but also the newly formed (Pu239). The price for which the plutonium can be sold to the U.S.A.E.C. is at present 12 dollars/gram.

The burn-up cost formula for the throw-away cycle becomes simply the cost of the fissile material charged to the reactor. In the case of recycling the fuel by reprocessing, the burn-up cost formula becomes A - B - C, in which A is the cost of the fissile material charged to the reactor, B the value of the recovered uranium 235, and C the value of the isolated plutonium 239. It is clear that B + C have to be larger than the reprocessing costs to make this recycling operation economically worthwhile. The value of B + C becomes appreciable as soon as enriched material is utilized, but it is shown in the following table that also the rest value of natural uranium after irradiation is not negligible, especially if these values are expressed in mills/kwh electricity.

TABLE 2

Residual value of fuel in natural and partially enriched cycles (10)
(Initial uranium resonance escape probability = 0.8)

	Value, dollars per kg U after irradiation			Potential value in mills/kwh.
	U	Pu	Total	
2000 MWD/t irradiation natural uranium	20	14	34	2.9
1% U235	50	18	68	5.7
2% U235	175	14	189	15.7
3% U235	352	13	365	30.0
4000 MWD/t irradiation natural uranium	8	50	58	2.4
1% U235	31	31	62	2.6
2% U235	151	26	117	7.4
3% U235	297	25	322	13.5

TABLE 2 (continued)

	Value, dollars per kg U after irradiation			Potential value in mills/kwh.
	U	Pu	Total	
10000 MWD/t irradiation				
natural uranium	1	55	56	0.9
1% U235	5	55	60	1.0
2% U235	102	54	156	2.6
3% U235	205	53	258	4.4

The importance of recycling the irradiated material may be best illustrated by the following examples: The net burn-up costs for 2% enriched material (dollars 11/gram U235) are approximately 2 mills/kwh. An irradiation to 4000 MWD/t and no recovery increases the burn-up costs to 9 mills/kwh. According to table 2, the final burn-up cost will be 1.6 mills/kwh. Another example is the costs for natural uranium, irradiated to 10000 MWD/t. The net burn-up costs are 0.6 mills/kwh, but according to table 2, reprocessing of this material would give a burn-up "profit" of 0.3 mills/kwh.

3. FUEL FABRICATION COSTS

The cost of fabrication and in the case of reprocessing the irradiated material, the cost of refabrication of the fuel elements will be the subject of the next lecture (3) in this course. Here, only the dependency of achieved burn-ups on the fabrication costs has to be mentioned. It seems not unreasonable to allow for fabrication costs 0.7 mills/kwh (4,5) or 35% of the allowed total recycle costs including burn-up costs, in the desired 2 mills/kwh bill. Today most fabrication costs figures will be appreciably higher.

4. "ALLOWABLE" REPROCESSING COSTS FOR COMPETITIVE POWER

Before we will be able to calculate the allowable reprocessing costs for the adopted 2 mills/kwh fuel cycle cost, we have to mention some additional items. To start the fuel cycle one needs some working capital to buy at least one reactor charge or to rent the enriched material. One can argue in how far such first expenditures should be included in the capital investment. Furthermore, even by reprocessing all irradiated material, the recovered products will not directly be

suited for charging again the same reactor. An additional factor, the replaceable core cost will increase the total fuel cycle costs. It becomes then rather obvious that the allowable reprocessing costs are very low indeed with the present knowledge of fuel fabrication and the price of fissile material. Returning to our 2 mills/kwh figure for total fuel recycle costs including burn-up the reprocessing cost should not exceed 0.5 mills/kwh. The results of the determination of residual value of fissionable and fertile materials given in table 2 indicate further that decontamination and conversion costs below 50 dollars per kilogram of natural uranium are economical for burn-ups as low as 2000 MWD/ton, that for all higher uranium 235 enrichments up to 3% and higher burn-ups the residual value of fuel exceeds 50 dollars per kilogram.

In conclusion, it will be clear that one is not justified to speak in terms of "allowable" reprocessing costs. For each reactor design an economical optimum will have to be calculated. Keeping the fuel fabrication or refabrication together with fuel working capital and replaceable core cost as constants for a given reactor the achieved burn-up and the price for the recovered products will dictate the choice of the fuel cycle, rather than the cost in mills/kwh.

Before leaving the throw-away cycle it may be of interest to list the savings obtainable by throw-away and the added costs due to throw-away. (6).

Savings are:

a) Shipping cost irradiated fuel.

b) Inventory charge while cooling fuel.

c) Decontamination cost including waste disposal.

d) Conversion charges from nitrate to saleable or reuseable product.

e) Any incremental fabrication costs due to residual radioactivity.

f) Reduced U236 load on the diffusion cascades.

Additional costs are:

a) Loss of value of residual uranium.

b) Loss of value of plutonium.

c) Loss of fission product and higher transuranium sales other than Pu.

d) Cost of disposal of fuel elements.

5. REPROCESSING COSTS

Reprocessing costs of irradiated material can be subdivided in shipping costs including insurance, storage both at the reactor site and at the reprocessing plant, radiochemical separation costs, waste storage and disposal costs, conversion of nitrates to saleable or reuseable products and inventory charges.

5.1. Transport costs

In an earlier lecture in this course (7) various means of transport of irradiated fuel have been discussed. As an example the shipment of fuel over some 1000 km, irradiated to 10000 MWD/ton and a cooling time of 100 days at the reactor site has been mentioned. Assuming the transport will be carried out in casks with a ratio of 1:50 for fuel weight and weight of the cask, the costs in Europe will be somewhere between 1.00 dollar and 1.50 dollars/kg irradiated fuel, representing, again depending upon the burn-up, 0.02 - 0.1 mills/kwh. In any case, it may be concluded that the shipment of radioactive material over moderate distances does not contribute significantly to the power costs and large, multipurpose reprocessing plants may be envisaged, as soon as legal and administrative difficulties for the transports of large amounts of radioactive material have been overcome.

5.2. Storage costs

The second lecture of Rometsch (7) dealt with the storage ponds for irradiated fuel, both at the reactor site and at the reprocessing plant. As these facilities are integrated parts of either the reactor or the reprocessing plant, the storage costs are usually first calculated as either lease or inventory charges of the nuclear material involved. The capital and operating costs of the storage ponds are included in the total costs of reactor and reprocessing plant.

5.3. Radiochemical separation costs

Various methods for separating uranium and plutonium from fission products have been discussed in detail during this course (8,9). As has been pointed out above, the needs for reprocessing irradiated material are difficult to estimate due to the variation in types of fuel and the different burn-up achieved. The experience in the U.S.A.

with the Idaho Chemical Processing Plant, as well as with other facilities like those at Hanford, Savannah River and Oak Ridge has shown that the reprocessing plant cost is relatively insensitive to the type of chemical process and that the important variables in unit cost may be chemical plant capacity and fuel burn-up (10). Figure 1 shows the dependance of investments for a reprocessing plant on the daily capacity. Figure 2 shows the dependance of annual operating costs on the daily capacity.

Although these figures have been published some years ago, it is generally accepted that reprocessing of irradiated material in small plants will not become economical. Consequently, it is not foreseen that in the development of a nuclear power program reprocessing facilities will be attached to the individual stations. The cost studies are based on the use of solvent extraction as the main separation process. As there are no comparable plants based on different processes in operation yet, our discussion will be limited to the use of so-called aqueous reprocessing methods. A cost comparison between the different decontamination cycles will be the subject of the forthcoming lectures in this course (11,12).

The following conclusions have been drawn from figures 1 and 2 (10):

1) To achieve chemical processing costs (products as nitrate solutions) of less than 0.5 mills/kwh of electricity, a radiochemical separation plant will have to process fuel from 6000 - 10000 MW of installed reactor electrical generating capacity, or as much as 40000 MW of heat at 25% thermal efficiency. At 4000 MWD/t, the chemical plant would therefore have to process the equivalent of 10 tons of natural uranium per day. Making allowances for variation thermal efficiency and the inaccuracies of the study, it was concluded that a chemical plant of less than 5 tons/day capacity at an average burn-up of 4000 MWD/t could not yield processing costs of less than 0.5 mills/kwh.

2) Amortization of capital and relatively fixed operating charges will make up most of the cost of operation. Therefore, a radiochemical plant should operate with a high on-stream efficiency.

3) Because of the diversity of the types of fuel being developed, it was further concluded that a large radiochemical plant should be a multipurpose facility, one in which it would be possible to process fuel from different types of reactors within an economic shipping radius of the chemical plant.

The diversity of the types of fuel is complicating the dissolution process and asks for several head-ends as has been pointed out during this course (13). The high percentage of fixed charges in the cost of operation is reflected in the cost figure for reprocessing of irradiated material of the U.S.A.E.C. Originally set at 15,300 dollars per day plant operating cost, it has been recently increased to 16,260 dollars per day plant operating cost. The basis for this figure has been the operating costs of a hypothetical plant inside the U.S.A. treating 1 ton per day of natural or slightly enriched uranium. It is, however, doubted if this figure is a realistic one (17). The uncertainty of the reprocessing costs may be illustrated by comparison of the investment costs of some U.S. installations:

TABLE 3

Investment and operating costs of some existing facilities in the U.S.A.

	Capacity	Investment cost	Operating cost
Hot Semi Works, Hanford	200 kg/day nat. U	Dollars $5 \cdot 10^6$	Dollars 73000/month
ICPP, Idaho	1200 kg/day nat. U [x)]	" $19 \cdot 10^6$	" 263000/month
Metal Recovery Plant, Oak Ridge	500 kg/day nat. U	" $1 \cdot 10^6$	60000/month
Thorex pilot plant	400 kg/day nat. U [xx)]	" $1,5 \cdot 10^6$	80000/month

x) The Idaho chemical processing plant can process high enriched fuels and has no plutonium recovery facilities. The mentioned 1200 kg ratural uranium per day is a potential capacity.

xx) The Thorex pilot plant can process irradiated thorium fuels and has no plutonium recovery facilities. The mentioned 400 kg natural uranium per day is a potential capacity.

The facilities, mentioned in table 3, with the exception of the Idaho plant are not equipped with several head-ends, which might be an explanation for the large difference in investment costs. To

arrive at a better cost comparison among the four plants, Schwennesen (14) based the investment costs as a function of the amount of shielded process area or process cell volume since such an area or volume represents the basic nucleous of plant. As can be seen from table 4 the investment costs are quite comparable taking into account the different locations of the plants, the different duties and the numbers of auxiliaries.

TABLE 4.

Comparison of investment costs on basis of plant size.

	Hot Semi-Works	ICPP	Metal Recovery	Thorex
Comparative Investment Cost	$5,000,000	$19,000,000	$1,000,000	$1,500,000
Total Volume, cu.ft. Radioactive Process Areas	71,000	247,575	19,700	32,400
Comparative Cost $/cu.ft. Process Area	$ 70	$ 77	$ 51	$ 46
Total Area, sq.ft. Radioactive Process Areas	2,480	9,775	784	900
Comparative Cost	$ 2,020	$ 1,940	$ 1,280	$ 1,670

The projected cost of a multipurpose reprocessing pilot plant in Belgium with a capacity of 350 kg natural uranium/day is $10 \cdot 10^6$ dollars. This facility will be equipped with several head-ends to meet the needs for reprocessing of irradiated natural and slightly enriched uranium in Europe. As it will be difficult to draw another conclusion from the above-mentioned figures, than a great uncertainty in the cost although it is obviously quite expensive, one of the main objects with the European facility is to obtain better founded cost data for the evaluation of an industrial reprocessing plant in Europe.

5.4. Waste storage and disposal costs

It is well known that the reprocessing of irradiated fuel creates a number of problems by the necessity of the treatment and disposal of radioactive effluents. Although the disposal of fission products and other radioactive wastes has not been the subject of this course, any discussion on reprocessing costs would be incomplete without some consideration of the radioactive waste problem.

The highly active effluent, originating from the first separation step has to be stored. It is still an open question in which form these large amounts of fission products can be stored in a safe and cheap way. Utilizing the aqueous processes like Purex, the amount of highly active effluent is approximately 3 liter/kg U, which is at present in most cases stored as concentrated nitric solutions in stainless steel tanks. The minimum cost of this type of storage is 7 cents/liter (15) but other estimates (16) are more than double this amount, although still negligible in percentage of the total fuel costs. The increasing amount of stored highly radioactive liquid waste once a nuclear power program has been developed is not a final solution to this problem and large efforts are made to come to a satisfactory solution for the solidification of this type of radioactive waste.

While the principle applied to the disposal of high active liquid waste is concentration and storage, two different methods can be used for medium and low active wastes. The large volumes of low active waste make concentration and subsequent storage very expensive and dilution and dispersion is used in many cases. The same procedure may be done with medium active waste, decladding solutions, after intermediate storage for decay. The possibility of dilution and dispersion requires the presence of sufficient water in which the radioactive waste can be released.

As a result most reprocessing facilities are built in the neighbourhood of large rivers or at the coast. In the last years health and safety regulations predict however, the steady control over radioactive waste and release is limited to very strict regulations. Under these circumstances, the treatment of low active and definitely of medium active wastes becomes necessary and will add appreciably to the cost of reprocessing of irradiated material.

As an illustration may be mentioned that the investment costs of the waste disposal facilities of the Idaho reprocessing plant amount to 8 million dollars. Due to location of this facility possibilities of release are very limited. The same difficulty, but for different reasons, is faced in Belgium, where the density of the population prohibits any excessive release of radioactive waste. The projected cost for waste treatment and storage facilities for this facility is approximately 2 million dollars. It is rather difficult to estimate

the operating cost for additional treatment of low and medium active waste as the amount will highly depend on the fuel type which is reprocessed.

A further problem is the release of gaseous waste. Normally, reprocessing plants are located in remote areas where release to the atmosphere does not meet particular difficulties. Reprocessing plants in densely populated areas will have to be provided with additional auxiliaries for proper containment of gaseous radioactive waste, again adding to the total cost for reprocessing of irradiated material.

5.5. Conversion of nitrates to saleable or reuseable products

The conversion of uranyl- and plutonium-nitrate to UO_2 of UF_6 and Pu-metal will be described in detail in a further lecture of this course (11). A charge of 5.60 dollars per kg. of uranium has been published by the U.S.A.E.C. for the conversion of uranylnitrate to the hexafluoride and a charge of 1500 dollars per kg. of plutonium for the conversion of the nitrate to plutonium-metal.

6. SUMMARY

From the rest values of irradiated material, we concluded a reprocessing cost not exceeding 50 dollars/kg irradiated material to keep radiochemical separation still an interesting economical proposition.

Today reprocessing costs will amount to:

1)	Transport costs (incl. insurance)	dollars:	1.50/kg
2)	Storage costs, inventory charges 4% per annum (minimum 120 days) 2% U235 material	"	3.00/kg
3)	Radiochemical separation costs (AEC-figure)	"	16.26/kg
4)	Waste storage and disposal costs	"	2.50/kg
5)	Conversion of nitrates, dollars 5.60/kg U (4 g Pu/kg U) 6.00/kg U	"	11.60/kg

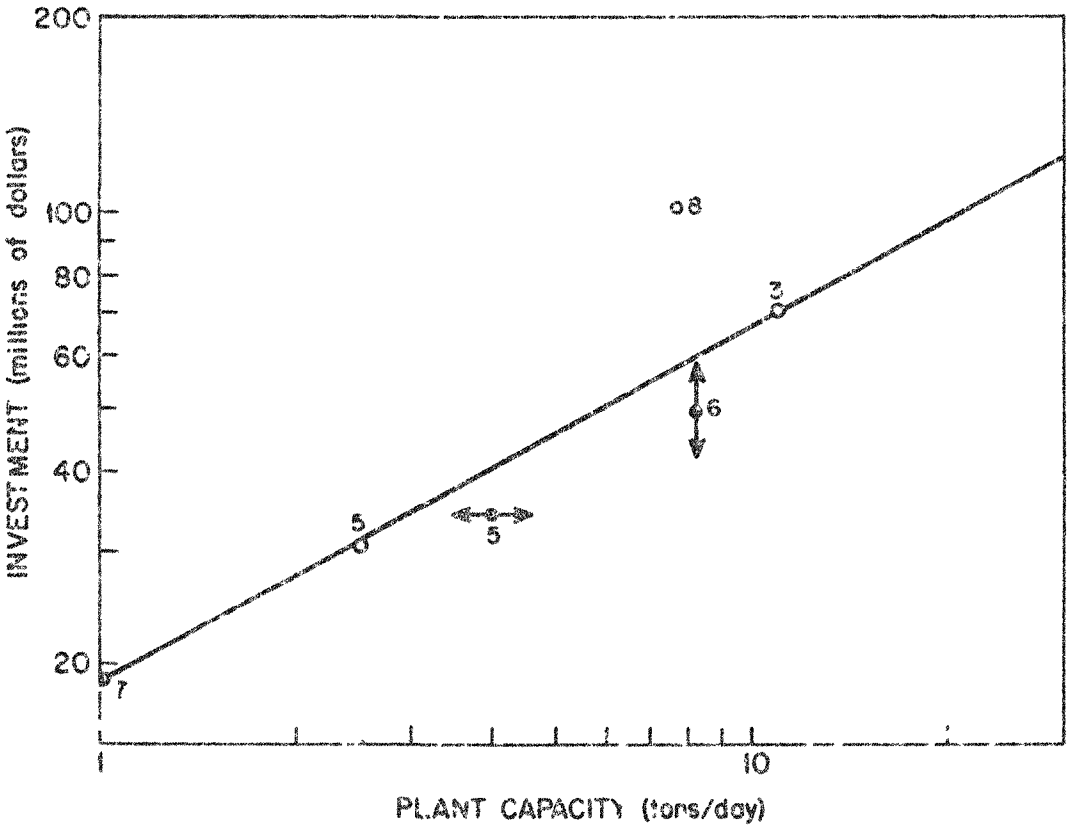
Although the final figure looks rather promising, it should be realized that the transport costs may be appreciably higher due to safety regulations, necessity of escort and insurance. According to a recent

publication (17) the real separation costs may be 2.5 times the published U.S.A.E.C. figure and finally the cost of waste storage will be dependent upon the nature of decladding solutions, the salting out agent used and the location of the plant.

However, it seems to be possible to keep reprocessing costs within 30 dollars/kg uranium, provided an optimum can be reached as regards plant capacity and a satisfactory solution for the waste problem can be realized. Further research to limit the waste volumes, either by improving the existing methods or by development of new ones is necessary.

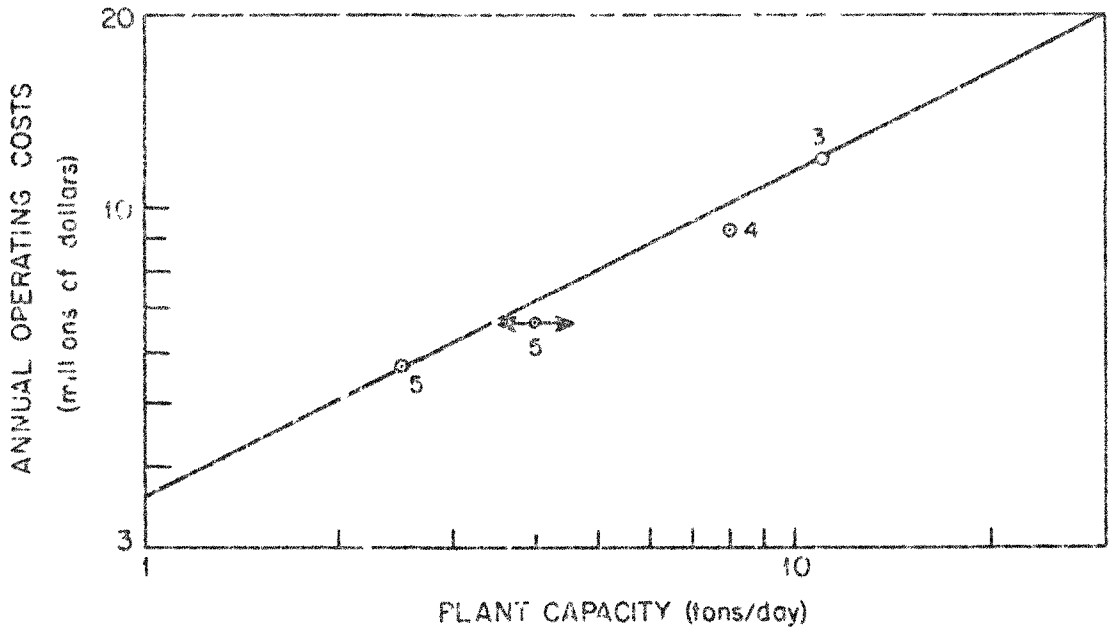
REFERENCES

1. Civilian Power Reactor Program, Part II. TID-8517.
2. J.A. Lane, Nucleonics 18 (4) 71 (1960).
3. S. Aas, Fuel Element Costs, Advanced Course on Fuel Elements for Water Cooled Power Reactors, Aug.-Sept. 1960, Kjeller, Norway.
4. E.L. Zebroski, Proceedings on Reactor Fuel Technology, May 6-7, 1958. St. Petersburg Beach, p. 56.
5. W.H. Zinn, ibid, Introductory Notes
6. J.W. Ullmann, "Throw-away Fuel Cycle", ORNL-2273.
7. R. Rometsch, Transport and Storage of Irradiated Fuel Elements, Advanced Course on Fuel Elements for Water Cooled Reactors, Aug.-Sept. 1960, Kjeller, Norway.
8. K.P. Lindland, Introduction to Aqueous Reprocessing of Uranium, ibid.
9. R.C. Vogel, Chemistry of Fluoride Volatility Processes, ibid.
10. F.L. Culler, General Economics of Chemical Reprocessing for Solvent Extraction Processing, Symposium on the Reprocessing of Irradiated Fuels, Brussels, May 1957, TID-7534.
11. R.C. Vogel, High Decontamination Fuel Cycles, Advanced Course on Fuel Elements for Water Cooled Power Reactors, Aug.-Sept. 1960. Kjeller, Norway.
12. J.H. Schraidt, Low Decontamination Fuel Cycles, ibid.
13. Å. Hultgren, Chemical Decanning and Dissolving of Fuel Elements, ibid.
14. J.L. Schwennesen, Capital and operating cost information on several existing U.S. nuclear fuel processing plants. Symposium on the Reprocessing of Irradiated Fuels, Brussels, May 1957. TID-7534.
15. C.R. Anderson & C.A. Rohrman, Proceedings of the First Geneva Conference on the Peaceful Uses of Atomic Energy, 9, 940 (1955).
16. E. Glückauf, ibid, page 3.
17. Reactor Fuel Processing, 2 (4), 1 (1959).



3. 6 tons/day Natural U Plus 50 kg/day U^{235} (no volatility plant)
5. 25 kg/day U^{235} and 25 kg/day U^{235} plus 1-2 tons/day Natural U
6. 8.3 tons/day Natural U
7. 1 ton/day Natural U
8. 8 tons/day Natural U

Fig. 1—Reprocessing plant investment vs. plant capacity. Basis: 2% enriched uranium; 10-kg capacity for highly enriched assumed equivalent to 1 ton/day of 2% enriched.



3. 6 tons/day Natural U Plus 50 kg/day U^{235} (no volatility plant)
4. 8 tons/day Natural U
5 25 kg/day U^{235} and 25 kg/day U^{235} Plus 1-2 tons/day Natural U

Fig. 2-Direct operating costs vs. plant capacity. Basis: 2% enriched uranium; 10-kg capacity for highly enriched assumed equivalent to 1 ton/day of 2% enriched

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Section VII

FUEL CYCLE COST

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FUEL CYCLE COSTS

by

S. Aas.

1. Introduction.

The title of this lecture is Fuel Cycle Costs. This cost is only part of the total power cost, but has been so limited in order to remain within the scope of this course. Fuel cycle costs constitute for present water cooled power reactors about 30 % of the total power cost. It would therefore be unproper to embark directly upon a treatise on fuel costs without first, at least briefly, also consider the remaining 70 %. In this lecture we will consequently first discuss total nuclear power cost from a more general point of view before the actual presentation of fuel cycle costs is given. This particular discussion is by no means meant to be anything near comprehensive but is merely included in order to place the topic of this lecture in a wider context.

2. Nuclear Power Costs.

Nuclear power costs can be said to be represented by the sum of three items: capital charges, fuel cycle costs, and operation and maintenance (including insurance).

There are a number of factors which affect actual figures for these items. These factors can be of technical, economical and even political nature. As an example can be mentioned that the fixed charges on capital investment is around 15 % in the US and in most European continental countries, while 8% is normal in Great Britain. Further examples are the differences that exist, certainly between nations and may be even between different districts within the same country, in equipments cost, labour rates, efficiency, overhead rates, accessability of low interest, governmental funds etc.

It will be understood that widely different cost figures may result for identical reactors depending upon the local conditions and practices. Published cost figures should therefore be approached with

cautionsness unless the exact method of calculation or a detailed break-down of the total costs is published as well.

It should also be realized that it is only recently that reasonably good cost data have become available for second generation reactors in which experiences from prototypes and general progress of the art have presupposedly been utilized. Cost data for prototypes can still be at fault by a factor of 100 % or even more. Earlier prophesies of nuclear power costs are therefore likely to be wrong and appear to be exclusively on the optimistic side.

Published specific capital investment costs for prototypes (1) are about 1000 dollars/kw for the smaller EBWR, while the larger PWR (second core), Yankee and Dresden have a specific capital investment cost of about 800 dollars/kw, 400 dollars/kw (estimated) and more than 230 dollars/kw respectively. AEC's estimates for 300 Mwe light water moderated plants is 320 dollars/kw. (2) Conventional steam-electric plants of the same capacity were built with an investment cost of about 150 dollars/kw in 1955. We see that capital costs for nuclear power plants are appreciably higher than the cost for conventional power plants.

There are two conclusions we can draw from this. The first one is that in as much as at least 60 % of the power cost stems from capital charges, there is a strong incentive for development work aimed at lowering the capital cost. This is certainly a sweeping statement as it embraces the major part of the development work that is being carried out in all fields with power reactors. Nevertheless, it might be useful to emphasize this as an always present conciousness of this situation is not necessarily a virtue of those engaged in this field. As one single specific example of how capital cost can be cut, is mentioned more extensive use of the less expensive carbon steel instead of stainless steel. The second conclusion is that as it can be argued that the capital costs for a nuclear power plant will always remain higher than the costs for conventional plants, thus the only way nuclear power can be competitive is that fuel cycle cost is correspondingly lower.

Fuel cost in coal and oil fired power stations in the US and England appears to be approximately 3 - 4 mills/kwh. This is then the immediate goal for nuclear fuel costs.

The total cost from conventional plants is 7 - 8 mills/kwh in high cost areas in the US. And this would be the immediate target to meet for overall nuclear power cost.

Published figures (3,4,5) for fuel cycle cost for operating water cooled power reactors, and for reactors under construction show that this cost varies considerably but is alone near to or even above the overall power cost from conventional power plants, or 4 - 9 mills/kwh (as high as 22 mills/kwh for Shippingport). In comparison it can be mentioned that fuel cost from the British Calder Hall reactors is about 2 mills/kwh.

Fig. 1 gives the essentials of a recent assessment by AEC regarding power reactors economics for plants is building starts to-day and for to-morrow's plants (2,5,6).

One should note the low fueling cost envisaged for the heavy water moderated reactor (Canadian). We will return to this in some detail later.

Fig. 2 shows the power cost for the various reactors as function of capital charge rate. We note here how a low rate favourizes gas cooled reactors of the British type and the D_2O natural uranium reactors. The shaded areas represent the gap which is expected to be closed through the development work now being carried out.

3. Fuel Cycle Costs.

3.1 General.

It has previously been pointed out that if specific capital investment for nuclear power reactors remains higher than that for conventional power stations, the only way nuclear energy can become competitive is by having lower fuel costs. It has also been shown that such is not the case as of to-day, despite the fact that the energy contained in ome gram of natural uranium is extremely high compared with the energy in one gram coal. The reason for this is well known, the uranium has to be processed, canned and reprocessed and these operations together with the inventory charge add significantly to the fuel cost (usually expressed per kg fuel).

In the following paragraph the various steps in the fuel cycle will be presented and discussed briefly. In a later paragraph the effect on cost of various fuel element design variables will be reviewed.

3.2. The fuel cycle.

Fig. 3 shows scematically the various steps in a fuel cycle for low enriched uranium dioxide fuel elements. A natural uranium cycle would not have the UF_6 step and dependent upon the specific reactor conditions, the reprocessing of spent fuel may and may not be included.

Since UO_2 is almost universally adopted as fuel for water cooled reactors, we will assume that this is the fuel used.

The costs of the various steps in the fuel cycle as presented in fig. 3, can be summarized as follows:

1. Net fuel materials cost (Burn-up cost).
2. Fuel fabrication cost.
3. Reprocessing cost.
4. Inventory charges (including eventual base charges).
5. Structural elements to be replaced per core.

The methods of evaluation of these factors follow reference 7.

3.2.1. Net fuel materials cost.

This cost is determined by the value of the uranium in fresh fuel including the processing losses minus the value of the uranium in the spent fuel minus the credit given for the plutonium recovered.

If natural uranium is used, the uranium value can be obtained by quotations from commercial or other suppliers of UO_2-material. The cost of such material varies slightly. A fair price would be about 30 - 35 dollars/kg.

Enriched material is normally only obtainable through AEC, i.e. from a US source. It is customnary to use the AEC price list for such material and this list is included in table form as fig. 4. Shipping cost must eventually be added.

The value of spent material uranium fuel is usually nil. The value of recovered uranium in the enriched case is dependent upon burn-up (MWD/ton) and initial enrichment. Again the AEC UF_6 price is normally used for the actual content of U 235 left. (Conversion of UO_2 to UF_6 during the reprocessing cycle is part of the reprocessing cost).

The value of the plutonium formed has been much discussed. AEC pays 12 dollars/gram for this material, which may and may not be recovered in case natural uranium is used. It is, however, debatable whether plutonium has such a high value at higher burn-ups, 10000 MWD/ton or more, because of the appreciable quantities of the non-fissile Pu 240 which is formed.

3.2.2. Fuel fabrication costs.

The fuel fabrication costs are made up of the sum of the following factors:

a. Conversion of UF_6 to UO_2 (for the enriched case) including freight to site of fabrication.
b. Fabrication of UO_2 pellets (fabrication losses are included in the value of the fresh fuel).
c. Fabrication.
d. Shipping of fresh fuel.

Conversion of UF_6 to UO_2 is to-day done by commercial firms. The charges paid is dependent upon quantity and enrichment.

Firm bids from one supplier states 25.20 dollars/kg UO_2 for smaller batches (less than one ton), 1.5 % enriched. This figure falls to around 15 dollars/kg UO_2 for ton-lots. (13.45 dollars/kg for 5 tons). For 3.5 % enrichment the conversion cost is 17.40 dollars/kg for ton lots. Another supplier quotes 35 dollars/kg for smaller lots of 1.5 % enriched UO_2. It is doubtful that the conversion cost will drop substantially below the 13.45 dollars/kg cited above.

Fabrication of UO_2 pellets is a massproduction process and thus amenable to the standardization and automation techniques typical for such processes. Fabrication of UO_2 pellets ought to be a relatively cheap step.

With the equipment and experience available today, it should also be possible to produce pellets within satisfactory dimensional tolerances directly, i.e. without grinding. Grinding may nevertheless be a useful operation if the inner diameter of the canning tubes vary too much, which is often the case.

The unit cost of pelletizing is dependent upon the diameter of the pellet, while the cost per pellet is practically constant. On the basis of the experience of this institute a direct cost per pellet of 0.20 - 0.30 dollars is definitely possible in plants with moderate research and development charges (based on European labour costs). To the mentioned price must be added charges for reprocessing of rejects from the sintering process. A reasonable charge would be in the reange 5 - 10 dollars/kg depending upon lot-size.

With pellets of a diameter of about 1/2" and 3/4" length, a reasonable pelletizing cost becomes: 15 dollars/kg - 30 dollars/kg. In comparison can be mentioned that firm bids from a commercial supplier run around 50 dollars/kg fob New York for a 250 kg lot 1.5 % enriched material. This appears to be excessive.

Fabrication costs include canning materials, fixtures, plugs, assembly, inspection etc. This cost is dependent upon canning material is used (zircaloy, stainless steel), the design of the fuel element and the amount of inspection which is deemed necessary. Actual figures are thus dependent upon reactor design, they may reflect lack of performance experience, e.g. whether thought of difficulties are real ones and whether say ten per cent failures in the reactor can be tolerated or a failure rate of only a hundredth of a per cent is maximum.

Due to this lack of experience and with possible hazards in mind, fuel element designs tend to be conservative, this means increased costs.

For the same reasons mentioned above, inspection costs are very high. This concerns inspection of incoming canning tubes and other raw materials as well as running process control. (Estimated cost: 10 dollars/kg.) It is not the intention to discuss the effect of design variables on fabrication costs at this point as these will be reviewed later. We will therefore limit ourselves to giving a few base prices as they appear in the literature or as quoted by commercial firms.

Regarding canning materials, little confidence can be placed on the figures quoted in the literature as they definitely seem to be future figures. Figures around 40 dollars per kilogram zircaloy-2 tubing are often found, while firm bids from commercial suppliers run from 60 - 80 dollars/kg for ton-batches. Cautionsness is definitely recommended.

High quality stainless steel tubes have been produced for a long time and the prices quoted are fairly reliable. For wall thicknesses around 0.20 - 0.50 mm the tubing prices do not vary with diameter and wall thickness. This means that prices quoted per unit weight should be used with care, while prices per unit length are more convenient. Three dollars/meter is in the high range. Welding cost, assembly cost etc. are difficult items to assess, dependent as they are on design, technique etc. and will not be discussed in detail. It may be more interesting to look at the total fabrication cost. This cost including pelletizing cost and is usually given in dollars per kilogram contained uranium or uranium dioxide.

AEC guarantees Euratom countries 100 dollars/kg for stainless steel canned fuel elements and 140 dollars/kg for zircaloy-2 canned fuel elements. It is very difficult to know to which degree these latter costs are realistic or not with to-day's experience and amounts produced. What is clear, however, is that this cost is excessively high for anything near economic power production. Figures as low as 40 - 60 dollars appear to be desirable in the near future (8,9,10). Whether this level can be reached is dependent upon larger production volumes, more reactor experience, simplification of design, cheaper raw-materials and optimization of operation variables like heatflux, heat rating etc. for the reactor and fuel element in question.

It can be mentioned that the second fuel charge to the Halden reactor, 2 tons 1.5% enriched UO_2 in zircaloy-2 is delivered for around 125 dollars/k_g, not including the UF_6 cost. It is not known to what degree this unit cost is "commercial". These fuel elements have been described in detail in a previous lecture in this course (11). The spiking elements previously described (12), were produced at a cost of about 36 dollars/kg.

3.2.3. Reprocessing costs.

The reprocessing costs are made up by the sum of the following components:

a. Shipping of spent fuel.
b. Recovery of U and Pu nitrate from UO_2.
c. Conversion of U-nitrates to UF_6.
d. Conversion of Pu-nitrate to Pu metal.
e. Recovery of Pu and U scrap.

Reprocessing costs have been discussed in detail in a previous lecture (13) and will not be considered further here. We should note, however, that reprocessing costs per se make up maximum 10% of total power costs.

3.2.4. Inventory charges.

The inventory charges are the interest to be paid on the capital needed for purchase of the first fuel loading, (including insurance and eventual taxes). This interest will have to be paid for the period the first fuel charge remains in the reactor. The actual charges are thus dependent upon burn-up as well as the rate of interest.

Another way of considering the inventory charges, is by capitalizing only half of the fuel that is in the reactor as it can be argued that the fuel earns its replacement value while in the reactor.

Inventory charges can also be considered as fixed charges as they are independent of the plant use and should be included in the capital cost and not in the operating expenses. When comparing nuclear fuel cost with conventional, inventory charges should not be added to the fuel cost if local practice considers expenses on central oil or coal inventory as fixed charges.

The AEC lease-charges are only applicable for U.S. consumers.

3.2.5. Structural parts to be replaced.

This cost is dependent upon reactor design and operation. If the whole core is changed at the same time, new fixtures and fastenings will have to be supplied along with the new core. This may also mean replacement of instruments and control rods. With the reference reactor design described in ref. 7 this cost amounts to 2 dollars/kg fuel or only 0.03 mills/kwh.

3.2.6 Fuel cycle cost and energy cost.

In order to determine the energy cost, the various component cost (dollars/kg fuel) is merely divided by the average burn-up (kwh/kg fuel) times the plant efficiency. The total contribution to the energy cost from the fuel costs is then the sum of the components.

Regarding the relative importance of the various factors, published estimates show that fabrication costs and burn-up costs alone account for about two thirds of the total fuel cycle costs (14,15).

Examples of fuel cycle costs are shown in table form as fig. 5.

It has previously been stated that the fuel cycle costs range from 4 to 22 mills/kwh for to-day's plants, while about 2.7 mills/kwh is average in the U.S. for conventional power plants.

The AEC estimates for plants if building started to-day was 3.4 mills/kwh, as mentioned. It is clear that present day fuel cycle costs will have to be cut by a factor of 2 - 3 at least in order to get down to about 2 mills/kwh, which is necessary taking into consideration the higher capital costs for nuclear power reactors. The Caradians claim that they in their Candu reactor will have a fuel cycle cost of no more than 1.32 mills/kwh. (See fig. 5). This is achieved by using a relatively simple fuel element design with consequent low fabrication costs, by utilizing natural uranium (heavy water reactor) and by no reprocessing of spent fuel. For further details is for example referred to reference 10.

It has been assumed that with improved fabrication techniques and larger through-puts, at least the fabrication cost will come substantially down. Although reductions are likely, it may be doubtful that these reductions are so substantial that they will reduce the power cost appreciably. It should be remembered that only 10 - 15 % of the total power cost stem from fabrication costs, which means that with a highly efficient fuel element factory a reduction in total energy cost of perhaps only 0.3 - 0.4 mills/kwh can be envisaged. (2,16).

Additional reductions are possible when more experience has accumulated so that for example optimization of design variables can be done with greater confidence. The trend-effects of design variations will be discussed next. The presentation will closely follow reference 17.

4. Influence of Fuel Element Design Variations on Power Costs.

The design variables of particular interest are enrichment, burn-up, heat rating, surface heat flux, canning material. Only a few of these are independent variables. It is therefore important to know how they affect each other before an optimum design with regard to minimum fuel costs can be arrived at. In comparing fuel elements where design factors have been varied it is necessary to refer to the same reactor. This is necessary as factors like size, temperature, pressure etc. all will appreciably affect total power costs. Where fuel element design variations might influence reactor lay out for optimum conditions, this will naturally be indicated. The conclusions in following discussion is based upon calculations for the Advanced Pressurized Water Reactor which is described in ref. 18. Let us make a discussion of possible canning materials our starting point.

Stainless steel and zircaloy-2 are the two canning materials which have proven themselves technically feasible in water cooled reactors. Certain aluminium alloys are still no more than promising. The choice between the two materials has been debated for a long time and various companies have decided for one or the other (PWR and Dresden with zircaloy-2; Savannah's reactor and Yankee have stainless steel cladding.) The economic consequences of an improved neutron economy with zircaloy as opposed to the lower fabrication cost with stainless steel are very difficult to evaluate as they must be based on calculated reactivity life time and rather uncertain fabrication costs. A final answer can therefore not be given to-day. However, under specific assumptions regarding these factors, and others, as we will see, we know enough to draw certain conclusions.

A group under the direction of M. Benedict has evaluated the merits of zircaloy and stainless steel in a much cited study (e.g. 19,20). For a watercooled reactor, the specification for which is given and by using the 140 dollars/kg and 100 dollars/kg in fabrication cost for zircaloy and stainless steel previously reported, the conclusion is that zircaloy offers an economic advantage at burn-ups greater than about 12000 MWD/ton. The initial cost is lower for stainless steel and short exposures favour this material. Extended exposure will reduce the fabrication charges and increase the relative contribution of the burn-up cost to the total fuel cycle cost. Thus, long exposures

will tend to favourize zircaloy. The break-even point was, as mentioned, 12000 MWD/ton under the specific circumstances, which assumed among other things, the same specific power (kw/kg fuel) for the two cases. (Part of the results have been plotted and appear as fig. 6.)

Rickert (17) point out, however, that specific power must also be considered.

Increasing the specific power means smaller diameter fuel rods to keep the centre temperature below a specified maximum. Fabrication cost will increase with decreasing diameter. This increase is offset because the inventory charges are reduced. This reduction comes about because increased specific power shortens the core life in years and increase the energy obtained per kilogram per year, the average burn-up and enrichment having been selected. The conslusion is that with all other conditions fixed, there is an optimum specific power for minimum fuel cost. This is illustrated in fig. 7.

Rickert also shows that as the burn-up is increased, so is the optimum specific power. Since the average burn-up is increased by increasing the enrichment and since zircaloy utilizes lower enrichment, zircaloy clad fuel should be designed for lower specific power than stainless steel clad fuel in order to achieve optimum fuel cost.

The immediate conclusion is that a comparison between the two fuel materials at fixed specific power is very likely to be misleading. The optimum specific power for the two cases is shown in fig. 8. We see the optimum specific power for stainless steel is about twice that of zircaloy. In order to obtain cost figures under these new circumstances, we will have to assign fabrication costs for the two materials. If the same costs as before are used (100 dollars/kg and 140 dollars/kg) the fuel costs at constant specific power and optimum specific power as function of average burn-up are as shown in fig. 9. The break-even point is at about 14000 MWD/ton in the former case, in good agreement with (19), while in the latter case stainless steel appear to be the cheapest one as the design burn-up is increased above a certain (low) level.

This conclusion is based upon estimated fabrication costs. One should therefore be cautious in drawing further conclusions, as the break-even cost of zircaloy increases rapidly with increasing fabrication cost for stainless steel under the same optimum conditions. Again we see

that realistic fabrication costs are badly needed.

In this context it is interesting to note that General Electric who made their Dresden reactor fuel elements with zircaloy, is now recommending stainless steel (21). This decision might have its cause in the cracks discovered in the zircaloy used for the Dresden elements or doubts regarding the integrity of zircaloy-2 at high burn-ups (22). The switch is nevertheless worth noticing also in light of Rickert's results.

The higher optimum specific power for stainless steel also means that for a given average burn-up, a core with stainless steel will attain optimum fuel cost at a higher total power out-put. Or if the total power out-put is constant, a core with zircaloy would be larger than one with stainless steel for optimum fuel cost. In either case the capital costs would be lower for the stainless steel case at first approximation. One should realize, however, that the surface heat-flux increases when the specific power is increased. The limiting factor will finally become burn-out. Burn-out is also function of coolant pressure, flowrate and temperature, thus the entire primary circuit becomes affected. The final consequences of this has not been evaluated.

Finally it is added that since stainless steel is a high neutron absorbing material, there is a strong incentive for reducing the stainless steel cladding thickness. In further development work deems this possible, the future appears even brighter for stainless steel, as comparatively little is gained by reducing zircaloy cladding thickness in reactors utilizing enriched material.

If natural uranium is decided upon (Canada), zircaloy is the only technically and economically feasible canning material to-day. In the Canadian case even aluminium has been ruled out at longer exposures for neutron economy reasons. If slightly enriched is material used, aluminium can still only be considered a promising material. The fabrication costs are about equal to those of stainless steel and the neutron absorption considerably lower. The disadvantage is the low mechanical strength at 200 - 300°C. This can at least partly be compensated for by using finned material. This naturally means more canning material in the core. Another disadvantage is the high corrosion rate, which is 0.10 - 0.15 mm/year at 260°C in pressurized water, and maximum

0.45 mm/year in boiling water at the same temperature for the 1 - 2 % Ni alloys. With 11 kw/kg specific power and 15000 MWD/ton average burn-up we have a core life of more than 4 years. This means a canning thickness of about 2.6 mm compared with about 0.7 mm for zircaloy and 0.3 for stainless steel under comparable conditions. This means that the total absorption of neutrons in the reactor, would roughly be in the proportion 1:6:9 for zircaloy, aluminium, and stainless steel respectively. In boiling water reactors aluminium does not offer any economic advantages over stainless steel due to the high corrosion rate with to-day's alloys.

Regarding average burn-up in general, it is well recognized that a high burn-up will reduce the fuel cycle costs. This is due to the fact that an increase in burn-up, or increase in energy produced per ton fuel, reduces the contribution per unit energy of all the costs which is dependent upon the amount of fuel contained (e.g. fabrication costs, reprocessing costs etc.).

Increasing the burn-up will eventually mean higher enrichment and the increase in cost due to this factor will finally off-set the reduction. Another question is whether the long life in the reactor will threaten the integrity of the fuel element. In a few experiments, UO_2 has been irradiated to 50000 MWD/ton. Thus a local maximum burn-up of 25000 MWD/ton appears to be a safe one to use today. In order to increase the average burn-up, flux flattening over the core as well as along the element itself is an important factor, effective in reducing the fuel cycle cost.

Summary.

Summarizing it can be stated that energy from water cooled power reactors is not competitive with energy from conventional oil and coal fired plants. This is due to higher capital and fuel costs, which make up around 60 % and 30 % respectively of the total cost.

As a consequence of the high capital costs, development work aimed at lowering these costs is highly important.

There are reasons to believe that capital costs for nuclear reactors will always remain higher than capital costs for conventional plants. The only way nuclear energy can become competitive is therefore by operating with lower fuel costs. To-day these range from 4 - 22 mills/kwh, while

a figure less than 2 mills/kwh is necessary. Of the fuel costs, fabrication cost and reprocessing cost make up about two thirds. These are industrial processes, and there should excist possibilities for substantial improvement in the future through bettering of techniques and through larger volumes produced.

Further advances must be sought through improvement in design and in optimization of design variables.

With present day fabrication cost figures, stainless steel appear to be the most economic canning material for slightly enriched reactors. Reactors utilizing natural uranium have to-day no choice but zircaloy.

With more experience fuel elements which permit higher specific power, and higher heatfluxes up to higher burn-ups may be developed. This will reduce the fuel cost as well as the capital cost.

LITERATURE.

1. J.A. Lane. Nucleonics 16, (1), pp 46 - 47, (1958).
2. Nucleonics 18, (4), pp 71 - 82, (1960).
3. W.E. Shoupp, R.J. Coe. 2nd Geneva Conference (1958) Paper A/conf/P/1038.
4. Nucleonics 15, (6), pp 72 -75, (1957).
5. Power Cost Normalization Studies, SL 1674 (Jan.1960).
6. Civilian Power Reactor Program, Part II: Economic Potential and Development Program as of 1959. TID. 8517.
7. Survey of Initial Fuel Costs of Large U.S. Nuclear Power Stations. EEI Publication No. 59 - 150 (Dec. 1959.).
8. Nucleonics 18, (1), pp 68 -72, (1960).
9. Boiling Water Reactor Study, TID 8500 (Jan. 1960).
10. J. Howieson. Economics of the Natural Uranium Fuel Cycle. O.E.E.C. Stresa Conference 11 - 14 May 1959, part 3. pp. 23 -35.
11. H. Mogard. Second Fuel Charge for HBWR. Advanced Course on Fuel Elements for Water Cooled Power Reactors. Aug. - Sept. 1960, Kjeller, Norway.
12. S. Aas. Spiked Fuel Elements for HBWR. Advanced Course on Fuel Elements for Water Cooled Power Reactors. Aug. - Sept. 1960, Kjeller, Norway.
13. T.J.Barendregt. Reprocessing Costs. Advanced Course on Fuel Elements for Water Cooled Power Reactors. Aug. - Sept. 1960, Kjeller Norway.
14. E.L. Zebroski. Proceeding of a Meeting on Reactor Fuel Technology, May 6 - 7 1958. St. Petersburg Beach, Florida U.S.A. pp. 56 - 66.
15. W.H. Zinn. ibid. pp. 3 - 7.
16. H. Hardung-Hardung. Possible Fuel Fabrication Cost Reductions us.Kwh/h Price IAEA Symposium on Fuel Element Fabrication with Special Emphasis on Cladding Materials. Vienna 10 - 13 May 1960.

17. R.J. Rickert. Economic Consequences of Design Variations in Water Reactor Fuel Elements. ibid.

18. Advanced Pressurized Water Reactor Study. Phase I. TID 8502

19. M. Benedict. Summary Report: Economic Comparison of Zircaloy and Stainless Steel in Nuclear Power Reactors. Colombia National Corp. Cambridge Mass. U.S.A.

20. N. Beecher, M. Benedict. Which for Minimum Fuel Cost- Zircaloy or Stainless Steel Clad. Nucleonics 17 (7), pp. 64 - 67, 100. (1959)

21. Nucleonics, 18, (6) p. 21 (1960).

22. L.M. Howe, W.T. Thomas. AECL 809. (1959).

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Nuclear-Power Economics For Seven Reactor Types

	PWR	BWR	OMR	SGR	GCR	D_2O	FBR
AEC predicts these nuclear power costs for tomorrow's 300-Mwe plants...							
Total capital cost (10^6)	64.0	64.5 (58.5)††	53.2	67.1	69.5	88.6	65.0
Power costs (mills/kwh)							
Capital charges	4.40	4.31 (3.91)††	3.53	4.47	4.63	5.80	4.43
Fuel cycle**	2.56	2.29 (1.96)	1.83	2.00	2.62	1.21	1.99
Operation and maintenance	0.59	0.61 (0.61)	1.09	0.70	0.49	0.91	0.79
Nuclear insurance	0.25	0.24 (0.23)	0.22	0.25	0.24	0.28	0.25
Total	7.80	7.45 (6.71)	6.67	7.42	7.98	8.20	7.46
...if these development expenditures are made during 1960-1970 (10^6) †							
Research and development	27†	59‡‡	72	84	107	90	143
Gross construction	126‡	136	104	165	121	193	179
Net construction§	65	66	38	99	52	106	101
Total gross	153‡	195	176	249	228	283	322
Total net	92‡	125	110	183	159	196	244
Same size plants built today would have these costs...							
Total capital cost (10^6)	73.4	78.9	66.0	90.9	114	108	76.5
Power costs (mills/kwh)							
Capital charges	5.05	5.26	4.39	5.05	7.60	7.08	5.10
Fuel cycle**	3.38	3.47	5.72	7.68	3.35	4.22	7.10
Operation and maintenance	0.59	0.61	1.09*	0.70	0.61	0.93	0.79
Nuclear insurance	0.26	0.27	0.25	0.29	0.33	0.30	0.26
Total	9.28	9.61	11.45	14.72	11.89	12.50	13.25
...and a reference design based on these typical reactor parameters							
Heat balance							
Total reactor power [Mw(th)]	810	690	260	240	830	860	440
Gross turbine power [Mw(e)]	213	212	79	80	240	214	160
Net plant power [Mw(e)]	200	200	75	75	200	200	150
Net plant efficiency (%)	24.8	29.0	28.5	30.8	24.1	23.2	34.2
Turbine cycle conditions		Pri. Sec.			(High) (Low)		
Throttle temperature (° F)	480	540 460	550	850	650 450	366	780
Throttle pressure (psig)	555	950 460	585	785	500 100	150	850
Steam flow (10^6 lb/hr)	3.03	1.44 1.21	0.936	7.19	1.77 0.785	3.03	1.46
Final feedwater temperature (° F)	340	565 405	360	300	260	251	380
Reactor description: core							
Active diameter (ft)	8.6	10.5	9.5	13.4	50	12	3.0
Active height (ft)	9.0	9.75	9.5	13.5	29	15	2.54
Reactor description: fuel elements							
Burnup (Mwd/metric ton)	13,000	11,000	4,500	11,000	3,000	3,960	15,900
Fuel material	UO_2	UO_2	U(3.5 w/o Mo)	U(10 w/o Mo)	nat. U metal	nat. U metal	U(10 w/o Mo)
Cladding material	ss	Zr-2	Al	ss	magnox	Zr-2	ss
Fuel enrichment (%)	3.34	1.5	1.6	2.85	nat.	nat.	25
Fuel element geometry	rods	rods	cylinder	rods	finned rods	cylinder	rods
Cladding thickness (in.)	0.029	0.030	0.035	—	0.020	0.030	—
Fabrication cost ($/kg U)	110	140	60	110	50	50	480
Reactor description: material inventories							
Fuel (metric tons)	52	66.5	41.4	36.7	274	27.2	0.509
Uranium (metric tons)	41.7	52.3	41	33	274	27.2	0.463
Initial U^{235} (kg)	1390	785	656	940	1970	188	430
Plant-performance data							
Primary coolant outlet temp. (° F)	574	545.3	575	945	710	480	900
Primary coolant inlet temp. (° F)	533	505	490	607	323	414	600
Reactor temperature drop (° F)	41	40.3	85	338	387	66	300
Primary system pressure (psia)	2200	1015	150	atmos.	200	750	115
Primary coolant flow rate (10^6 lb/hr)	53.1	1.43	19.8	8.44	28.3	39.6	16.4
Maximum core heat flux (10^6 Btu/ft²/hr)	39.5	27.7	11.2	30.2	96.0	77.7	116.7
Average core heat flux (10^6 Btu/ft²/hr)	8.618	9.77	2.8	12.1	56.0	33.5	67.5
Max. clad. surface temp. (° F)	636	585	750	1000	730	575	1000
Maximum fuel temperature (° F)	4500	4500	—	1260	1200	880	1050
Core coolant velocity (ft/sec)	14.1	—	15 (max)	11.4 (max)	—	15	31.2
Peak-to-average power ratio	4.55	2.92	4.0	2.5	1.72	2.32	1.44
Core specific power (10^3 kw/metric ton U)	19.5	13.2	6.34	7.27	3030	31.6	947

* Includes organic make-up cost at 13¢/lb.

† Includes research, development and construction funds supplied by private industry in cooperative arrangement with AEC but not private-industry costs outside arrangements with AEC.

§ Includes cost of test and experimental facilities plus cost for prototype and large power plants that is over cost for conventional plants of the same size.

‡ Does not include estimated 125×10^6 for research and development nor 5×10^6 construction cost required for Shippingport.

** Fuel-cycle assumptions: Reprocessing = $15,300/day (8 + mt of U); AEC schedule for UF_6 cost; Shipping cost (irradiated fuel) = $12.45 kg; Conversion of uranyl nitrate solution to UF_6 = $5.60/kg; Conversion of plutonyl nitrate solution to Pu metal = $1.50/gm; Pu buyback (credit) = $12/gm.

†† Costs with superheat (1,500 psi and 1,000° F); similar reductions in costs would result for pressurized water reactor using superheat.

‡‡ Proposed expenditures for BWR include money for superheat development.

Fig. 1.

89

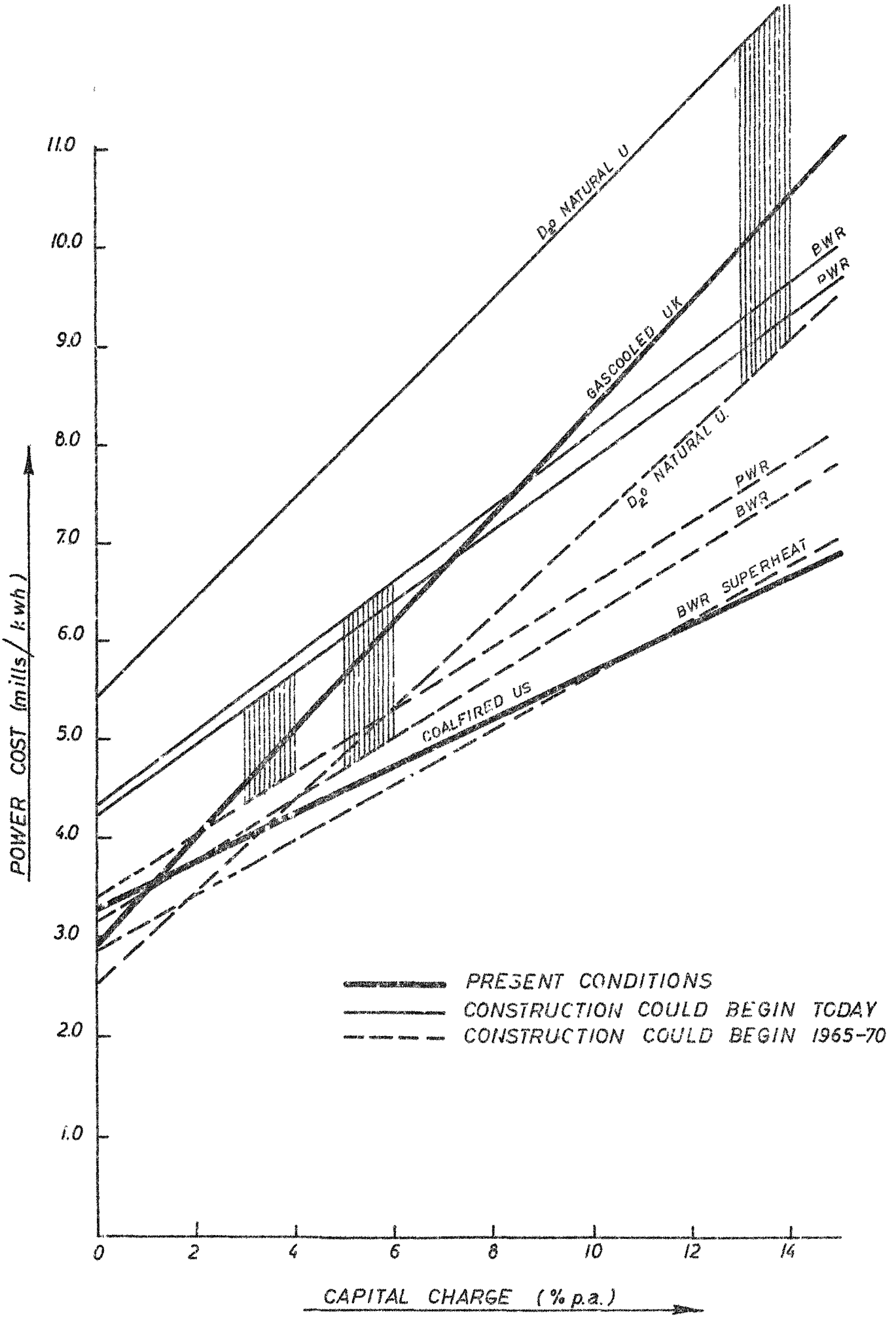


Fig. 2

Fuel Cycle Costs.

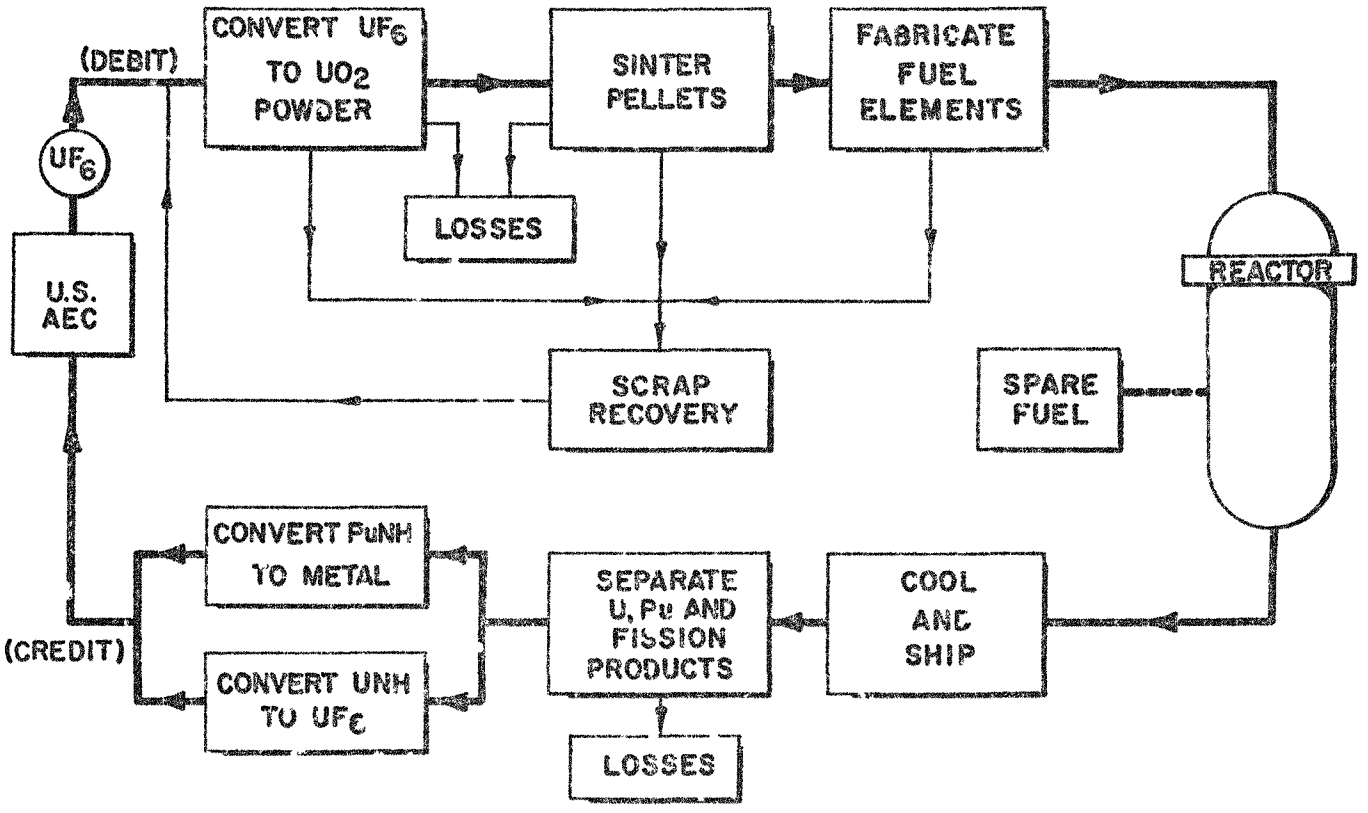


Fig. 5. Fuel cycle for low enrichment uranium dioxide.

Fig. 4.

Enriched Uranium Prices.

Following are base charges for enriched uranium as UF_6, f.o.b. Oak Ridge, varying with enrichment:

Weight fraction U^{235}	Charge ($/kg contained U)	Charge ($/gm U^{235} content)
.0072	40.50	5.62
.0074	42.75	5.78
.0076	45.25	5.95
.0078	47.50	6.09
.0080	50.00	6.25
.0082	52.50	6.40
.0084	55.00	6.55
.0086	57.50	6.69
.0088	60.00	6.82
.0090	62.75	6.97
.0092	65.25	7.09
.0094	67.75	7.21
.0096	70.50	7.34
.0098	73.00	7.45
.010	75.75	7.58
.011	89.00	8.09
.012	103.00	8.58
.013	117.00	9.00
.014	131.25	9.38
.015	145.50	9.70
.020	220.00	11.00
.025	297.00	11.88
.030	375.00	12.52
.035	455.00	13.00
.040	535.50	13.39
.045	616.50	13.70
.050	698.25	13.96
.060	862.50	14.38
.070	1,028.00	14.68
.080	1,195.00	14.94
.090	1,362.00	15.13
.10	1,529.00	15.29
.15	2,374.00	15.83
.20	3,223.00	16.12
.25	4,078.00	16.31
.30	4,931.00	16.44
.35	5.793.00	16.55
.40	6,654.00	16.64
.45	7,515.00	16.70
.50	8,379.00	16.76
.55	9,245.00	16.81
.60	10,111.00	16.85
.65	10,979.00	16.89
.70	11,850.00	16.93
.75	12,721.00	16.96
.80	13,596.00	17.00
.85	14,475.00	17.03
.90	15,361.00	17.07

Fig. 5.

Fuel Cycle Costs in mills/kWh. (ref.10)

	Shipping-port	Indian point	Dresden	Candu
Net cost of U or Th fissioned transformed or lost	2.20	2.65	1.45	0.47
Credit for Pu(₡ 12/gm)	0.70	None	0.89	None
Net fuel material costs	1.50	2.65	0.56	0.47
Fuel fabrication costs	17.82	2.36	2.20	0.71
Spent fuel processing	0.71	0.27	0.53	None
Fuel working capital	1.78	0.46	0.74	0.14
Fuel material lease	0.34	1.16	0.40	None
Replacable core cost	0.59	0.05	0.14	None
Total	22.74	6.95	4.67	1.32
Range of costs mills/kWh		5.2 to 12.5	2.8 to 5.85	0.79 to 1.72
Uncertainty %		+ 80 - 25	+ 25 - 40	+ 30 - 40

Factors Affecting Fuel Costs.(ref. 15).

		stainless steel	zircaloy
1.	Assumed burn-up MWD/ton	11.020	11.020
2.	Specific power kw/kg	9	9
3.	Enrichment %	3	2
4.	U-235 consumed gm/kg	12.3	10.7
5.	Cost of U-235 consumed ₡/kg	189.75	153.50
6.	Pu produced gm/kg	7.2	7.68
7.	Value of Pu produced ₡/kg	86.40	92.16
8.	Net fuel depletion cost ₡/kg	103.35	61.34
9.	Reprocessing ₡/kg	40	40
10.	Cost of Pu ₡/kg	0.86	0.86
11.	Conversion to Pu metal ₡/kg	10.70	11.50
12.	Cost of U-235 ₡/kg	1.86	0.67
13.	Conversion of UF_6 to UO_2 ₡/kg	30.00 25.00	23.00 14.00
14.	Conversion cost U-235 ₡/kg	7.80 1.95	2.50 0.50
15.	Fabrication cost ₡/kg	170 100	200 140
16.	Conversion of salt to UF_6 ₡/kg	5.60	5.60
17.	Use charges before loading ₡/kg	7.80	4.60
18.	Use charges fuel in storage ₡/kg	2.50	1.50
19.	Use charge, fuel in reactor	48.80	24.90
20.	Use charge, irradiated fuel	8.05	2.90
21.	Transportation of new fuel	2.00 1.00	2.00 1.00
	Fuel cost:	3.9-4.8 mills/kWh	3.36-4.1 mills/kWh.

(Capital charges on fabrication cost has been added to plant capital charge (50 ₡/kg)

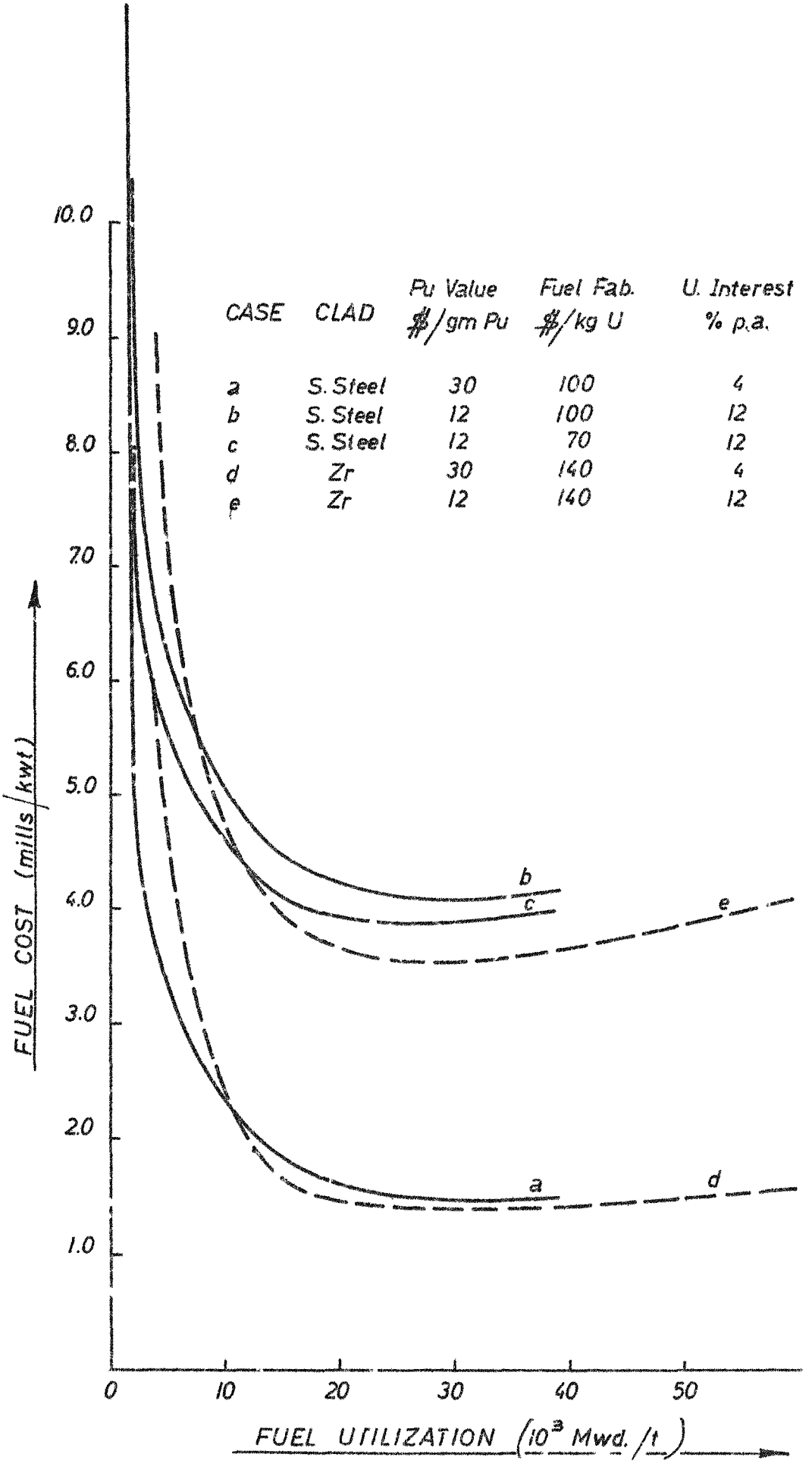


Fig. 6
Fuel Cycle Costs.

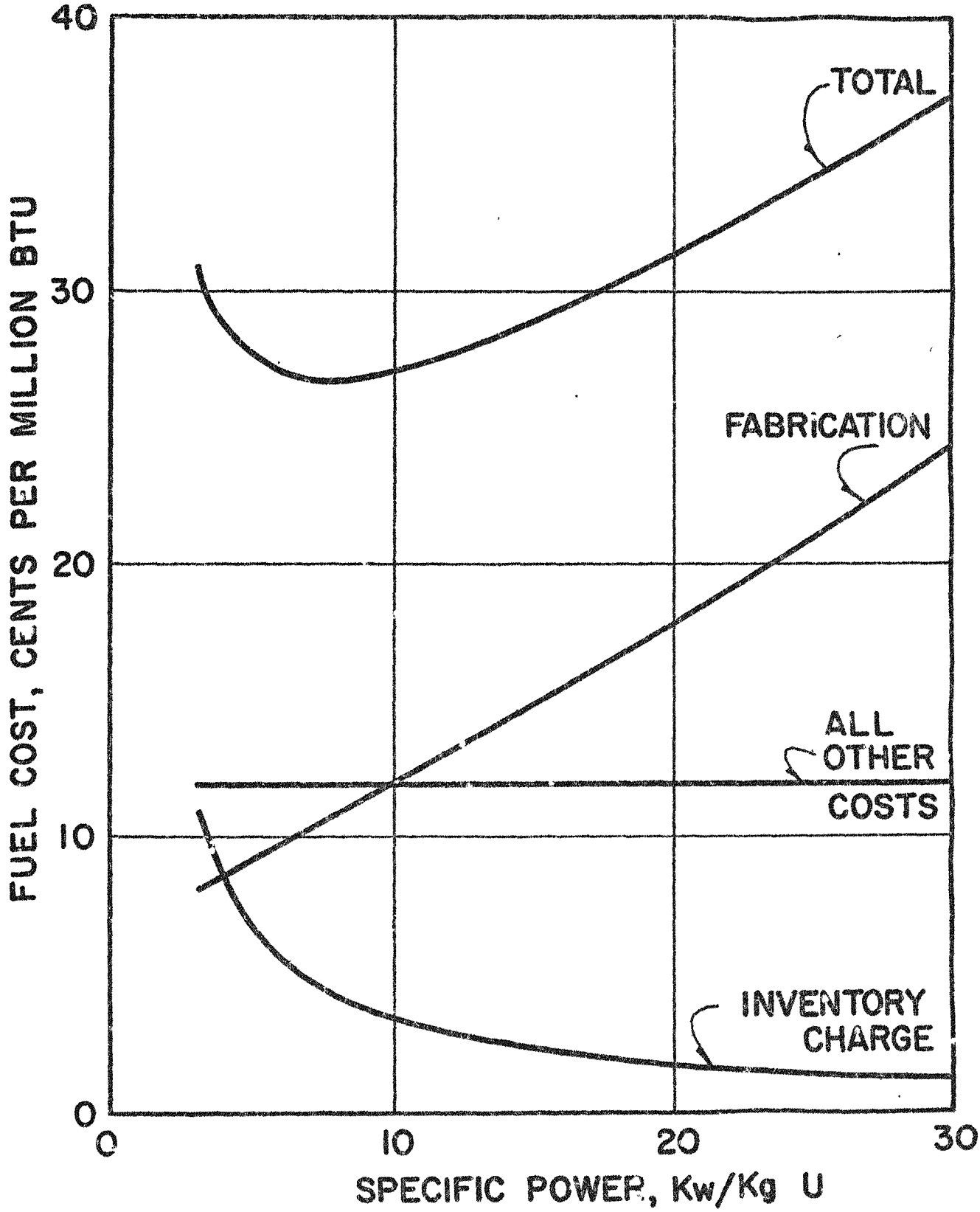


Fig. 7. Fuel cost optimization for zircaloy clad fuel 1.8 weight per cent enrichment for an average burnup of 11,000 megawatt-days per metric ton.

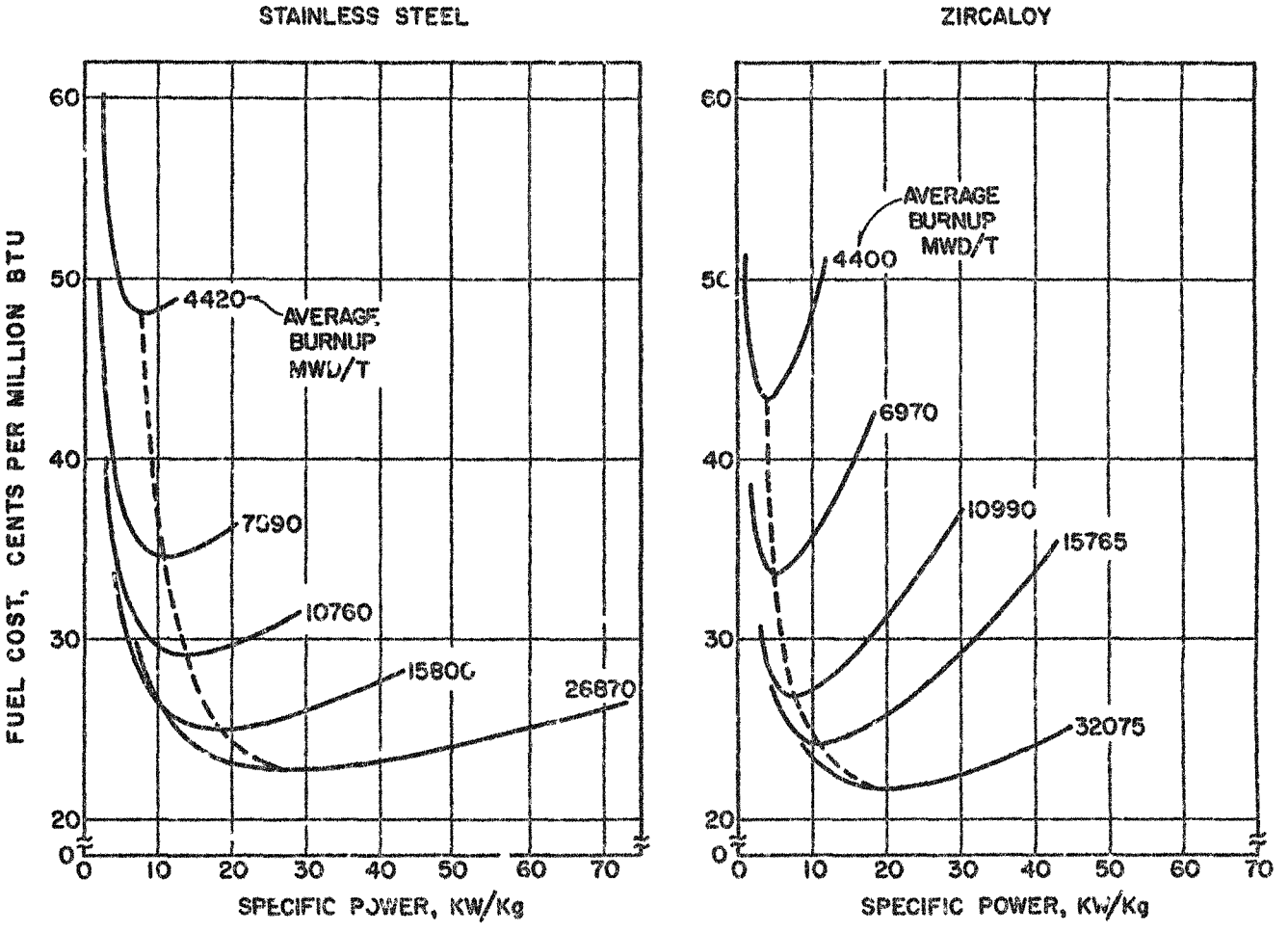
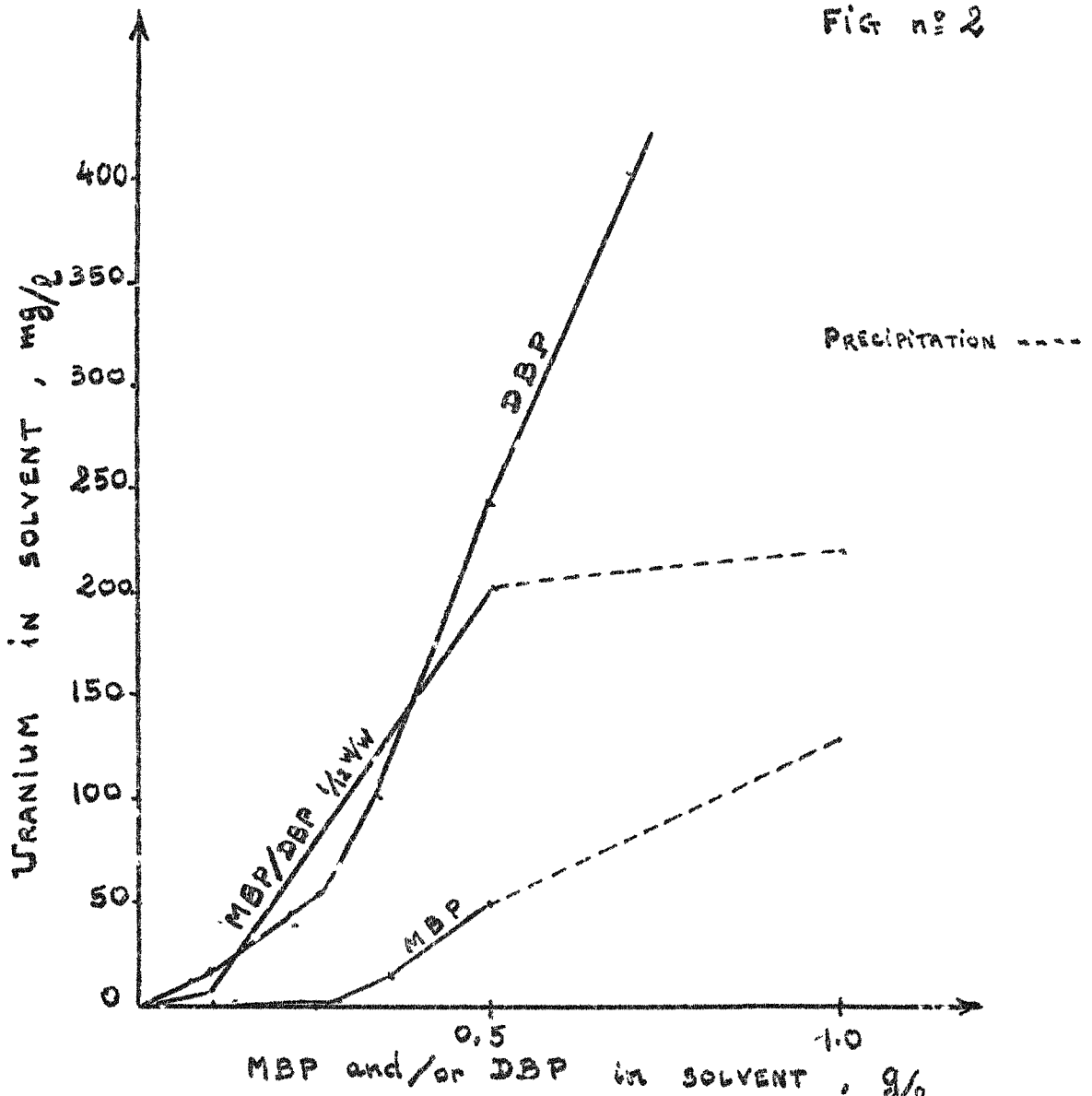


Fig. 8. Fuel cost optimizations for stainless steel and zircaloy clad fuel for several values of average burnup.

RETENTION OF URANIUM

FIG n° 2



SOLVENT : 20% TBP-OK Aqueous Feed 40% U in 3M NO_3H BACKWASHED 3 x 2 vol NO_3H 0,01 N

FROM T. RIGG and W. WILD
Process Chemistry vol 2 p. 328.

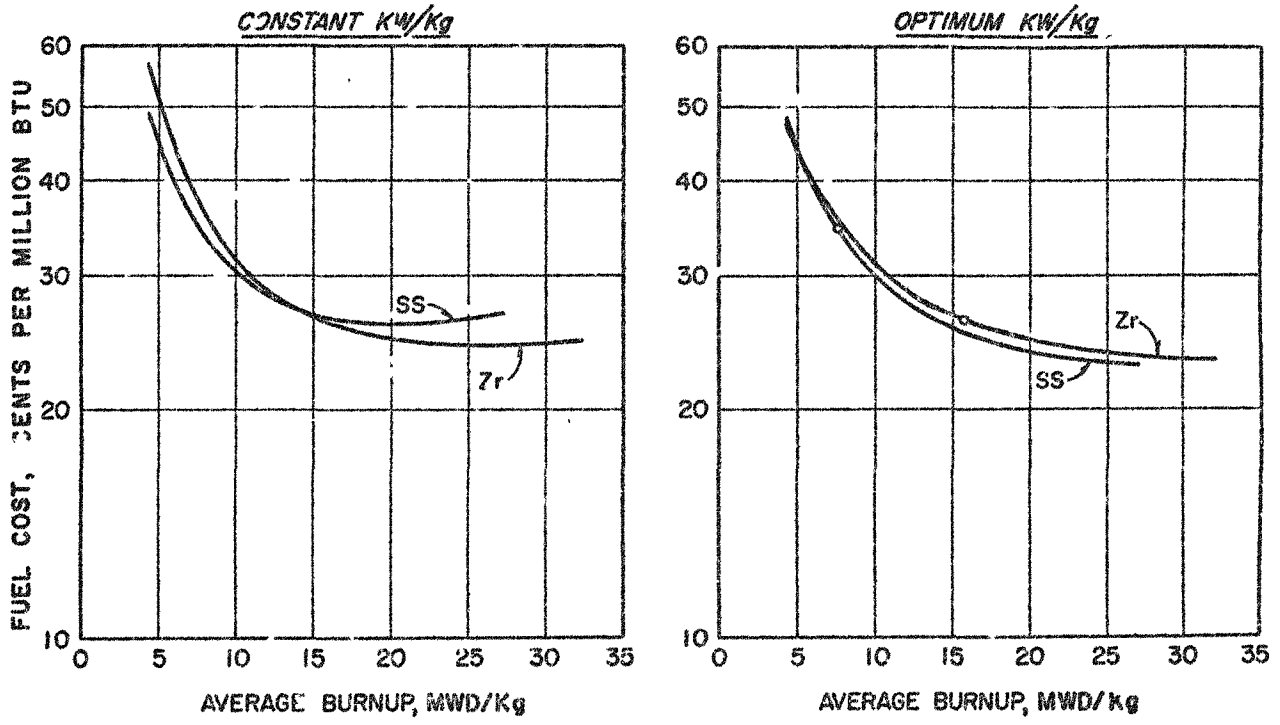


Fig. 9. Comparison of total fuel costs for stainless steel and zircaloy clad fuel as a function of average burn-up on the basis of constant specific power and optimum specific power.