

放射性廃棄物の環境中での物理・化学形態変化に与える 因子に関する研究(II)

(動力炉・核燃料開発事業団 委託研究成果報告書)

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放射性廃棄物の環境中での物理・化学形態変化に与える因子に関する研究（Ⅱ）

埼玉大学

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要 旨

核燃料サイクル施設から放出される放射性廃棄物の環境影響評価は、これまでソースターム、放射性物質の環境での移行等を考慮したモデルにより評価されているが、移行に大きな影響を与えると考えられる物理・化学形態に関する考慮はなされていない。そこで、より現実的な評価を行う観点から、施設から放出される放射性廃棄物の物理・化学形態及び環境中での物理・化学形態変化について調査し、環境影響評価に与える影響について研究を行った。

本報告書は、動力炉・核燃料開発事業団の委託により実施した研究の成果である。

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1. 緒論

再処理施設から放出される放射性廃棄物の環境影響評価は、これまでソースターム、放射性物質の環境中での移行等を考慮したモデルによる評価がなされてきた。今後、より現実的な評価を行なう観点から、施設内の放射性廃棄物の物理・化学形態、また、環境中でのこれら物理・化学形態の変化が、その環境影響評価に与える影響について調査することが必要と考えられる。

使用済燃料の再処理において発生する放射性気体には、 ^3H 、 ^{14}C 、 ^{85}Kr 、 ^{129}I 、 ^{131}I 等の気体状放射性物質が含まれるが、被爆線量当量は ^{129}I が最も大きく、ヨウ素の施設内および環境中での挙動が極めて重要と言える。ヨウ素は軽水炉燃料中ではペレット中にヨウ化物（主に CsI ）として均一に分散されていると考えられている。燃料の溶解工程では酸化ウランの硝酸による溶解の際に生成される亜硝酸によって酸化され、 I_2 としてオフガス中に大部分が放出されるが、一部は溶解液中に残存する。残存ヨウ素は共除染工程以後の工程に取り込まれ、有機ヨウ素の形態で槽類オフガス中へ移行すると考えられている。また、高レベル廃液には ^{242}Cm 、 ^{244}Cm が含まれていることから、これらの核種は自発核分裂によって ^{131}I を発生する。従って、ヨウ素の除去のみならず、放出時のヨウ素の物理・化学形態を知る上でもヨウ素の再処理プロセス内の挙動を的確につかまえておくことが必要である。

その他Tcの再処理工程内での挙動に関心が持たれており、それらについても再処理工程内の挙動を的確につかまえておくことが必要である。

本調査研究ではヨウ素の物理・化学形態を考えたヨウ素捕集対策をどう考えたら良いかについて検討し、又、再処理施設工程内でのTcの挙動について、最近の文献を中心に調査し、その概要をまとめた。

2. ヨウ素吸着剤設計

再処理プロセス内でのヨウ素の化学形態はプロセス条件によって変化する。又、ヨウ素除去をどの工程で行なうかによって除去条件が異なってくる、ヨウ素吸着剤を考える場合、対象とするヨウ素の化学形態をどのように考えるか、又、共存する化学種及びプロセス条件がどうなっているかを配慮する必要がある。ここでは、ヨウ素吸着剤を機能性粒子の一つと考え、現在、研究が進められている機能性粒子の設計-その設計の考え方-を示すと共に、それに基づく若干の研究成果を調査した。

機能性粒子 ～その設計の考え方～

埼玉大工 (正) 松本史朗

はじめに

ハイテクノロジーと呼ばれている先端技術分野では、極微小レベルの著しい発達が見られる。半導体産業に見られるこのような極微小レベルな精緻な技術をマイクロエンジニアリングと呼んでいる。ここでは、マイクロエンジニアリングの観点から機能性粒子の概念と設計の考え方について述べることにする。

機能性粒子の概念

マイクロエンジニアリングにおいては、対象とする物に対する原理的・基本的技術の高度化、微視的計測、制御技術、現象解析、評価技術が基本的に重要と考えられている。最近の科学の動きでは、物質の原子、分子レベルに遡って解明が行われて来っており、同時に、原子、分子レベルでの物質の設計、組立、制御に目が向けられている。中でも、組立は物質の構造設計として新素材開発における重要な技術となる。そこには微視的な現象評価を基にした科学における極微小レベルの精緻な技術への挑戦がスタートしているといえる。その成果として、新たな機能を持った物の出現あるいは今までより飛躍的な質的向上につながるシステムの確立が期待される。

このことがマイクロエンジニアリングの観点からの機能の概念と考えることにする。

マイクロエンジニアリングでは、物それ自身を小さくすることにより、質的に飛躍することを期待していることも含まれる。かつての超微粒子への熱い期待はまさしくそこにあったといえ、今でもその期待は大きい。また、均一さを極めて良くすることによっても質的变化が期待されている。例えば、クロマトグラフ用充填剤が極めて均一性を要求されるゆえんもそこにある。

以上のことより、機能性粒子として物それ自身の機能のみならず、それを利用した応用技術においても飛躍的な質的向上が期待されるものと考えらるべきであろう。

なお、科学技術会議による「物質・材料系科学技術に関する研究開発基本計画について」に対する昭和62年に提出された答申の内容は機能性粒子の研究開発の方向性を示すものとして参考になる。それを以下に示す。

第1に理論的体系的に新物質・材料を開発していくためにはミクロレベルにおける現象の解明を中

心とした研究が重要であり、物質・材料に係わる新現象を探索するとともに諸現象について理論的に解明する。

第2に新たな概念に基づくものを含め、反応環境の制御、構造の制御、生体機能の応用、物質・材料の設計といった手法を駆使することにより、革新的な機能を有する物質・材料の製造をめざした研究開発を推進する。

第3に基礎的研究によって得られた知見等を、積極的に活用する事により、広範な分野各々に必要な高度な機能を有する材料の開発を図るとともに、加工技術や信頼性技術等を確立するなどニーズに対応した材料開発を推進する。

第4にこのような基礎的研究をはじめとした幅広い研究開発を効果的に推進するため、ビーム発生技術、極限環境発生技術、解析・評価技術等、共通・基礎的技術の開発を図る。

機能性粒子設計の考え方

機能性粒子の粒子設計として、図1に示すような枠組みで、粒子の製造技術およびその応用技術との関連から考えることを基本的考え方としている。機能としては、表面機能（原子、分子レベルでの機能をも含む）、粒子構造およびそれらの一様性（サイズを含めた機能の適切な配置）に注目することとしている。表面機能に関しては、既存の機能性物質や現在盛んに研究が行われている分子設計の成果を取り入れることができるであろう。問題は応用技術に照らし合わせた機能発現が十分備わった粒子の製造技術をどのようにして確立していくかである。粒子製造法の確立なしには粒子設計は何ら意味を持たないことになる。ここでは各製造法についての詳細な吟味については省略し、機能性粒子製造法の確立におけるKey Pointは何であるかについて、現在筆者らが考えていることを述べることにする。一つの重要なポイントは製造プロセスにおける「現象あるいは反応場の制御」ということである。例えば、多孔体の細孔構造は反応性、物質移動等を左右する重要な因子であることから、ある種の機能を備えた多孔性粒子を製造する場合、この細孔構造をどう制御するかは重要な意味を持つことになる。また、最近の均一な粒子製造技術においては、現象の制御および反応場の制御によって均一粒子の製造が容易に行われるようになってきている。

以上のように、機能性粒子の設計はその応用技術および粒子製造技術の両面から検討される必要があるが、特に、粒子製造技術は粒子設計において極めて重要な位置づけにあると考えられる。

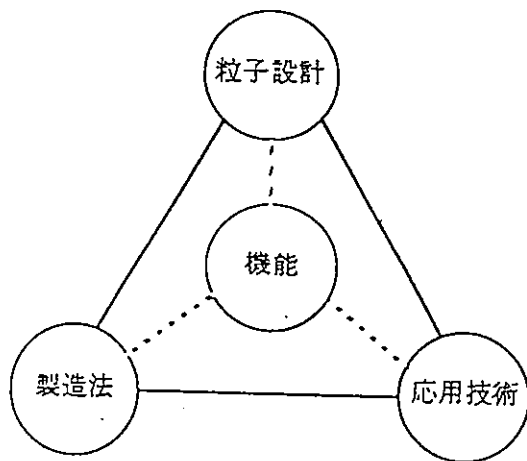


図1 機能性粒子の設計と考え方

均一液滴の生成とその応用

単孔ノズルから流出する液体 jet に振動を付加すると、jet は規則的に分裂し、均一な液滴が生成される。このことは Rayleigh¹⁾、Weber²⁾ の液体 jet の不安定性の解析から説明される。Rayleigh の解析では、最大不安定となる波長 λ と jet 径 d との関係は次式で与えられる。

$$\lambda = 4.508 d \quad (1)$$

このときの最大不安定振動数 f は jet の速度 u を用いて、

$$f = u / (4.508 d) \quad (2)$$

で表される。この振動数で単孔ノズルを流出する jet に機械的振動を与えると図2に示されるように均一な液滴が生成される。また、この方法による均一液滴生成法では、生成される液滴は加えられた振動数に相当する液滴が生成することから、供給流量 Q 、振動数 f を用いて、粒径 d_p は次式で与えられる。

$$d_p = (6Q / \pi f)^{1/3} \quad (3)$$

この方法による均一液滴の生成は、外部的に振動を付加し、液体 jet の分裂過程の現象を制御することによって可能となったことを示している。ノズル

振動法による均一液滴生成法は均一粒子の製造法として極めて有効な方法であり、二重ノズルを利用してカプセル化技術へと展開され^{3), 4)}、さらに均一多孔性粒子の製造法へと発展し⁵⁾、種々の機能性粒子の開発が進められている^{6), 7)}。図3に均一多孔性粒子の写真を示す。数百 μm から数 mm の範囲で均一粒子の製造が可能となっている。また、この粒子に抽出剤を固定化し、固体抽出剤が開発され、ランタノイド等の抽出クロマトグラフへの適用が検討されており、粒子設計が可能になりつつある。



図2 ノズル振動法による均一液滴の生成

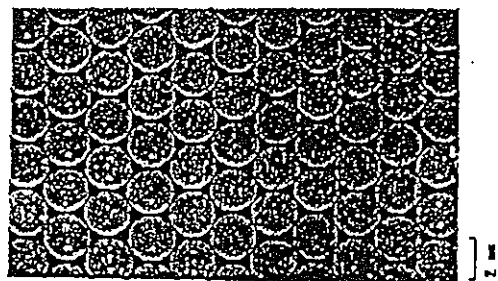


図3 均一多孔性粒子

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疎水性銀添吸着剤粒子の構造とヨウ素の見掛けの反応速度

まず、同一の細孔構造を持つSDB粒子にそれぞれ、26,31,40wt%の銀を添着させた吸着剤粒子によるヨウ素吸着に伴う吸着剤重量の時間変化（図1）よりヨウ素吸着速度は銀添着率が高いほど初期の吸着速度は大きいですが、銀添着量が大きすぎると理論吸着量になかなか達しない。このことより、単に銀添着量を増やせば吸着剤としての性能が良くなるとは言えない。吸着量が評価しやすい添着量を設定することが必要である。

次に、吸着剤担体の細孔容積のヨウ素吸着挙動への影響を検討している。（図2）この結果より細孔容積0.59cc/gと細孔容積の小さな担体を用いると、理論吸着量になかなか達しなく、吸着速度も細孔容積あるいは平均細孔径の大きい担体に比べて小さくなることがわかる。このことは担体の平均細孔径が大きい方がヨウ素の吸着剤内の拡散速度が大きく、ヨウ素と銀との反応に基づく細孔構造の変化の影響を受けにくいことを示している。これらの結果より、吸着剤担体の細孔容積もしくは平均細孔径が大きい方が吸着速度が大きくなり、理論吸着量との整合性もあり、吸着剤の構造設計上好ましいことがわかる。

以上の基礎データをもとに、平均細孔径の異なる担体において、添着銀の未反応率の時間変化を検討した結果が図3である。横軸に反応時間、縦軸に未反応率を表している。平均細孔径の小さな吸着剤では未反応率の減少速度は遅く、平均細孔径が大きくなるにつれて未反応率の減少速度は大きくなる。これらの関係より、時間 t における吸着剤単位重量当たりの吸着量 $C(t)$ は

$$1 - \frac{C(t)}{C_{\infty}} = \exp(-kt)$$

として表され、 k が見掛けの反応速度定数で、 C_{∞} は平衡吸着量である。

図4,5は吸着剤の平均細孔径と見掛けの反応速度定数、銀添着量と見掛けの反応速度定数の関係を示している。銀添着量を増すより吸着剤の平均細孔径を大きくするほうが見掛けの反応速度を大きくすることができることになる。

以上の結果より、吸着ベットでのヨウ素の吸着挙動の解析を行えば、ヨウ素吸着捕集方法の設計が可能となる。

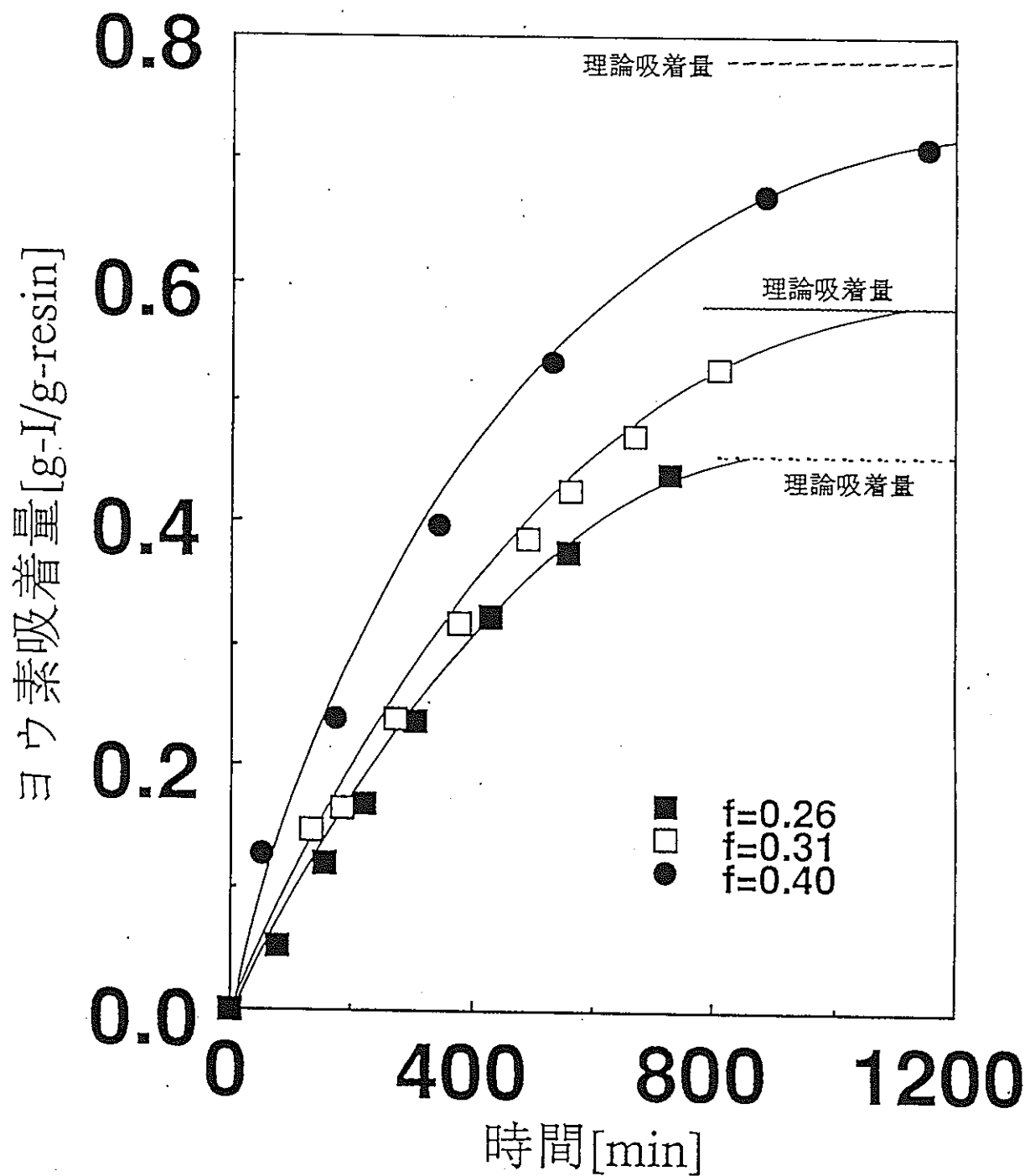


図 1 銀添着量 (f) を変化させた場合のヨウ素吸着量

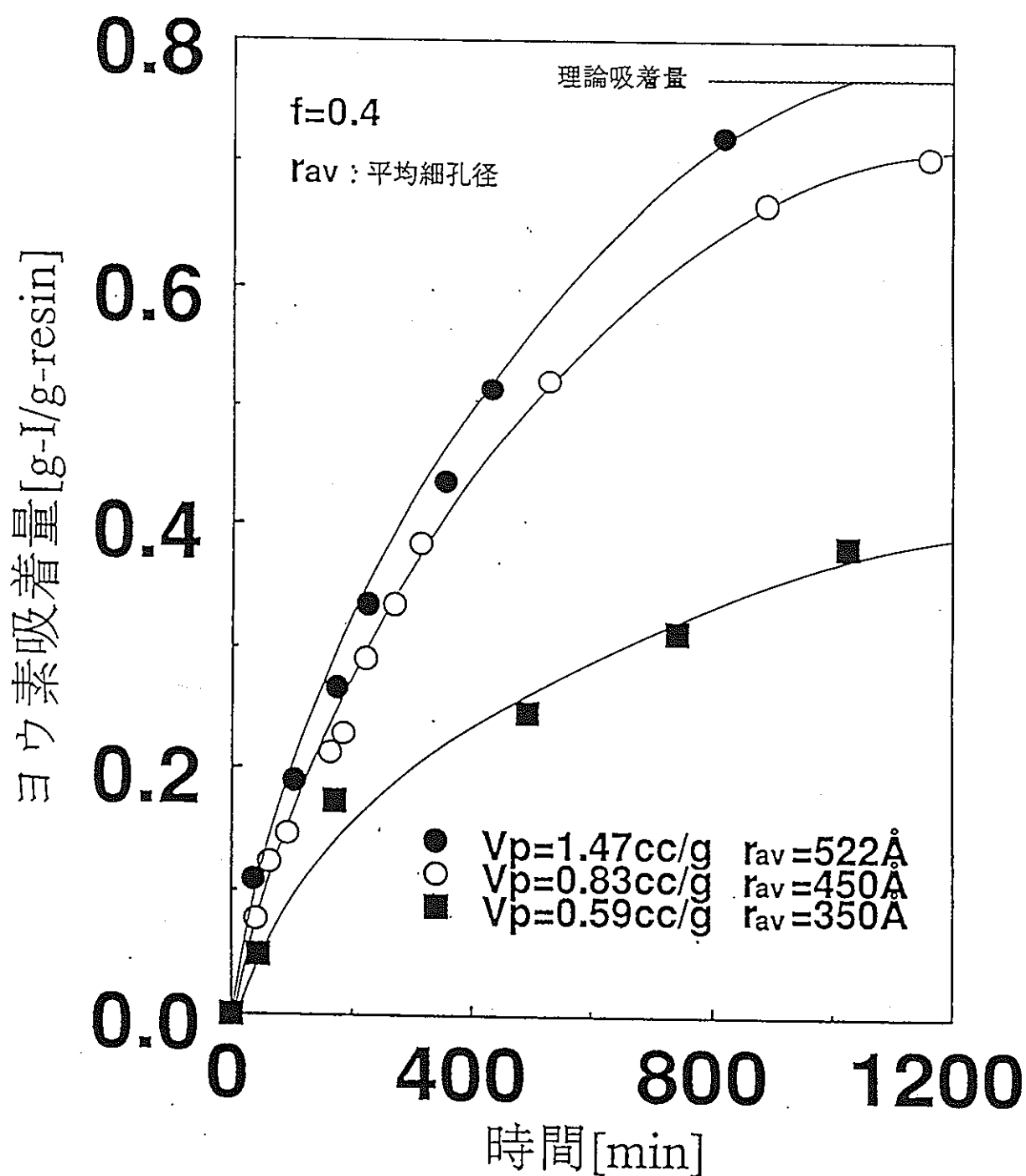


図 2 吸着剤担体の細孔容積 (V_p) のヨウ素吸着挙動への影響

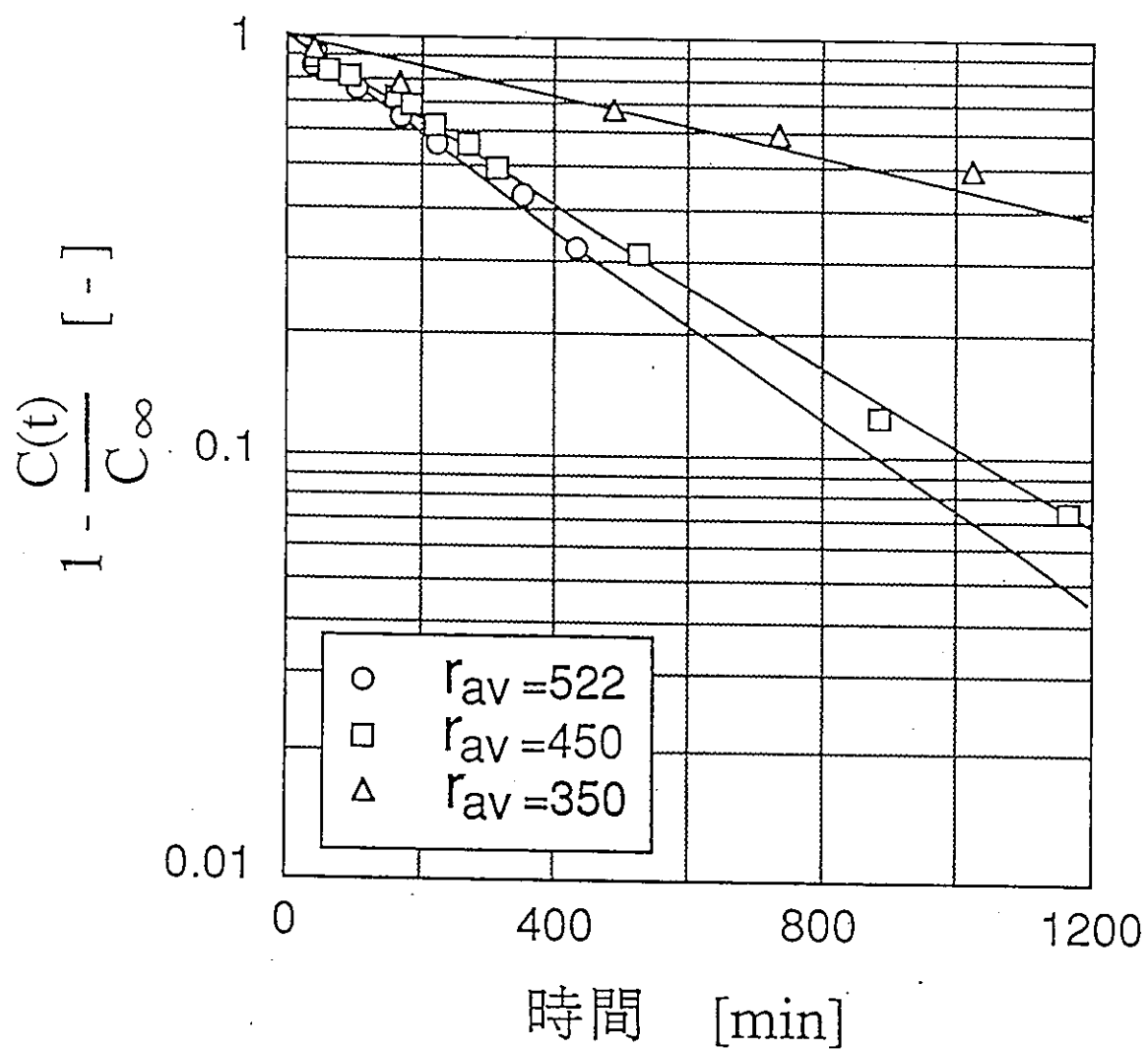


図 3 未反応率の時間変化

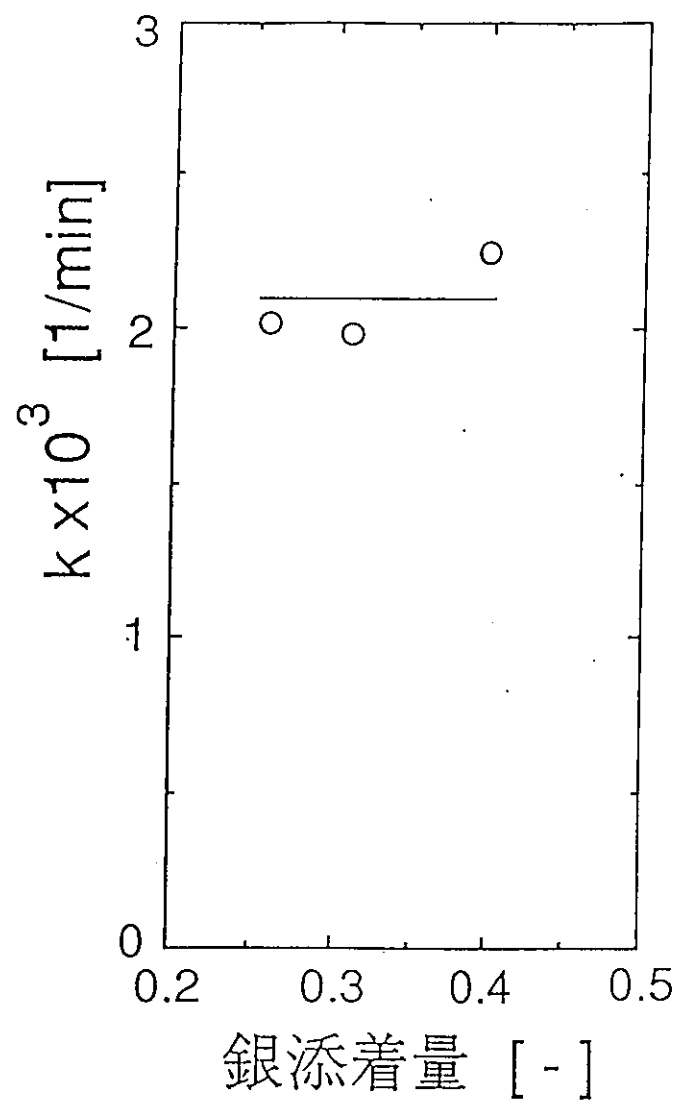
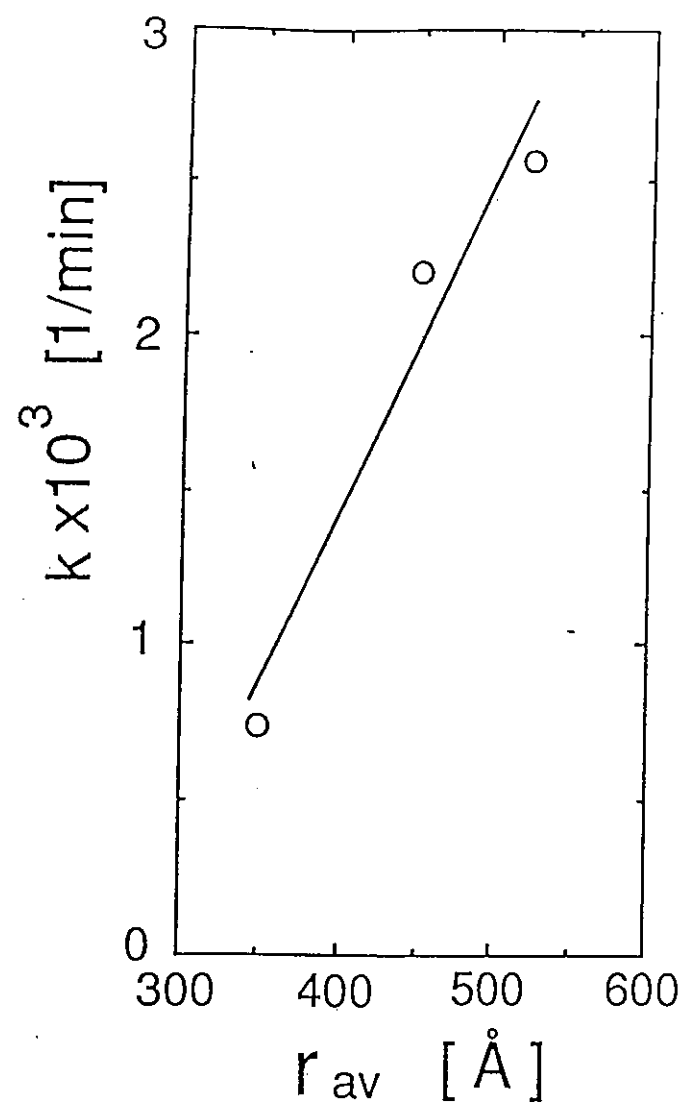


図 4 平均細孔径 vs. 速度定数 図5 銀添着量 vs. 速度定数

3.再処理プロセスにおけるTcの挙動

The development of a flowsheet to separate uranium and plutonium present in irradiated oxide fuel

I.S.Dennis等 (英国、BNFL)

THORPのU/Pu分配カラムの最適運転条件探索の立場から、Tc及びPu分離に関する各種の試験結果を報告している。

分配塔におけるTc及びPuの分離性能は物質移動により支配され、適切な流動条件の付与によりヒドラジンによるTc消費反応やPuのU系への移行は防止できるとしている。

U/Pu separation in an organic continuously operated pulsed column

J.Schon等 (西独、KFK)

Tc-ヒドラジン (N_2H_4) 反応が比較的起こりにくいとされる有機相連続の場合について、MINKA施設を用いて種々の条件下におけるTc、Pu分離挙動について報告を行なっている。

分配塔を有機相連続で運転を行なってもプロセス変動を考慮するとTc- N_2H_4 反応の発生は否定できないので、分配塔以前での分離又は原子価制御が望ましいとしている。

Tc rejection flowsheet

R.Baker等 (英国、UKAEA)

分配塔でのTc- N_2H_4 反応を回避する立場から、分配塔の前段でTcを選択的に洗浄除去する方法について実験的検討を行っている。

5M硝酸による洗浄により、97%のTcを除去し、且つ洗浄廃液中へのU及びPuのリークは0.04%以下に出来たと報告している。

THE DEVELOPMENT OF A FLOWSHEET TO SEPARATE URANIUM AND PLUTONIUM
PRESENT IN IRRADIATED OXIDE FUEL

I S DENNISS and C PHILLIPS. R&DD, BNFL SELLAFIELD

The solvent extraction and redox behaviour of technetium was shown to interfere with the original U/Pu separation flowsheet by causing excessive consumption of the hydrazine used to stabilise the process. Various methods of reducing the consumption of hydrazine were then examined and the adoption of a solvent continuous uranium/plutonium separation column was shown to be the best option. Extensive work was then carried out to develop and prove the new process.

INTRODUCTION

Magnox fuel has been reprocessed at the Sellafield site of British Nuclear Fuels for twenty-five years using the Purex process. Recently a new plant (THORP) to reprocess oxide fuel from Advanced Gas-cooled and Light Water Reactors has been developed using a range of pilot plant facilities.

The major innovations in this new plant are the adoption of pulsed columns to process the plutonium-bearing stream (to aid criticality control) and the use, wherever possible, of chemicals which leave no residues in the waste streams (salt-free reagents).

The flowsheet for the first solvent extraction cycle, where plutonium and uranium are separated first from fission products and then from each other, is shown in Figure 1. The active feed containing U, Pu and fission products is fed to a combined extract and scrub column (HA) where U, Pu and some fission products are extracted into solvent (30% tributyl phosphate in odourless kerosene). The loaded solvent is then passed to a heated scrub column (HS) where further fission products are removed from it.

Plutonium is then converted to the inextractable three valent form in the 1BX column where it transfers into the aqueous phase which is passed into the 1BS column. In the 1BS, residual uranium is extracted from the plutonium stream and recycled to 1BX.

Uranium leaves 1BX in the solvent phase which is sent to the 1BXX "plutonium-polish" mixer settler, any plutonium removed in this contactor is recycled to 1BX.

The most significant use of a salt-free reagent is in the uranium/plutonium separation contactor (1BX) in the first solvent extraction cycle (Figure 1). Here uranous nitrate (U(IV)) is added to reduce Pu(IV) to inextractable Pu(III) together with a stabiliser, hydrazine, to react with any nitrous acid generated and hence prevent oxidation of U(IV) and Pu(III).

Early trials of the flowsheet in miniature scale (1/6000) alpha and fully active pilot plants showed that the fission product technetium behaved in an unexpected manner. In the active feed, technetium is present as Tc(VII) which forms extractable complexes with uranium and the fission product zirconium. The latter causes the complete extraction of Tc in the HA(E) column and it is carried forward to the IBX column where it is reduced to inextractable Tc(IV) which follows the plutonium product. It also takes part in a complex series of redox reactions in the IB system in which it catalyses the destruction of the hydrazine stabiliser by nitrate ions. This behaviour was reported by Garraway at Extraction '84 (1).

The initial design of the process included aqueous continuous (solvent dispersed) LBX and LBS columns operating at 35°C. In the case of LBX this was to maximise the aqueous residence time since the rate of reduction of Pu(IV) to Pu(III) in this phase was believed to control the degree of separation of Pu from U (DF Pu) achievable across the contactor. The combination of the aqueous continuous column with a long aqueous residence time and the technetium hydrazine reaction therefore led to the requirement for a relatively large concentration of hydrazine to stabilise the process which was largely consumed by a parasitic reaction.

The amount of hydrazine required could be safely added to the process but it was judged to be undesirable that such a large proportion of the essential stabiliser should be consumed in the process. It was also thought that the large concentrations of hydrazine which might be present in the process when technetium was absent (eg at start up and shut down) could pose operational problems.

Methods to limit the extent of the technetium hydrazine reaction in the LBX and LBS columns were therefore examined. This paper describes some of the work carried out to investigate the alternatives and develop and demonstrate the chosen method.

METHODS TO LIMIT THE TECHNETIUM-HYDRAZINE REACTION

The alternatives available are to reduce the amount of technetium getting through to the LBX column or to reduce the rate of reaction or time for it to occur within the LBX/LBS system.

Reagents such as thiocyanate, thiourea and ascorbic acid which reduce technetium and render it inextractable were rejected because they can complex or reduce uranium and plutonium and will also form undesirable breakdown products. Zirconium is complexed by fluoride, sulphate and oxalate (1,2) which would prevent the co-extraction of technetium and zirconium. However potential plant corrosion problems and the complexing of plutonium with oxalate led to the rejection of these methods.

Introduction of further solvent extraction steps to backwash technetium prior to the LBX column was also considered but rejected because of the increased mechanical complexity introduced and the production of an extra waste stream.

The next option examined was to reduce the rate of reaction in lBX and lBS by chilling the system to 20°C. This gave about a three-fold reduction in the rate of hydrazine destruction in miniature alpha and fully active pulsed columns. At the same time however, DFs for Pu and Tc across lBX were also reduced by factors of 20-50. The resulting increased amounts of Pu and Tc in the solvent product from the lBX column (lBXSP) were backwashed in the "plutonium polish" mixer settler (lBXX see Figure 1) and so did not adversely affect the rest of the process, but the increase in the amounts of these species reaching the mixer settler and being recycled to the lBX column was judged to be undesirable.

Parallel trials using a uranium-only test rig which simulates the HA cycle at full size and which has been described elsewhere (3,4) also indicated difficulties with the operational control and mass transfer efficiency of the aqueous continuous lBX column at both standard and lower temperatures.

In summary, these trials investigated the mass transfer efficiency and throughput capacity of the HA cycle pulsed columns. Attention was paid to the operational stability of this series of linked pulsed columns, particularly the behaviour of the dispersed phase hold-ups (DPHUs) (3). The most relevant findings are summarised below.

It had long been realised that axial mixing in the lBX aqueous phase was likely to be significant because of the unfavourable phase ratio and hence low aqueous superficial velocity and that limitation of this axial mixing would be necessary to obtain satisfactory plutonium DFs. Trials of the lBX column at 35°C on the full size rig showed that control of the dispersed phase hold-up (DPHU) and interface position was also difficult because of the high solvent to aqueous and hence dispersed to continuous phase ratio.

It was found that the lBX column would operate stably in either high (more than 50%) or low (less than 30%) DPHU regimes, depending on throughput and pulse energy (Figure 2). Operation in, or passage through the transition region between the two regimes, however, led to wide and erratic variations in DPHU which made column control very difficult and also increased the axial mixing. A similar phenomenon has been reported by other workers (5). If the transition region was to be avoided, it would clearly be necessary to operate the plant in the low DPHU regime. This, however, limited the pulse energy that could be applied, and hence the liquor throughput achievable to values that gave a rather limited margin above the plant requirement. Reducing the lBX temperature to 20°C exacerbated these difficulties by lowering the pulse energy and throughput boundaries at which the transition region was entered. These difficulties could be resolved by increasing the diameter of the column, but this would of course increase the aqueous residence time, thus defeating the object of reducing the temperature.

Reducing the temperature of the lBX column was therefore rejected as unsatisfactory, but the measure was adopted for the lBS column where there were no deleterious consequences. This left reducing the time for reaction in lBX as the only remaining option available.

Reducing aqueous phase residence time

The most satisfactory means of reducing aqueous residence time is to operate the 1BX with solvent as the continuous phase. Initial scoping trials on the full size test rig showed that the aqueous DPHU would be approximately 10% giving a low aqueous residence time. There are other advantages too, the superficial velocities of both phases in the column are high, leading to a minimisation of axial mixing and it was found that the column operated very stably indeed with none of the DPHU transitions and interface control difficulties experienced with aqueous continuous operation.

To counterbalance these advantages there was initially uncertainty as to whether acceptable decontamination factors could be achieved for plutonium and technetium across 1BX and whether hydrazine, which is inextractable, could adequately scavenge nitrous acid from the bulk solvent phase and hence stabilise the system.

The results of the initial trials in the 1/6000 scale alpha active test rig were however encouraging; the flowsheet was chemically stable and good decontamination factors were obtained. A full development programme was therefore carried out. This involved experiments in miniature alpha and fully active pulsed columns, intermediate alpha active pulsed columns and a purpose built, full scale uranium active 1BX operated in the solvent continuous mode. The major findings of this programme are summarised below.

DEVELOPMENT OF THE SOLVENT CONTINUOUS 1BX PULSED COLUMN

The consumption of hydrazine and stability of the system was examined in a series of alpha active batch and miniature counter-current trials. These showed that the time-dependent reaction between technetium and hydrazine occurs in both aqueous and solvent continuous columns but there is an additional consumption independent of technetium and time in the latter case. The same reaction occurs in mixer settler U(IV) flowsheets (6) and is caused by the oxidation of U(IV) in solvent catalysed by Pu(IV). The chemical stability of the 1BX was subsequently confirmed in the miniature fully active pilot plant and in the intermediate (1/200) scale alpha active pulsed column facility at Dounreay. In the latter case it was shown that varying the dispersed (ie aqueous) phase hold-up had no effect on the chemical stability of 1BX. This demonstrated that hydrazine can adequately stabilise the solvent continuous process. The flowsheet has now been operated for over 1000 hours and has been shown to be chemically stable with a remarkable tolerance to minor feed variations.

The most detailed information on the mass transfer efficiency of the 1BX column was obtained from the 1/200 scale rig at Dounreay where column profiles and the dispersed phase hold-up (DPHU) and drop sizes could be measured. The pulsed columns in this rig were 5.3m high (packed height) and 25.4mm internal diameter. Each was constructed from 7x0.75m glass sections with full sampling facilities installed between each section. Each section was packed with stainless steel nozzle plates (3.2mm diameter holes, 23% free area) suspended on a tie rod at 5 cm intervals. The rig was operated over a range of flowrates and pulse amplitudes to investigate the effect of changes in throughput and pulse energy on the mass transfer efficiency of 1BX.

Measurement of average DPHU showed a characteristic dependence on the pulse amplitude (Figure 3) over a range of hydrodynamic conditions. Drop size measurements over the same range of conditions showed no significant variation of specific surface area (Table 1) and so a constant value was used in the analysis of mass transfer data.

Under active conditions the rig was operated with two sets of flow rates chosen to duplicate the specific throughputs to be used in the THORP 1BX column. A linear relationship was found between $\log DF_{Pu}$ and DPHU for each set of flow rates and if an allowance is made for residence time the relationship is independent of flow rates. This is illustrated in Figure 4 which assumes that mass transfer is the rate controlling factor in a pseudo first order process; the logarithm of the DF is therefore plotted against the product of the inter-facial area and solvent residence time in the column. The results have been analysed in terms of simplified mass transfer or chemical rate controlled processes (see Appendix 1) and found to give better agreement with the former assumption (Table 2). This is supported by the further finding from the Dounreay rig of a relationship between the DF_{Pu} and acid profile across 1BX (see Figure 5). This figure shows that the acid present in the solvent feed to 1BX is backwashed more rapidly, giving a steeper acid profile, as the DF for Pu across the column increases.

A purpose-built solvent continuous 1BX column which replicates the THORP design has been installed and operated in the full scale uranium active test rig at Sellafield. This column is taller than that used at Dounreay (ca 10 and 5.3 m packed heights respectively) and so, since both are operated at the same specific throughputs, the residence times are longer in the full scale column. Trials using this column have confirmed the hydrodynamic stability and ease of control shown previously.

Preliminary investigations of the DPHU values achievable in the full scale 1BX column have shown similar dependence on pulse amplitude and throughput to that observed in the Dounreay column. Similar average DPHUs can also be obtained (Figure 6) and this, together with the fact that there is a longer residence time in the full scale column indicates that satisfactory DFs will be obtained for Pu and Tc in the THORP column.

This prediction is based on a comparison of the hydrodynamic characteristics of the Dounreay and full scale columns and this is confirmed by the acid profiles measured in the full scale column which are "steeper" than those measured at Dounreay (Figure 7). Acid is backwashed more efficiently in the full scale column and so it should also backwash plutonium and technetium at least as efficiently as the Dounreay 1BX column.

CONCLUSIONS

This work has demonstrated the value of carrying out flowsheet development work in parallel in small and full scale facilities to test the chemical and engineering design of the process. It has also shown the importance of fully active trials to demonstrate unexpected effects caused by the mix of components in irradiated fuel.

The mechanisms and rates of reactions involving the hydrazine stabiliser in the uranium-plutonium separation contactor have been fully investigated as described in reference (1) and this has allowed the hydrazine feed requirement for the reprocessing plant to be established.

Study of the behaviour of plutonium in relation to the hydrodynamic condition of the uranium-plutonium separation column has indicated strongly that separation performance is governed by plutonium mass transfer. Comparison of the results from the 1/200 scale alpha active and full scale uranium active pulsed columns has demonstrated that the THORP 1BX column will achieve the degree of separation of uranium and plutonium specified in the flowsheet.

ACKNOWLEDGEMENTS

The contributions made to this work by Dr J Garraway, Mr B N Prest and the members of the Solvent Extraction Group, R&DD, BNFL Sellafield and Dr P J Thompson, Mrs K Cartwright, Mr S Castling and the experimental and analytical staff of UKAEA Dounreay are gratefully acknowledged.

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TABLE 1

Measurement of representative
1BX drop-size photographs

| DPHU (%) | DF Pu | Total drop area (mm ²) | | | Total drop volume (mm ³) | | | Specific surface area (mm ⁻¹) | | |
|-------------|-------|---------------------------------------|--------|--------|---|--------|--------|--|--------|--------|
| | | Top | Middle | Bottom | Top | Middle | Bottom | Top | Middle | Bottom |
| 6.9 | 54 | 675 | 1569 | 1902 | 217 | 563 | 662 | 3.11 | 2.79 | 2.87 |
| 9.0 | 290 | 1397 | 1387 | 1433 | 483 | 372 | 416 | 2.89 | 3.73 | 3.45 |
| 11 | 1062 | 1089 | 1852 | 1911 | 318 | 632 | 580 | 3.42 | 2.93 | 3.29 |

Average of 11 sets 3.21 3.27 3.39

TABLE 2 Apparent first order rate constants calculated
assuming mass transfer and chemical control

| | Mass transfer | Chemical |
|--------------------|---|---|
| Dounreay S cont | $5 \times 10^{-3} \text{ cm s}^{-1}$ | $2.6 \times 10^{-2} \text{ s}^{-1} (35^{\circ}\text{C})$ |
| Sellafield S cont | $1.9 \times 10^{-3} \text{ cm s}^{-1}$ | $4 \times 10^{-2} \text{ s}^{-1} (35^{\circ}\text{C})$ |
| Sellafield Aq cont | $1.2 \times 10^{-3} \text{ cm s}^{-1}$ | $2 \times 10^{-3} \text{ s}^{-1} (35^{\circ}\text{C})$ |
| Literature | $5 \times 10^{-4} - 5 \times 10^{-3} \text{ cm s}^{-1}$ | $0.12 \times 10^{-2} \text{ s}^{-1} (25^{\circ}\text{C})$ |

APPENDIX 1

Kinetic Analysis of Mass Transfer Assuming
Simple Pseudo First Order Equation

$$\ln DF = kT$$

1 Chemical Reduction Control

k = reaction rate constant

T = aqueous residence time = $\text{DPHU}/\text{aqueous flow}$

$$\therefore \ln DF = \frac{k \cdot \text{DPHU}}{\text{aqueous flow}}$$

2 Mass Transfer Control

$$\ln DF = k^1 \frac{A T_s}{V_s}$$

k^1 = mass transfer rate constant

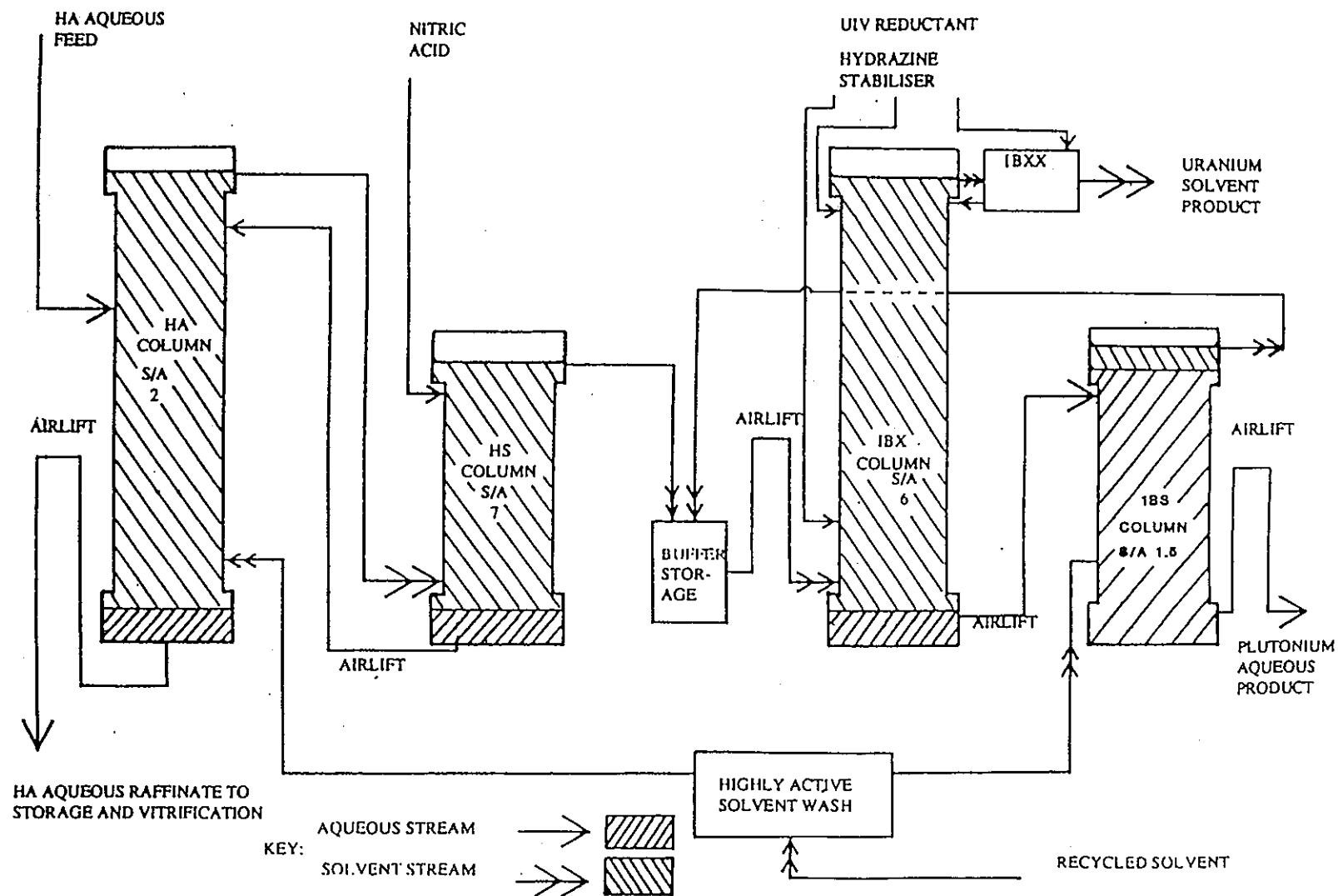
A = interfacial area = $\text{DPHU} \times S$ (specific surface area)

V_s = volume of solvent

T_s = solvent residence time = $V_s/\text{solvent flow}$

$$\begin{aligned} \therefore \ln DF &= \frac{k^1 \cdot \text{DPHU} \times S}{V_s} \times \frac{V_s}{\text{solvent flow}} \\ &= k^1 \frac{\text{DPHU} \times S}{\text{solvent flow}} \end{aligned}$$

FIG 1 THORP HA CYCLE AND PULSED COLUMN TEST RIG



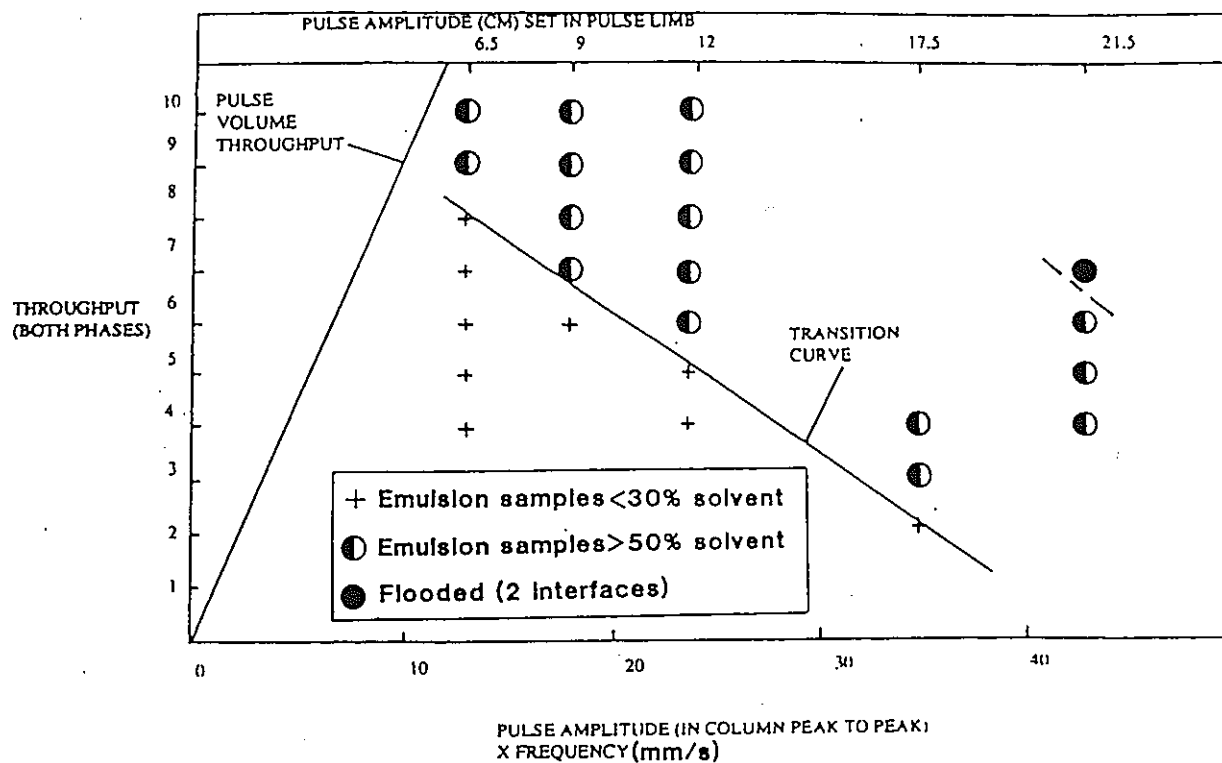


FIG 2 TYPICAL IBX COLUMN AQUEOUS CONTINUOUS FLOODING DIAGRAM

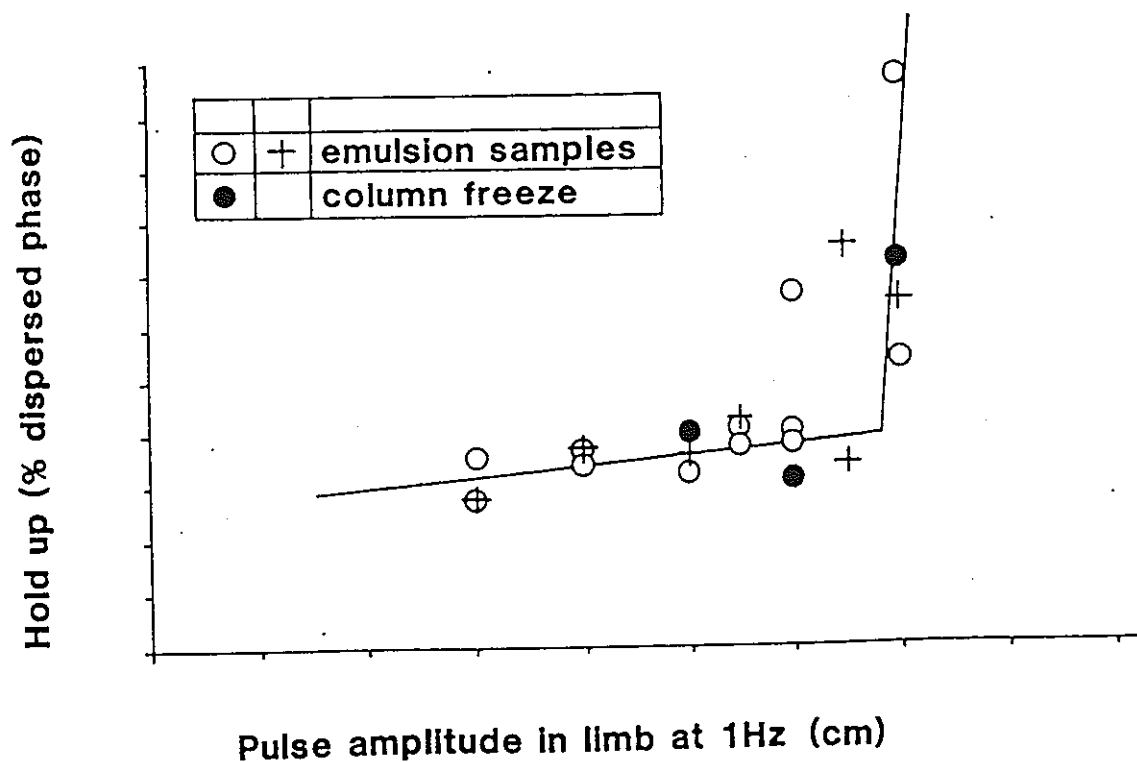


FIG 3 Dounreay solvent continuous 1BX column hydrodynamics in uranic operation 35°C, 1 Hz operation, specific throughput 34 m/hr

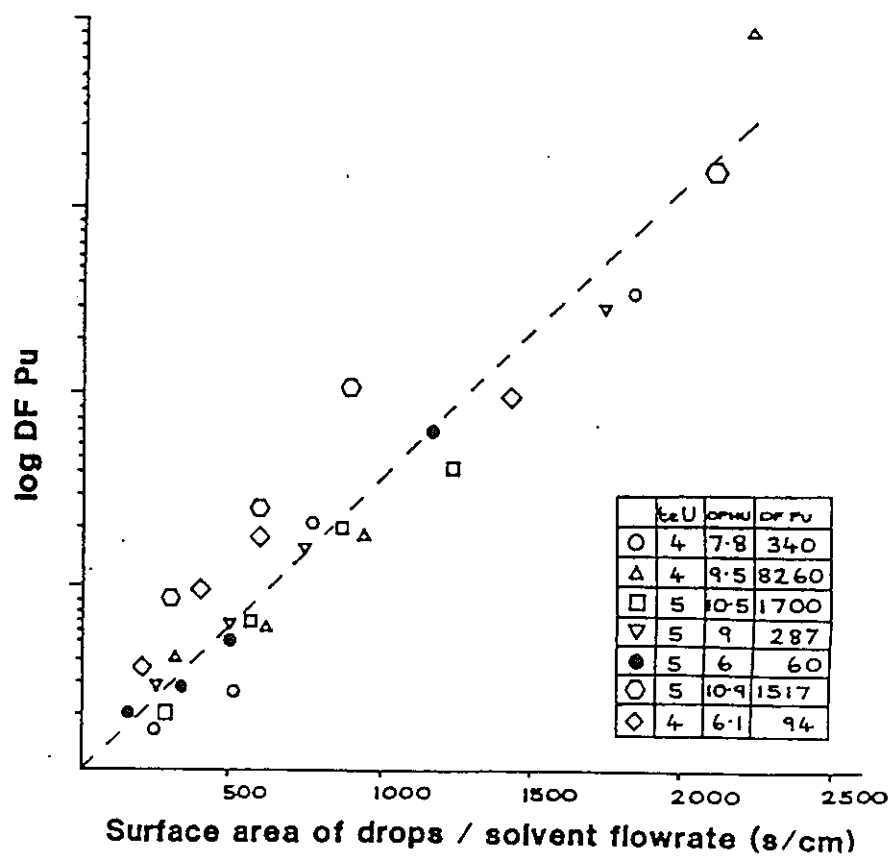


FIG 4 Dounreay solvent continuous 1BX column mass transfer performance

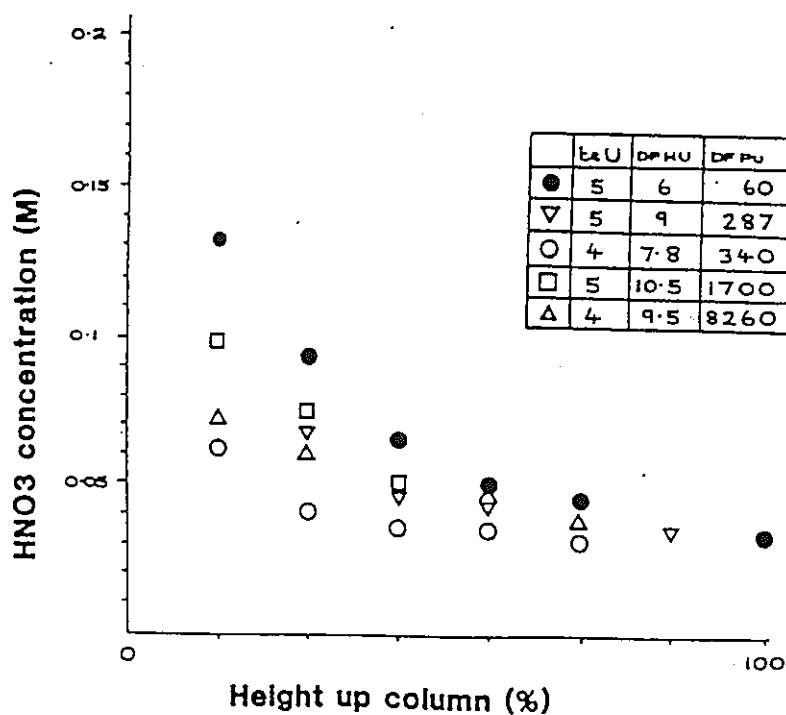


FIG 5 Solvent acid profiles in the solvent continuous Dounreay 1BX column

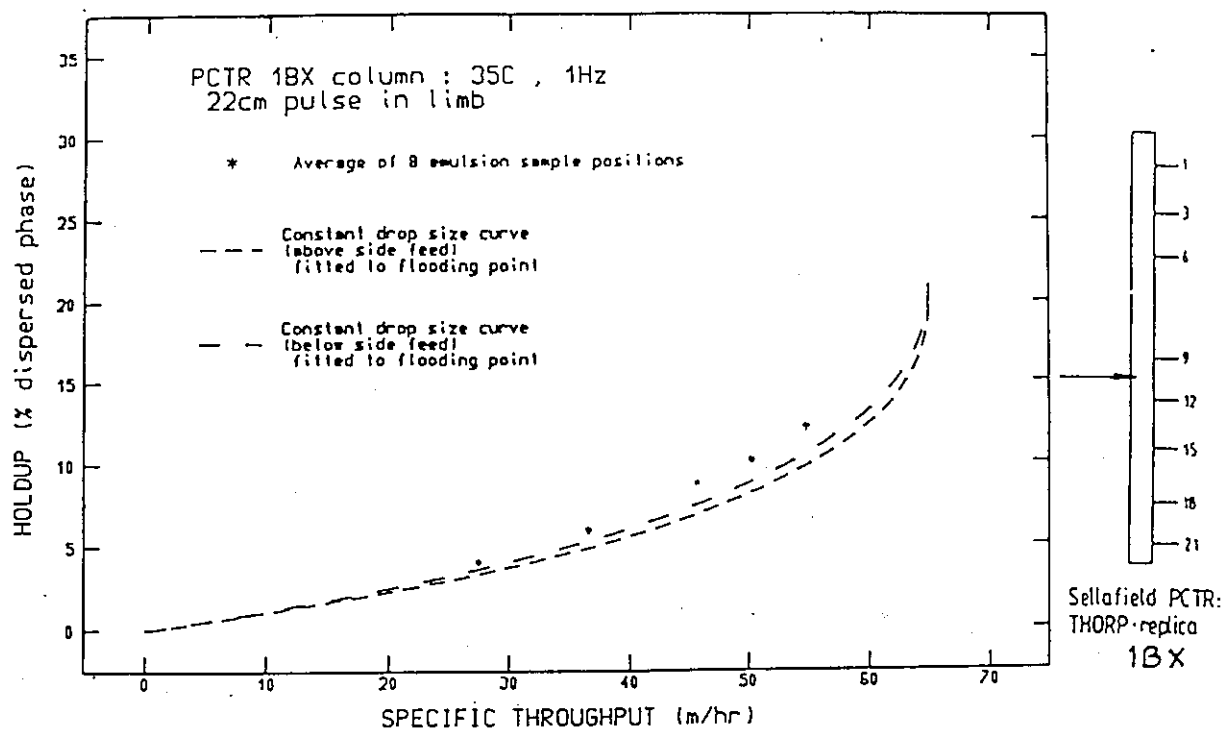


FIG 6 THORP replica solvent-continuous 1BX
Hydrodynamics in uranic operation

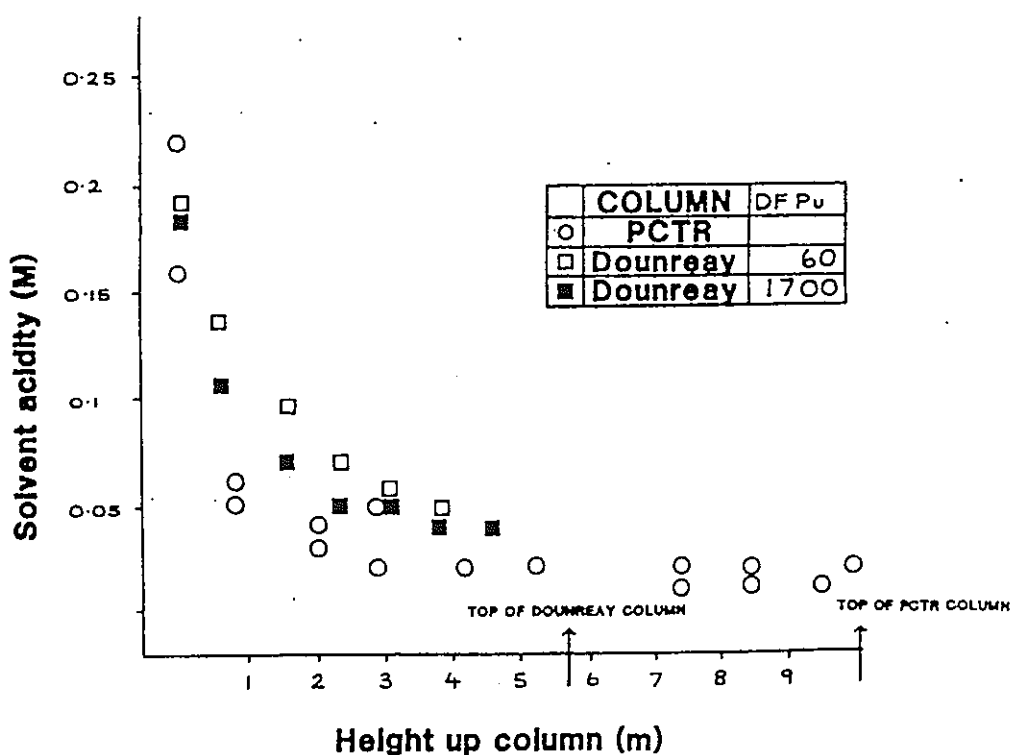


FIG 7 Solvent acidity profiles in the Dounreay and Full Scale
1BX columns

U/Pu SEPARATION IN AN ORGANIC CONTINUOUSLY OPERATED PULSED COLUMN

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In the MINKA pulsed column system of the Hot Chemistry Institute U-Pu separation was studied in an organic continuously operated BX column. It is reported here about experience gathered in operation of this separation system, about the influence of technetium on the U-Pu separation efficiency, and about the extration behavior of the elements Pu, U and Tc under these conditions of separation.

INTRODUCTION

Within the framework of flowsheet studies on the PUREX process U-Pu separation in a continuously operated organic BX partitioning column was investigated in the MINKA miniature pulsed column facility, installed at the Hot Chemistry Institute of the Karlsruhe Nuclear Research Center, as a potential alternative (Philipps (1) to electrochemical U-Pu separation (Petrich (2), (3), Schmieder et al (4), Baumgärtner and Schmieder (5).

It is reported here about experience gathered with the organic continuous partitioning system, with external U IV feed and about the influence exerted by technetium on the separation efficiency. Moreover, hydrazine destruction with technetium as catalyzer is discussed. The influence of technetium on Pu reduction was studied and by the example of the concentration profiles plotted of the organic and aqueous phases of the BX separation column the extraction behavior of U, Pu and Tc is indicated.

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EXPERIMENTALInterconnected Columns.

U-Pu separation was studied under the conditions prevailing in the first extraction cycle of the PUREX process. In MINKA four pulsed columns were interconnected for this purpose to form a closed extraction cycle. These interconnected columns are represented in Fig. 1 and the details of the columns are listed in Table 1.

In Fig. 1 P11, P15, etc. denote the metering pumps for the aqueous and organic process solutions, respectively, and B16, B36, etc. denote the transfer vessels. Mass flowmeters (MM) or volume flowmeters (VM) and balances, respectively, are used for flow measurements.

The MINKA pulsed columns have an extraction length of 3.5 m. At 0.5 m spacing each they are equipped with sample collectors for the two phases and with thermocouples.

Moreover, additional process solutions can be fed into the columns at these positions. The feed points are marked in Fig. 1 by the numbers in the columns, e.g. for K_1 feed into the column at levels 1, 7, 8, etc.

The A and BX columns are operated as organic columns in the continuous mode whereas the BS and C columns are operated as aqueous columns in a continuous mode. A detailed description of the extraction cycle with the related service units is given in (Schön et al (6), (7), (17)).

Flowsheet.

The composition of the organic feed solution of the BX column (Fig. 1: BXF) and the operating parameters of the BX separation column have been adapted to the usual design of the PUREX process for LWR fuel; see Table 2.

In order to be able to study the influence of technetium on U-Pu separation under unfavorable process conditions preseparation of technetium in the extraction and scrubbing parts of the A column was dispensed with. Therefore, technetium was continuously metered into the organic product of the A column during the experiment (Fig. 1: HAP) as an aqueous Tc VII stock solution. This resulted in a Tc concentration of 60 - 70 mg Tc/l in BXF. On the basis of earlier results on Pu accumulation (6), (7) and on U-Pu separation (Schmieder et al. (8)) the feed point of the BXX-U IV solution was fixed at a level 1 m above the BXF inlet (Fig. 1: BX column, level 3).

The experiments were performed in four steps. The individual steps differ by the routing of the organic scrubbing stream of the BS column (Fig. 1, BSU, either return into the BXF stream or into the C column) and by the interconnection of the BX and BS columns. The respective variants of the flowsheet and the related experimental periods have been compiled in Table 3.

RESULTS AND DISCUSSIONBX Separation Efficiency.

The separation efficiency of the organic continuously operated BX column is evaluated by the decontamination factor (DF) (9).

In Fig. 2 the development versus time of DF has been plotted together with the plutonium content in the organic discharge of the BX column (BXU).

A surprising finding is the clear drop in plutonium concentration in the BXU stream to values of about 0.2 - 0.5 mg Pu/l in the course of transition from single column operation (part 1 of the experiment) to BX-BS interconnected column operation (part 2 of the experiment beginning in the 34th hour).

In the third part of the experiment technetium was metered in (beginning in the 64th hour). The presence of technetium in the partitioning column was visible from considerable gas evolution as early as two hours after the onset of dosage which continued until the end of the experiment. However, the U-Pu separation efficiency was adversely influenced only at the end of 12 hours after the onset of technetium feed by a marked rise in Pu concentration in the BXU stream. As the experiment proceeded, the plutonium content in BXU showed the tendency to fall and disconnection of the BS column (part 4 of the experiment, 104th - 113th hour) had no influence on this tendency. Approximately starting in the 96th hour plutonium concentrations established in BXU which varied between 0.7 and 1.4 mg/l corresponding to a DF of 900 to 400. Hence, these values are clearly above the Pu contents of BXU which were analyzed in the absence of technetium (parts 1 + 2 of the experiment, up to the 64th hour).

Degradation of Hydrazine.

With the onset of technetium feed the nitric acid concentration in the aqueous phases of the BX and BS columns decreases due to oxidation of hydrazine with nitric acid as the catalyzer (Garraway and Wilson (10), Akopov et al (11), Boukis (12), Wilson and Garraway (13), Garraway (14), Zelverte (15). The development versus time of the hydrazine concentration in the BXP and BSP solutions has been represented in Fig. 3 for this MINKA experiment.

In the absence of technetium both solutions have almost the same hydrazine concentrations (Fig. 3, 0-64th hour).

By contrast, the values differ clearly in the presence of technetium (beginning in the 64th hour). After only 8 min. residence time of the aqueous phase in the BX column approximately 50% of the hydrazine feed has degraded. (Fig. 3: symbol: square). The subsequent residence time of about one hour duration in the bottom decanter of the BX column causes the hydrazine content in the aqueous phase to decrease to 0.06 to 0.08 M/l N_2H_4 (Fig. 3: symbol: circle). In the BS column con-

nected in series the residence time of the aqueous phase is again about 5 hours which leads to a further degradation of hydrazine down to values of $\leq 10^{-2}$ M/l (Fig. 3: symbol: cross). The low hydrazine concentration in the aqueous product solution of the BS column is still sufficient to stabilize the reduced Pu (17).

After the BS column has been disconnected in the 4th part of the experiment (104th - 113th hour) the hydrazine concentration in the aqueous phase of this column is further reduced. Approximately 8 hours after disconnection the hydrazine content in the aqueous phase of the BS column (level 3 at 1 m column height) has decreased to $\leq 5 \times 10^{-5}$ M/l N_2H_4 and in the solution which, in addition to ≤ 1 g U/l and 0.41 g Tc/l, contains 3.6 g Pu/l there is a clear reoxidation of plutonium.

During catalytic destruction of hydrazine by nitric acid ammonium (NH_4^+) and hydrazoic acid (HN_3) are formed as the products (10⁴ - 14). The development versus time of these reaction products in the aqueous phases of the BX and BS columns of MINKA was shown in (17). Under the conditions prevailing in this MINKA experiment an NH_4^+ concentration of $8 - 12 \times 10^{-2}$ M/l established in the presence of technetium in BXP and BSP, respectively. The corresponding values for HN_3 were measured to be 2×10^{-2} M/l in BXP and $7 - 10 \times 10^{-2}$ M/l in BSP. The organic BSU solution even contained $3 - 4 \times 10^{-2}$ M/l HN_3 .

Under the conditions prevailing in the MINKA experiment specific rates of formation for the hydrazine daughter products of 0.21 - 0.31 mole HN_3 per mole degraded N_2H_4 and for NH_4^+ values of 0.29 to 0.45, respectively, can be calculated from the amount of hydrazine consumed and from the measured NH_4^+ and HN_3 values, respectively.

In the absence of technetium about 2 mole N_2H_4 were consumed per mole of plutonium. In the presence of technetium the amount of N_2H_4 consumed in the BS column increased to 7.6 mole N_2H_4 per mole Pu and in the BX column to 8.2 mole N_2H_4 per mole Pu.

Supplementing the analyses of the process samples in a simulated aqueous solution the extraction behavior of the reduced Tc and Pu species was investigated with 30% TBP/kerosene, and the degradation of hydrazine was measured in addition (Dressler et al. (16)). The results have been plotted in Fig. 4. The concentrations of hydrazine in the aqueous phases and of the Pu and Tc species, respectively, in the organic phase have been plotted versus the contact time of the solution until extraction and hydrazine analysis, respectively. The concentrations have been plotted as relative values which are related to the composition of the initial solution = 100%. The simulated solution contained at the beginning of the investigation 1.4 M HNO_3 and 0.116 M N_2H_4 , as well as 0.7 g Pu/l, 4.7 g U IV/l, 1.4 g U VI/l, and 0.33 g Tc/l.

It is clearly evident from the figure that the hydrazine concentration diminishes with the length of holdup of the sample. The initial degradation of hydrazine down to concentrations

of $\sim 10^{-2}$ M/l can be described formally by a half-life $t_{1/2} = 120$ min. This value supplements the measurements made on real samples taken from MINKA (17) in which for comparable concentrations of U, Pu, HNO_3 and N_2H_4 half-lives of $t_{1/2} = 80$ min were determined for 0.43 g Tc/l and $t_{1/2} = 160$ min for 0.24 g Tc/l, respectively.

Another phenomenon worth noticing is the reduction behavior of plutonium and technetium in the simulated solution.

After e.g. 1 min. holdup about 95% of plutonium and about 30% of technetium have undergone reduction. This means that the presence of U IV speeds up the reduction of technetium (13), (15), Koltunov et al. (25), Ramazano et al (26) compared with the course of the reaction in the HNO_3 - N_2H_4 system (10 - 15). After about 30 min. the reduction of technetium has attained its final level. Any intermediates which might be formed during the process of technetium reduction through U IV are indicated in (15).

On the other hand, the reduction of plutonium in the presence of technetium seems to be incomplete which is evident from a comparison with literature values on plutonium reduction through U IV in the HNO_3 - N_2H_4 system Biddle et al. (18), Menchero (19), Schlea (20), McKay (21). We suppose that this change in the reduction behavior of plutonium in the presence of technetium is the principal cause of the poorer U-Pu separation efficiency in the BX column.

It is further evident from Fig. 4 that with diminishing N_2H_4 content in the solution reoxidation starts of the reduced plutonium and technetium species, respectively. In the simulated solution fast reoxidation started at hydrazine contents below 2×10^{-2} M/l N_2H_4 .

Concentration Profiles.

In Fig. 5 the concentrations have been plotted of HNO_3 , N_2H_4 , U, Pu and Tc in the aqueous and organic phases, respectively, of the BX column. A BX system free of technetium (left side of Fig. 5) is compared with a system containing technetium (right side of Fig. 5).

On both sides of Fig. 5 the concentrations in mole/l and g/l, respectively, have been plotted versus the column height. "Da" stands for the bottom aqueous decanter and "Do" for the top organic decanter of the BX column. The positions 1 - 8 correspond to the column levels: level 1 = feed at 0 m column height, level 3 = BXX feed at 1 m column height, and level 8 = BXS feed at 3.5 m height.

The profile on the left side of Fig. 5 was taken in the absence of technetium after 32 hours duration of the experiment. The profile on the right side of the figure was measured 25 hours after the onset of Tc feed (=89th hour). This profile is reproduced here as an example and it shows the characteristic

changes in the concentration plots in the presence of technetium.

In the top part of Fig. 5 the N_2H_4 and HNO_3 concentrations have been plotted. In the presence of technetium N_2H_4 undergoes strong degradation already in the top part of the column. In the bottom part of the column further reduction of N_2H_4 concentration is inhibited by the BXX feed.

The concentration profiles of uranium have been plotted in the figures in the middle. For the system free of technetium the U IV concentration profile of the aqueous phase has been entered in addition. It was determined by spectrophotometry (Schmieder et al (22)). In the presence of technetium this method of analysis cannot be applied in routine operation because the reduced technetium, in the range of 500 - 700 nm, gives rise to an enhanced background not constant with the time (12) so that the measurement of U IV is disturbed at 648 nm. Spectrophotometric measurements of technetium in the presence of U VI, U IV and Pu III are given (15), Borovinskij et al (24).

In the bottom part of Fig. 5 the concentration profiles have been plotted for plutonium and technetium. The comparison of the profiles shows that in the presence of technetium the plutonium concentration of the organic phase decreases at a much less steeper rate than in the profile free of technetium. In the presence of technetium about 1 m more column length is needed to attain the same plutonium concentrations as compared with the system free of technetium.

All the organic and aqueous Tc concentration profiles, respectively, have a distinctly flatter course than the respective plutonium profiles. Moreover, all organic technetium profiles exhibit in the zone of BXX feed a more or less pronounced jump in concentration. Moreover, the Tc profiles measured in the aqueous phase take a very flat course in the bottom part of the BX column (0 - 1.5 m height) so that nearly no changes in concentration occur from one sampling point to the next.

A possible cause of this unusual appearance of the profile, compared to the plutonium profile, could be the slow reduction of Tc VII by U IV (15), (25) (see Tc plot in Fig. 4) and/or internal reoxidations (see jump in Tc concentration in the organic phase; Fig. 5).

As already shown earlier (8) the separation efficiency of the organic continuously operated BX column is greatly influenced by the U IV concentration in both phases of the column. Of the U IV present an equivalent fraction is consumed for the reduction of Pu IV. In the presence of technetium another fraction is obviously consumed to reduce Tc VII so that the overall conditions of reduction in the BX column are adversely affected and contribute to a deterioration of the U-Pu separation efficiency. Therefore, an improved pre-separation of technetium in the extraction and scrubbing columns, respectively, of the first cycle of the PUREX process should clearly improve the partitioning conditions in the BX column. Multiple feed of the BXX solu-

tion at different levels of the BX column should produce the same effect.

It is planned to test the improved separation of technetium in the next campaign to be performed in MINKA within the framework of flowsheet studies on the IMPUREX process (Schmieder and Petrich (23)).

Acknowledgement

The authors wish to thank the operators of MINKA and the PUTE operation team for excellent experimental work and Mr. U. Galla for support in the interconnected operation of the PUTE-MINKA-MILLI facilities. We would like to extend our thanks to the staff of the analytical group who performed quickly and precisely the analyses of the numerous process samples.

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TABLE 1 - Design of MINKA columns

| Column Function | A extraction + scrub | BX separation | BS Pu-scrub | 1C U-strip |
|--------------------|-------------------------|------------------|----------------|---------------|
| Mode | organic | organic | aqueous | aqueous |
| Heating [°C] | 25-60 | 25-60 | 40 | 25-60 |
| Diameter [cm] | 2.6 | 2.6 | 3.3 | 3.5 |
| Height [cm] | 300+50 | 350 | 350 | 350 |
| Sieve plates: | | | | |
| Spacing [cm] | 3 | 3 | 5 | 5 |
| Holes [cm] | 0.15 | 0.15 | nozzle | 0.3 |
| Pulsation: | | | | |
| Amplitude [cm] | 1.5 | 1.5 | 1.5 | 2.5 |
| Frequency [Hz] | 1.2 | 1.5 | 1.5 | 1.0 |

TABLE 2 - Flowsheet conditions of U-Pu-separation

| Process stream | ^{174P} BXF | BXS | BXX | BSX |
|---------------------------------|------------------------|------|--------------|--------------------|
| Relative flow rate | 1.0 | 0.14 | 0.03 | 0.17 |
| M HNO ₃ | 0.07 | 0.1 | 1.0 | 0.01 |
| M N ₂ H ₄ | - | 0.2 | 0.2 | - |
| g U/l | 80 | - | 140* | < 10 ⁻³ |
| g Pu/l | 0.8 | - | - | < 10 ⁻⁴ |
| g Tc/l | 0.08 | - | - | < 10 ⁻⁴ |
| % TBP | 30 | - | * > 70% U IV | 30 |

TABLE 3 - Parts of the MINKA experiment

| Part | Time [h] | Mode of Operation |
|------|-------------|--|
| 1 | 33 | BX, BS as single columns, BXP transfer into the BS column without BSU recycling into BXF |
| 2 | 31 | BX + BS columns interconnected, BXP transfer into the BS column and BSU recycling into BXF |
| 3 | 39 | Part 2 plus Tc |
| 4 | 7 | BX, BS as single columns, no BXP transfer into the BS column and no BSU recycling into BXF |

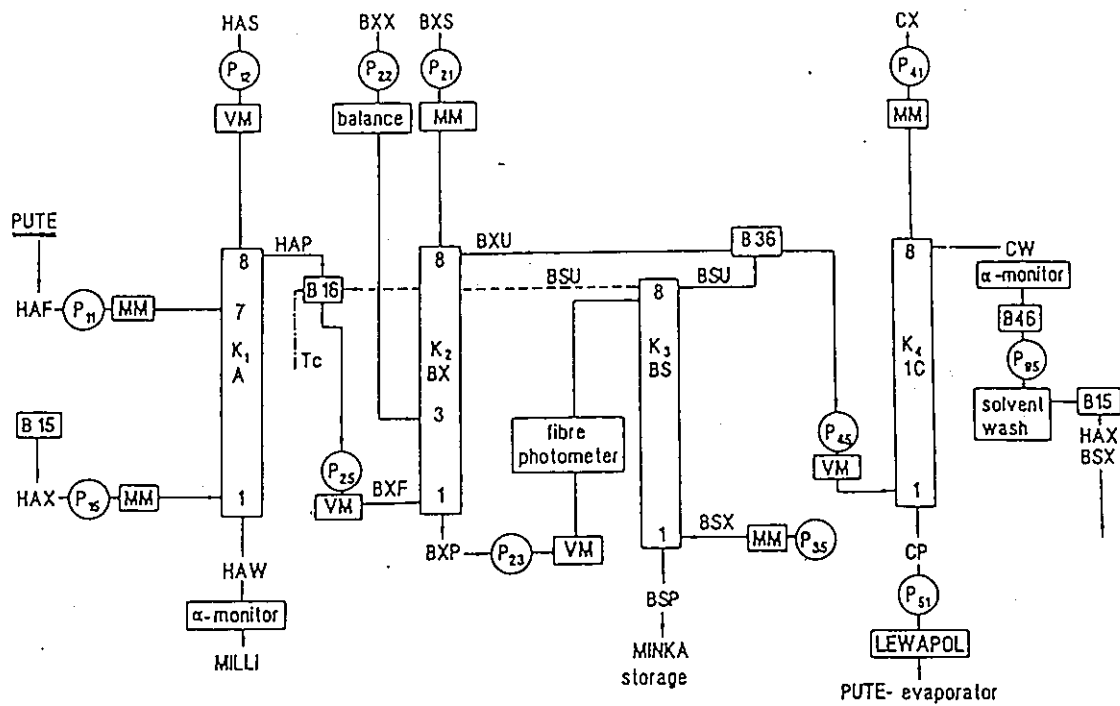
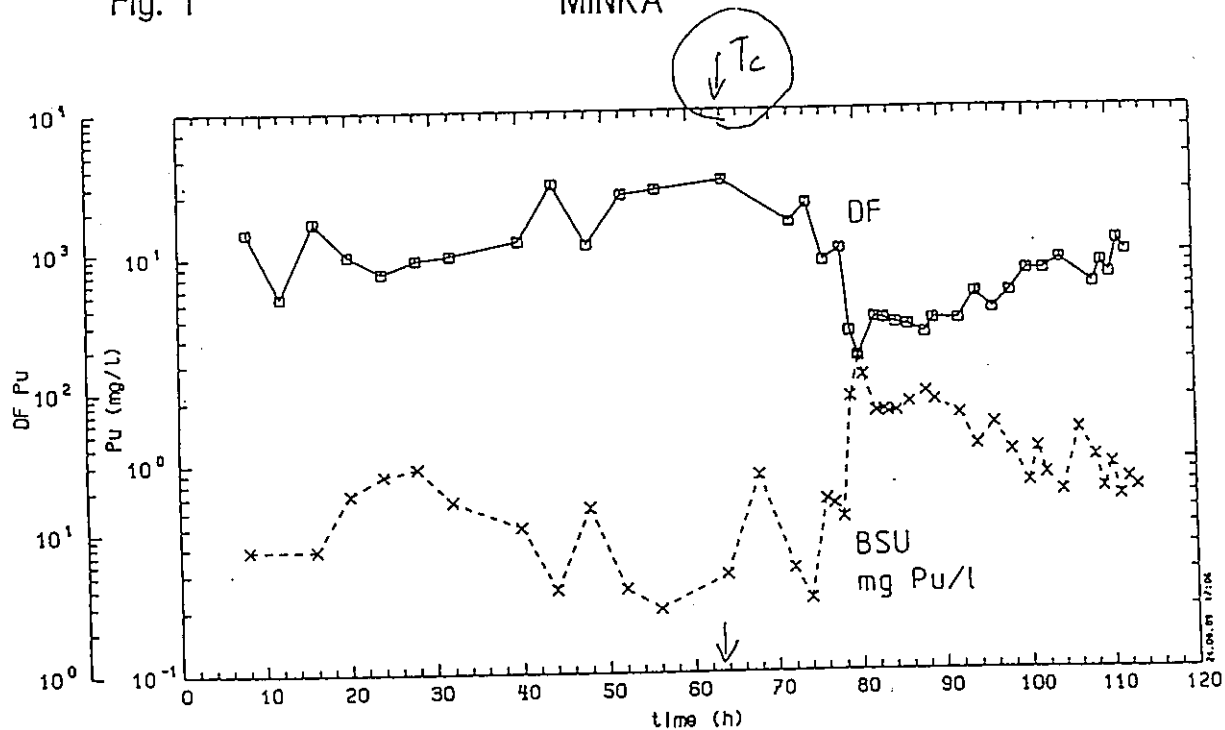
KfK
HCH

Fig. 1

MINKA

KfK
HCHFIG.2 DF_{Pu} AND ORGANIC CONCENTRATION OF PU IN THE BXUT_C (TV) v Gas form

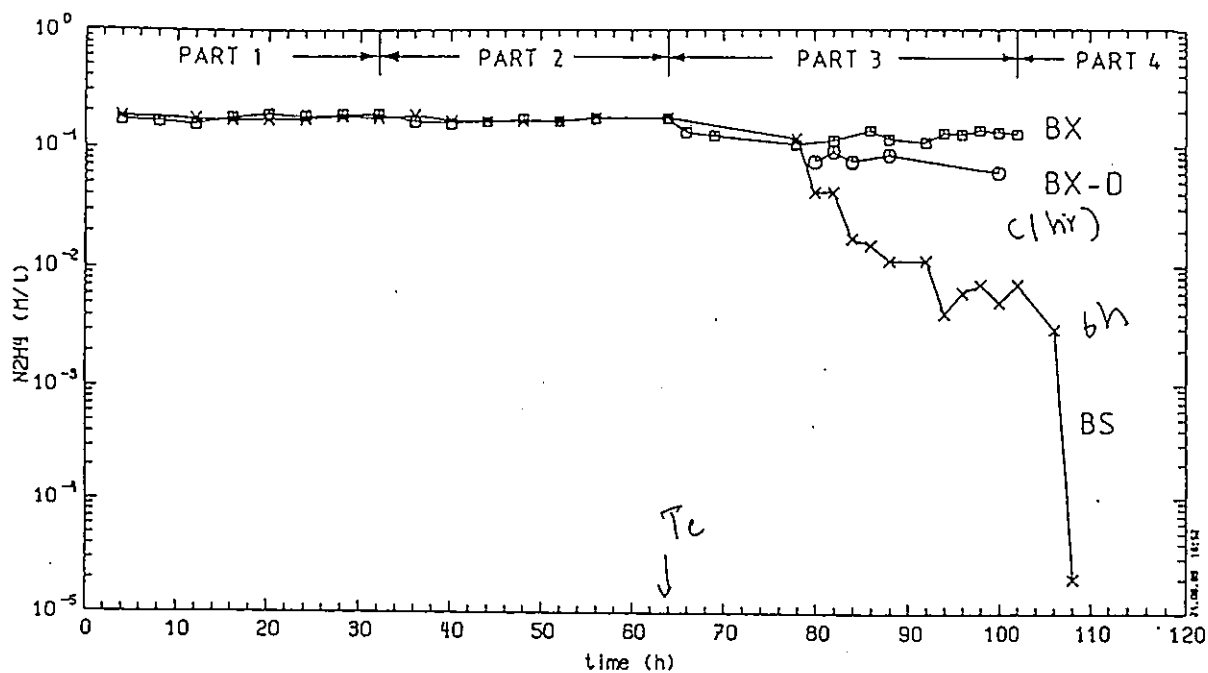


FIG.3 AQUEOUS CONCENTRATIONS OF N_2H_4 IN THE BX-BS COLUMNS

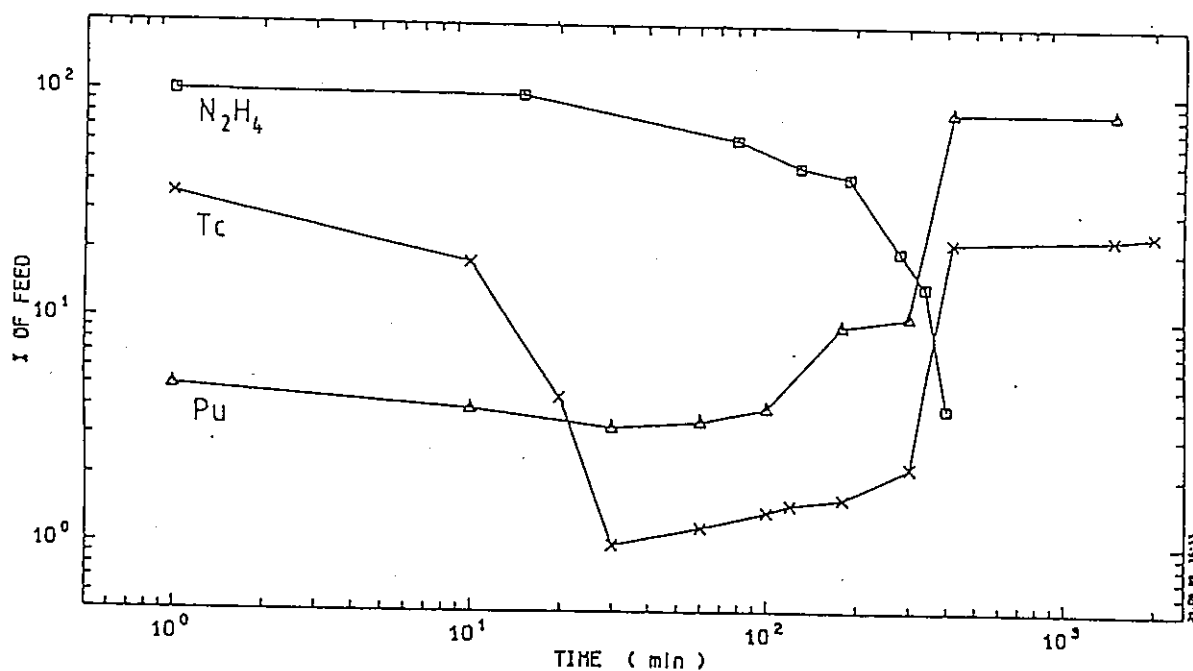
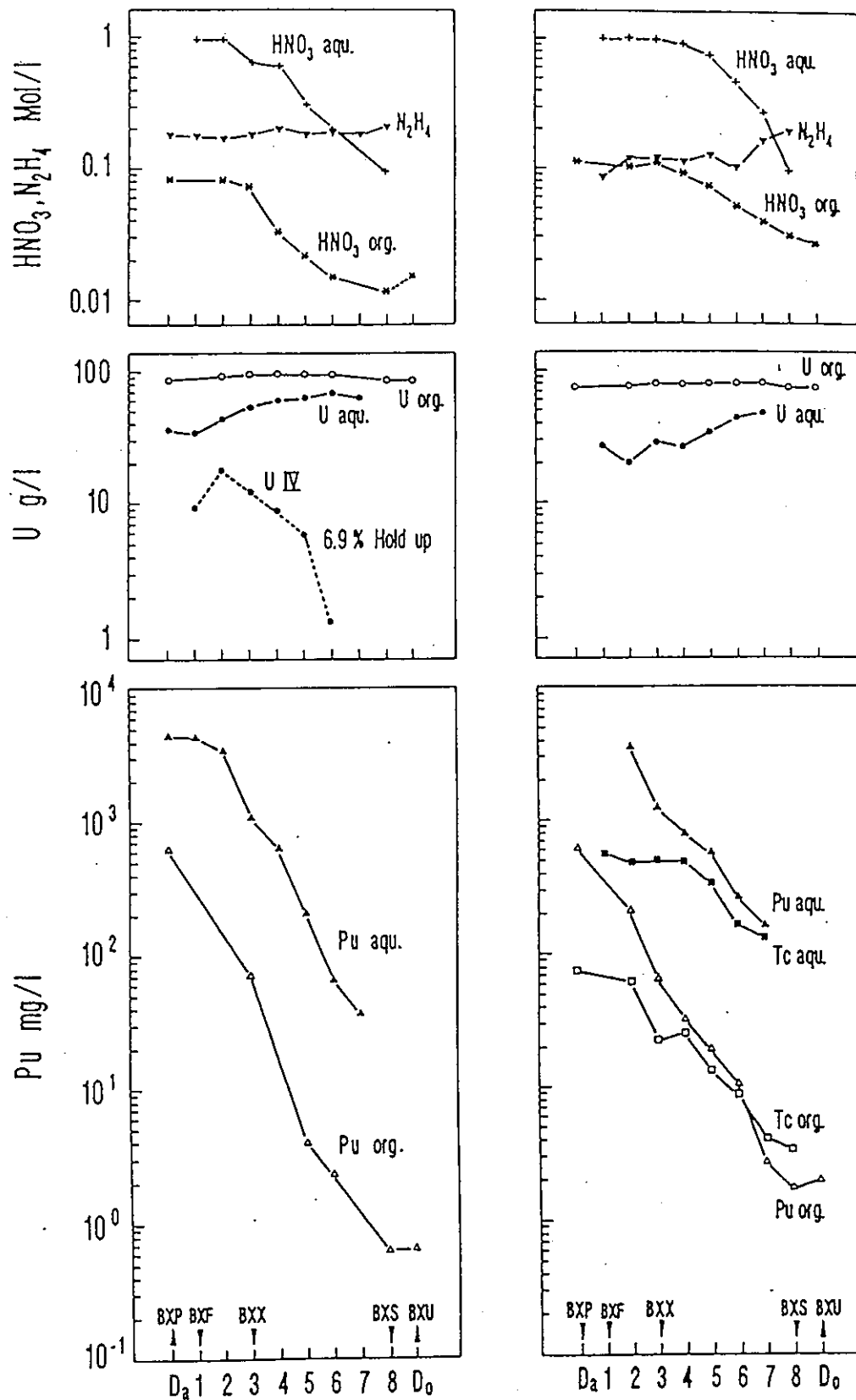


FIG.4 BEHAVIOUR OF N_2H_4 , Pu AND Tc



BX- CONCENTRATION PROFILES

KIX

INCH

A TECHNETIUM REJECTION FLOWSHEET

R. Baker*, J.H. Miles*, P.T. Roberts*

A single contactor unit has been designed which enables Tc to be removed from a TBP/diluent stream bearing U and Pu, by means of a 5M HNO₃ wash. A Tc waste stream is produced which is virtually free from U and Pu. The flowsheet has been tested firstly with U and Tc, then with U, Pu and Tc, and finally in a highly active facility with real PWR fuel solution. About 97% of the Tc was removed from the organic phase and U and Pu levels in the Tc waste have usually been below 0.04% of those in the product stream.

INTRODUCTION

The element technetium has many rare properties and one that is unique. It shares with promethium the distinction of being a fission product element not found in nature, and it shares with selenium, tellurium, antimony, molybdenum and perhaps germanium the distinction of being a fission product element which forms stable anions in nitric acid solution. It appears to be unique however in that this anion forms a complex with uranium which is extractable into TBP/diluent solutions.

It can be present in nitric acid solutions in up to 4 different valency states (IV, VI, VII and perhaps III); this number being rivalled only by that of plutonium (III, IV, V and VI). The 99 isotope has a long half life (2.12×10^5 years) and the pertechnetate anion, which is the stable form in natural oxidising media, is not absorbed on natural siliceous materials. This makes it a very important isotope in determining the dose to man from fission product material entering the biosphere in the far future (Hill (1)).

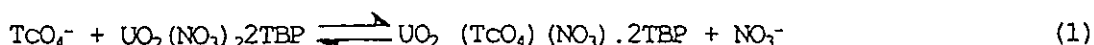
At the Extraction '84 Meeting Garraway (2) described the behaviour of technetium in a Nuclear Fuel Reprocessing Plant. Extraction of Tc in the extract and scrub stages is almost complete due to the involvement of extractable complexes with zirconium. In reductive U/Pu separation contactors on the other hand Tc is reduced to a mixture of the IV, and VI valent species, which are inextractable, but which react with hydrazine in a cyclic manner giving rise to excess consumption of this reagent.

Flowsheet Design

High concentrations of uranium in a TBP/diluent phase usually result in

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reduced extraction of fission products (FP) because there is less "free TBP" remaining to extract them. In the case of Tc however this will not be so since



uranium is required to form the extractable complex, its extraction in the absence of uranium being very small indeed. It will be clear from equation (1) however that high concentrations of nitrate ion will push this equilibrium back to the left and prevent the extraction of Tc. It is very convenient that the high concentrations of nitrate ion which prevent the extraction of Tc are ideal for the extraction of U and Pu which have maxima of extraction in the 4-8 M HNO_3 range.

If we therefore backwash an organic phase with strong HNO_3 we expect the Tc to revert to the aqueous phase, but the U and Pu to remain in the organic phase. This is carried out in stages 1 to 3 of the contactor in Figure 1. In order to prevent any trace of U and Pu leaving in this aqueous waste stream however, it is necessary to "strip" it with a low volume TBP/diluent wash, which is added to the main organic stream. (Stages 4-12 of this figure.)

High concentrations of HNO_3 in the organic phase leaving the contactor will be unwelcome in any U/Pu split contactor. All the known reducing and complexing reagents used for this purpose give poorer separation in the presence of high concentrations of HNO_3 . We have therefore experimented with the use of a single stage of low volume, low concentration, acid wash to reduce the amount of acid going forward. This is stage 0 in Figure 3.

Figure 1 lists the distribution coefficients (D) and extraction factors (E) for U(VI), Pu(IV) and TcO_4^- in all sections of the rejection contactor. We note that U as U(VI) is well extracted at all points in this flowsheet and that Tc(VII), (TcO_4^-) is equally well rejected ($E < 0.2$). For the strip section we have included two values for each element; the first is for the top stage of the strip section with high U concentration in the organic phase, the second is for the bottom stage where U concentrations will be very low indeed. We see that for Pu the extraction factor for Pu(IV) at the phase volume ratio chosen, falls just below unity in the high U concentration stage. This probably occurs over only one stage and does not affect the operation of the flowsheet. In all other stages the extraction factor will be above 2, and the Pu well extracted.

We have developed this flowsheet in three stages; starting with a simple uranyl nitrate-pertechnetate-nitric acid system, and then repeating this process with plutonium present. These stages were carried out with mixer-settler equipment in a glove box. Finally, the flowsheet was tested with real PWR fuel in a fully shielded α , β , γ cell.

EXPERIMENTAL

Counter-current contacting equipment

All the flowsheet trials were carried out in miniature mixer-settlers. For the "U + Tc active" and "U + Pu + Tc active" trials these were purchased from the Ceries organisation in Lyon, France, and had been prepared by drilling in a block of Altuglas plastic (Ceries type "Pollux A"). For the fully active trials similar mixer-settlers were used which were made at Harwell Laboratory from radiation resistant materials. The block was of stainless steel and incorporated windows of CeO_2 -doped radiation resistant

glass*. These windows were sealed onto a gasket of peroxide cured EPDM compound** (BNFL 30H) which is also resistant to radiation and to nitric acid and to TBP/OK.

For the "U + Tc active" trial an organic feed solution was prepared by extracting uranyl nitrate crystals and then ammonium pertechnetate solution[†] into purified TBP/OK. Only the Tc rejection contactor was operated.

For the "U + Pu + Tc active" trial an extract contactor was operated (Figure 2) and the feed solution was an aqueous solution of U and Pu nitrates in HNO_3 with NH_4TcO_4 added. Zr was not added to the feed solution and it was realised that this would greatly reduce the amount of Tc extracted in a normal extract and scrub contactor. The scrub section was therefore omitted and the organic phase passed direct to the Tc rejection contactor apart from passage through 3 "dead" stages of mixer-settler to allow aqueous haze to separate out.

A low acid backwash contactor was used after the Tc rejection contactor, in order to recover Pu and U in an aqueous phase.

The Fully Active Trial

In the fully active trial a sample of 510 g of long cooled (approximately 12 years) high burn-up (30,000 MWd/te) PWR fuel was dissolved in HNO_3 with careful scrubbing of the gases evolved. The method has been described previously by Brown (3,4). The solution was filtered through 0.45 μ millipore type HV Durapore filters fabricated from polyvinylidene fluoride. In this case an extract-and-scrub contactor and the Tc rejection contactor only were operated, and the aqueous wastes (highly active and Tc product) were collected in sealed cans and later disposed of in concrete. The organic product was absorbed in "Mor-Dri" which was later mixed into cement for disposal. Accurate solution flowrate control did not rely on metering pumps. The metering pump outlet was fed to a constant head cell and from there via a pre-set needle valve and electronic flow measuring equipment (Phase Separations Ltd. catalogue 900503), to the mixer-settlers.

The waste and product solutions were pumped out of the ends of the mixer settlers through a 3-way valve to the waste drum. Samples were taken from the valve at regular intervals. The working area was divided into "red" and "white" highly active and low active areas and different manipulator jaws used in each area. Control of the spread of contamination was excellent. Equipment removed from the cell after use averaged only 10 μSvhr^{-1} whereas the levels in the cell were about 2 Svhr^{-1} .

The B.220.29 facility at Harwell allows short periods of very highly active work to be done at comparatively reasonable cost. Hire charges for the facility in this work are cheap when compared with the very high charges for the construction of fixed pilot plants, which use heavy shielding and occupy a whole laboratory suite.

Analysis. Analytical samples were taken with an evacuated tube from hypodermic needles mounted in the top of the settlers. Analyses for Tc were

* Manufactured by Pilkington Ophthalmic and Special Glasses, St. Asaph, Clwyd.

**Manufactured by Rapra Technology Ltd., Shawbury, Shrewsbury, Salop.

[†]Amersham International catalogue no. TCS 1.

carried out by liquid scintillation in the first run but by the colorimetric technique of Howard and Weber (5) based on thiocyanate complexes for the other two runs. Uranium analyses were carried out by a fluorimetric procedure while acid determinations on organic phases used a potentiometric "gran plot" method, described by Rossotti and Rossotti (6).

Pu analyses were carried out by liquid scintillation techniques using Packard Insta-gel scintillant and a Beckmann LS 3800 instrument. This does not distinguish between α particles arising from Pu and those from Am but it was expected that the latter would be absent in samples from the last two contactors. In the case of the "U + Pu + Tc active" run this proved to be incorrect and it was shown by α -spectrometry that 93% of the α -count in the Tc waste was due to Am. The Pu concentration figures were corrected accordingly.

RESULTS AND DISCUSSION

The "U + Tc active" trial

Only one contactor was operated: it being fed with a synthetic TBP/OK phase. Only 2% of the Tc remained in the emergent organic phase and only 0.0006% of U came out in the aqueous "Tc waste" stream. The only unexpected feature was the hold up of some of the ^{238}U daughter isotopes (^{234}Th and ^{234}Pa) in the small quantities of organic phase left in the Tc rejection contactor in the stages below the feed point, after shut-down. This process is, if anything, an advantage because the associated γ activity is removed, for a time, from the uranium product. The isotopes will decay away in the organic phases from the contactor with a half-life of 24.1 days, and of course re-appear in the U product on the same time-scale.

The "U + Tc + Pu active" trial

This trial was carried out with 3 contactors according to the flowsheet of Figure 2. The first contactor was an extract contactor using an aqueous phase feed, and the third a backwash contactor to recover U and Pu in the aqueous phase. In order to encourage extraction of Tc the aqueous feed solution was made 1M in HNO_3 instead of the usual 3M so as to reduce interference by NO_3^- ion in the formation of the U-Tc complex (see Equation 1). The scrub section was dispensed with since in the absence of zirconium this would tend to backwash the Tc, but a short dead leg was incorporated in the hope that this would allow any haze of the aqueous feed solution, to drop out of suspension in the organic phase.

In this trial the proportions of Tc found in the emerging organic phase and in the final aqueous phase from the third contactor were below the limit of detection (estimated at 0.26% of the Tc going into the rejection contactor). The α -count profile across the Tc rejection contactor (Figure 4) fell rapidly across the stages 4-7 where, as explained above, Pu might not be expected to extract well, because of the high U loading. In stages 7-12 the α -count reaches a steady value and this has been shown by α -spectrometry to be 93% Am. Clearly the "dead stages" at the top of the extract column have not been sufficient to prevent some of the aqueous phase feed solution, with Am from the Pu stock, reaching the Tc rejection contactor. The use of the extract contactor without a scrub section was however vindicated by achieving 54% extraction of the Tc. The Pu remaining in the Tc waste is only 0.036% of that in the final aqueous product which is an adequate removal.

Acid concentration. The performance of the low acid scrub was disappointing. Analysis of the organic phase entering the Tc rejection contactor showed a level of only 0.16M HNO_3 which is not unexpected in view of the low (1M) aqueous acid concentration with which it has just been in contact in the extract contactor. The emerging organic phase however averaged 0.36M.

A McCabe-Thiele diagram suggests that the organic phase leaving the 5M acid in stage 1 should be 0.4M in HNO_3 but that this should fall back to 0.23M by operation of the low acid scrub. It is probable that the top stage of this mixer-settler was giving poor disentrainment of phases at the high phase volume ratio used.

The Fully Active Trial

The fully active trial was carried out in two sections. The first used 5M HNO_3 for the Tc rejection contactor but did not employ the low acid scrub (stage 0). In the second section the low acid scrub was included but the strong acid scrub was increased to 5.5M so as to keep the acid concentration in stages 1-11 at 5M.

The concentration of Tc at the inlet to the Tc rejection contactor was 49.5 mg l^{-1} and this fell to an average of 2.23 mg l^{-1} (4.5%) in the first section of the run and 1.53 mg l^{-1} (3.1%) in the second. The better performance in the second half reflects the additional stage in use although it is not optimised for Tc rejection.

The U concentration profile across the Tc rejection contactor fell gently from 7 g l^{-1} at stage 0 to about 4 g l^{-1} at stage 5 and then very rapidly to 0.3 mg l^{-1} at stage 10 (see Table 1).

Pu concentrations. The Pu concentration showed very little change in stages 0-8 and then fell by a modest factor of 3 (Table 1). (All these concentrations were determined on the aqueous phases.)

The failure to decontaminate from Pu is probably due to the absence of a conditioning step to convert Pu to the IV state before the run. The conditioning step was omitted because of the likelihood that it would lead to a spread of contamination. The boiling of the solution in the dissolver will have produced a high proportion of Pu(VI) and the concern expressed above about the extractability of Pu(IV) in the stage below the feed plate, will apply much more to Pu(VI), which is less extractable.

It may be noted however that all these aqueous phase concentrations are considerably below the organic phase product (840 mg l^{-1}) so that a modest decontamination factor of about 20 does apply.

Acid concentration. The acid concentrations in the organic stream entering the rejection contactor averaged 0.33M. This rose to 0.50M in the emerging stream when no low acid scrub was applied but fell back to 0.39M in the second section of the run when the low acid scrub was in use. It is not expected that the increase from 0.33 to 0.39M in this stream entering a U/Pu partition contactor, will have a serious effect on its performance.

CONCLUSIONS

Further attention needs to be paid to the conditioning of the feed solution and behaviour of the low acid scrub. Nevertheless the work provides

a very satisfactory demonstration of a simple process for removing Tc from highly active organic streams containing U and Pu.

ACKNOWLEDGEMENTS

This work was supported financially by the UK Departments of Energy and of the Environment, British Nuclear Fuels plc and the Central Electricity Generating Board. It received essential support from many different groups at Harwell Laboratory. The radiation resistant mixer-settlers were made in the workshops of the Engineering Division with help from the external organisations noted in the text. The highly active operations relied heavily on the B.220.29 Operations Team in the Chemistry Division and α -spectrum and uranium analyses, were carried out by members of Actinide Analysis Group in the same Division. Mr. C. Mason of our own Group carried out acidity determinations on organic phases.

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TABLE 1 - U and Pu Concentration Profiles across the Tc rejection Contactor
Aqueous phase Samples in the fully active Trial

| Stage No. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|------|---|------|------|------|------|------|------|--------|----------------------|----------------------|------|
| U conc. (g l ⁻¹) | 6.62 | - | 4.51 | 4.00 | 3.72 | 4.39 | 1.07 | 0.89 | 0.012* | 7x10 ⁻⁴ * | 3x10 ⁻⁴ * | - |
| Approx** Pu conc. (mg l ⁻¹) | 156 | - | 95 | 109 | 201 | 163 | 136 | 115 | 122 | - | 68.0 | 42.1 |

* Results obtained by fluorimetry. Remaining U figures by coulometry.

**Liquid scintillation counting results. Converted on the assumption that 7.4×10^6 Bq \equiv 1 mg Pu

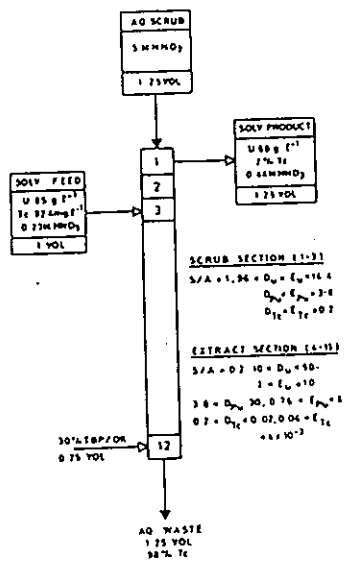


Figure 1. U + Tc active trial

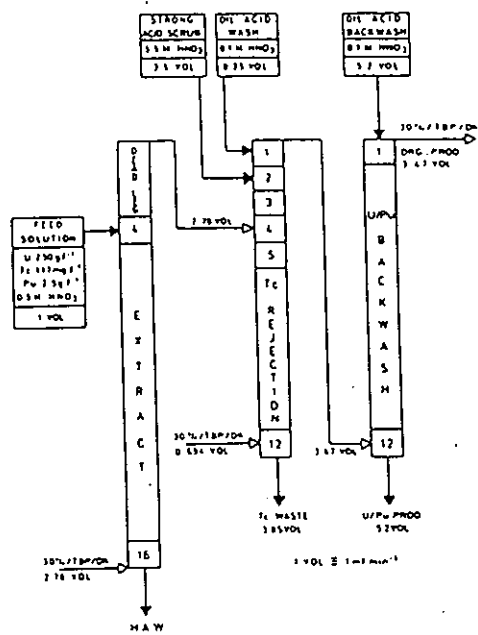


Figure 2. U + Tc + Pu active trial

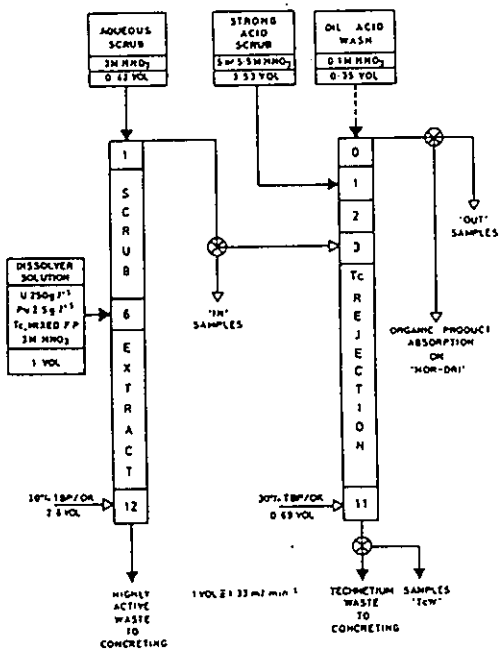


Figure 3. Fully active trial

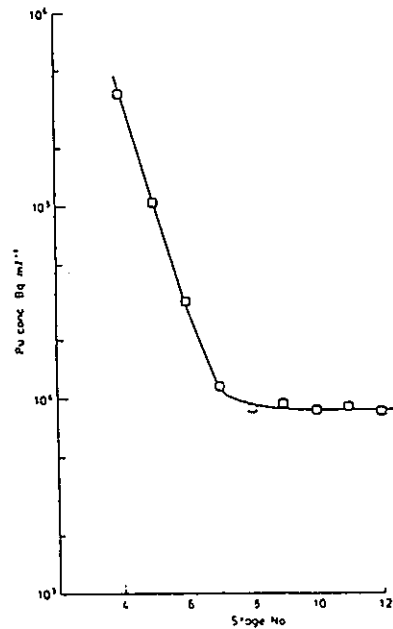


Figure 4. Pu concentration profile
Rejection contactor.
U + Tc + Pu active trial

4.再処理プロセス内でのTc制御の考え方

(1) 研究の動向

最近の高燃焼度燃料を対象とする大型再処理施設のフローシートでは、Tcの有するプルトニウム還元補助剤（ヒドラジン）の分解作用がU/Pu分配カラムの分離性能の低下やヒドラジンの過剰消費を通じて安全性にも影響を及ぼすかも知れないとする意見があり、共除染工程におけるTc制御法の研究は抽出プロセス化学における最近のトピックスの一つになっている。

制御法として、①分配カラムの前で分離する、②分配カラムの内部で分解反応速度を抑制するとする二つの考え方があり、Harwell及びKFK研究所からは①の観点から、BNFLはTHORPの設計方針である②の観点から研究が行われている。BNFLの研究では、分配カラムの連続相を有機相とし且つ分散相である液滴径の制御によりヒドラジンの分解を抑制でき、特別にTcを上流側で除去する必要はないとしている。KFKの研究では、高濃度のTcが分配カラムに供給された場合、分配カラムの連続相を有機相にして運転してもウランに対するPuのDF低下とヒドラジン分解の傾向は避けられないので、Tcはその上流側で除去することがより望ましいとしている。Harwellの研究では、分配カラム給液を高濃度の硝酸を用いて洗浄することによりDF10以上の効率でTcを除去することができるとしている。

(2) THORPフローシートにおけるテクネチウム制御の考え方

(i) THORP抽出プロセスの特徴

図-1に示したように、THORP施設の抽出工程の特徴として、

- ①U/Puの分配を第1サイクルで行なっていること、
 - ②U及びPuの精製工程の数を減らし、全体ではほぼ2サイクル精製フローシートを採っていること
 - ③抽出装置として共除染工程、U/Pu分配工程塔の第1サイクル及びプルトニウム精製工程においてパルスカラムを用いていること、
 - ④JNFSの六ヶ所再処理施設に比べると、Tcを除去する装置及びウラン系へのPuの移行を防止するプルトニウム洗浄装置が設置されていないこと、
 - ⑤一方、ヒドラジン分解生成物であるアザイドの処理工程を設けていること、
- 等の点をあげることができる。これら特徴の一部は(①、③、④及び⑤)は抽出工程にお

けるTc制御の考え方と密接に関連しているものと思われる。

(ii) テクネチウム制御の考え方

THORPではUP-3などと同様にU/Puの分配を第1サイクルで行なう設計（第1サイクル分離方法）となっているが、UP-3の様に分配カラムの前でTcを除去するTcバリヤを設けていない。

これは、ドーンレイの α テストリグ及びセラフィールドでのFull scale mock-up試験等での結果から、分配カラムの連続相を有機相とすると共に適切な物質移動条件（液滴界面積（液滴径及びホールドアップ）及び滞留時間）を与えることによりPu及びTcに関する充分なDFを得ることが出来ると判断したためとしている。特に、①分配カラムにおけるPu、Tc分離は、化学反応律速ではなく物質移動律速であること、②分離性能は有機相内の酸濃度の分布により決定されること（低酸濃度である程高いDFが得られる）等の知見に基づいている。

従って、Tcバリヤはもとより、分配カラム下部での温度制御（Tcのヒドラジン消費反応を制御するために低温部を設ける）などの対策は不要としている。流量等のプロセス条件の変動が生起した場合にヒドラジン消費反応が進み、その結果アザイドやアンモニウムイオン等の蓄積の恐れがあるが、THORPではこれらを含む廃液を蒸発濃縮する前に酸により処理する工程を設けている。

THE DEVELOPMENT OF A THREE-CYCLE CHEMICAL FLOWSHEET TO REPROCESS OXIDE NUCLEAR FUEL

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ABSTRACT

The Thermal Oxide Reprocessing Plant (THORP) is currently being built and commissioned at Sellafield. Initial assessment of the flowsheet performance required to process oxide nuclear fuel in THORP indicated that the most onerous aspects were likely to be the removal of technetium, neptunium and plutonium from the uranium product.

Theoretical studies and early laboratory work suggested that five solvent extraction cycles would be required. Uranium and plutonium would be separated in the first cycle ("early split") and each of these products would then be passed to two further purification cycles.

Subsequent laboratory basic chemistry studies and development work using alpha and fully active miniature pilot plants showed that careful control of technetium, neptunium and plutonium redox chemistry allowed product specifications to be met by the first of each of these pairs of purification cycles alone. It was therefore possible to delete two solvent extraction cycles from the plant and achieve a significant reduction in its size, cost and complexity.

A major contribution to the efficiency of the flowsheet is made by the novel principles which have been adopted for the control of neptunium in the uranium purification cycle. The element is converted to the inextractable five valent form in the feed to the cycle by controlled oxidation and then held in this state to give good separation from the uranium product.

1. INTRODUCTION

Magnox uranium metal fuel has been reprocessed at the Sellafield site of British Nuclear Fuels for over twenty-five years using the Purex solvent extraction process with tri-n-butyl phosphate (TBP) diluted with odourless kerosene (OK). The Thermal Oxide Reprocessing Plant (THORP), which is currently being built and commissioned at Sellafield, will reprocess uranium oxide fuel from United Kingdom, Japanese and European light water and advanced gas-cooled reactors. The Purex process was also selected for THORP but account had to be taken of the differences between Magnox and Oxide fuel. Due to the higher in-reactor irradiation of oxide fuel it has a plutonium content some five times greater and a fission product content up to eleven times greater than Magnox fuel.

The flowsheet design and chemical development work was therefore governed by two main factors. Firstly there was the need to meet product purity specifications against the increased input and different proportions of the fission products. Secondly it was necessary to reduce the environ-

mental impact and operator radiation dose of the new plant. The second factor was addressed by developing a flowsheet which minimised the number of waste streams and the overall size and complexity of the plant and which avoided adding indestructible reagents to the process which would emerge in waste streams and restrict their further treatment. "Salt free" reagents such as hydrazine, hydroxylamine and uranium (IV) were therefore used for valency adjustment.

For the first factor, the major difficulties with oxide fuel in comparison with Magnox are the higher residual content of U235 and the higher ratio of fission product and transuranic contaminants to uranium. The first of these provides a greater incentive to recycle the uranium product in new reactor fuel whilst the second means that a greater degree of purification of the uranium product is necessary to allow this recycle.

The Purex chemical flowsheet developed is shown in simplified form in Figure 1. Separation of uranium and plutonium from fission products and from each other is carried out in the first (HA) cycle using pulsed columns and this is followed by separate single cycles for uranium purification (UP) using mixer settlers and plutonium purification (PP) using pulsed columns.

This paper outlines the process chemistry flowsheet development work carried out for THORP and then describes in some more detail the work undertaken to ensure adequate removal of technetium, plutonium and neptunium from the uranium product.

2. FLOWSHEET DEVELOPMENT

The first step in the development of the flowsheet was to define a specification for the uranium product (Table 1); this allowed the decontamination factors* (DFs) required for the various species across the process to be calculated (Table 1). These requirements were then assessed in the light of the known performance of plants in operation and behaviour of the relevant species.

The bulk of the fission products had been studied during the design of previous reprocessing plants and so the principles required to obtain good DFs were known (Duncan, 1965). In addition, the most troublesome (Zr 95 and Ru 106) had short half-lives which allowed the concentrations to be decreased by increasing the cooling time of the fuel before reprocessing.

The long-lived fission product technetium was, however, believed to be a problem since it is produced in high yield in oxide fuel and was known to be relatively inextractable. It also forms a volatile fluoride which would cause

* Decontamination Factor (DF) for uranium stream -

Unit of impurity per unit of uranium in fuel feed

Unit of impurity per unit of uranium in product

problems in the uranium enrichment plant if too much technetium reached the uranium product.

TABLE 1

THORP product specification and required decontamination factors

| Species | Specification | Decontamination factor required (1) |
|---|---------------|--|
| Total alpha ($\text{Bq g}^{-1} \text{ U}$) | 250 | |
| Plutonium ($\text{Bq g}^{-1} \text{ U}$) | 208 | 7.65×10^5 |
| Neptunium ($\text{Bq g}^{-1} \text{ U}$) | 42 | 314 |
| Ruthenium ($\text{KBq g}^{-1} \text{ U}$) | 10 | 6.7×10^5 (2) 4.2×10^4 (3) |
| Other gamma ($\text{KBq g}^{-1} \text{ U}$) | 1.1 | |
| Technetium (ppm) | 4 | 274 |

(1) Decontamination factor (DF) = $\frac{\text{Contaminant/U in feed}}{\text{Contaminant/U in product}}$

(2) One year-cooled fuel

(3) Five year-cooled fuel

A second problem was considered to be the removal of neptunium and plutonium from the uranium product. Neptunium was known to exhibit complex chemical and solvent extraction behaviour and previous Magnox flowsheets had not reliably given good DFs. Plutonium DFs achieved in the Magnox flowsheets were good, but salt reagents (eg ferrous sulphamate) were used in mixer settler solvent extraction contactors. In contrast the first (HA) cycle of THORP uses pulsed columns for criticality reasons and salt free reagents are used in both this cycle and the uranium purification (UP) cycle; therefore existing flowsheet information was not necessarily relevant.

Process chemistry development work on the behaviour and control of technetium, neptunium and plutonium was therefore carried out using basic laboratory chemical studies and a range of pilot plant facilities. These included a 1/6000 scale full active replica of all the THORP solvent extraction cycles using irradiated oxide fuel as feed stock (the Miniature Pilot Plant), a 1/5000 scale alpha active glovebox facility using uranium, plutonium, neptunium and technetium as feed stock and a 1/250 scale alpha active pulsed column facility using uranium, plutonium and technetium. These pilot plants, together with a range of complementary chemical engineering pilot plants, including full size, uranium-active replicas of the HA and PP cycles, provided

all the data for the process and equipment design of the THORP Chemical Separation Plant.

3. TECHNETIUM AND NEPTUNIUM BEHAVIOUR IN THE HA SOLVENT EXTRACTION CYCLE

The HA solvent extraction cycle of THORP (Figure 1) separates uranium and plutonium from the fission products in an extract and scrub system and then separates uranium from plutonium in the 1B system using uranous nitrate (U (IV)) to reduce Pu (IV) to Pu (III). The reduced forms of uranium and plutonium are stabilised against nitrite re-oxidation by the addition of hydrazine.

3.1 Technetium

It was known that technetium and uranium co-extract in the Purex process (Siddall, 1959) and early alpha active trials of the HA cycle flowsheet indicated that a certain amount of the technetium present in the THORP irradiated fuel feed would extract in the first extract and scrub contactor and follow the uranium-plutonium stream. This technetium was shown to be largely backwashed with the plutonium in the 1B system, but the presence of the technetium in the 1B system was found to catalyse the consumption of the hydrazine stabiliser by nitrite leading to a requirement to increase the feed rate of the hydrazine.

Fully active trials in the Miniature Pilot Plant showed however that the zirconium present in irradiated fuel enhanced the extractability of technetium causing 100% extraction in the extract and scrub contactor (Garraway, 1984). The efficient backwashing of technetium in the 1B system ensured that the uranium product specification could still be achieved but a large amount of development work was necessary to minimise the effects of the technetium-hydrazine reaction on the 1B system whilst ensuring a satisfactory plutonium DF for the uranium stream. A description of this work is published elsewhere (Denniss and Phillips, 1990).

3.2 Neptunium

Neptunium is present in the irradiated fuel feed largely as extractable Np(VI). It therefore follows the uranium-plutonium stream from the first extract and scrub contactor into the 1B system. Here the uranium (IV) reducing conditions are sufficient to reduce neptunium to the extractable (IV) state and it therefore follows the uranium-in-solvent stream to the UP cycle. The DF for neptunium on the uranium stream in the HA cycle is thus poor and it was therefore necessary to design the UP cycle to remove the bulk of the neptunium as well as removing residual plutonium and fission products.

4. NEPTUNIUM AND PLUTONIUM BEHAVIOUR IN THE UP CYCLE

At the outset of THORP development the chemistry and solvent extraction behaviour of neptunium and plutonium was known, but no flowsheet had

previously been designed to give good removal of neptunium from uranium. Plutonium has three common valency states (III, IV and VI) and two of these are important in the solvent extraction process; Pu (IV) which is extractable and Pu (III) which is inextractable and can be produced by reduction of Pu (IV). Neptunium exists also in three common valency states (IV, V and VI) which can be readily inter-converted by redox or disproportionation reactions (Guillaume, 1984). Neptunium (IV) and (VI) are extractable but neptunium (V) is not (Guillaume, 1984).

4.1 Neptunium in the first UP cycle contactor

The most efficient way of separating neptunium from uranium was considered to be the formation of inextractable Np(V) followed by forward extraction of the uranium in the first UP cycle contactor, UP1 (Figure 2). The feed to the UP cycle contains 100% Np(IV) and so the requirements for an oxidising pre-treatment were examined by laboratory experiments. Heating Np(IV) at low acidity had been reported to form Np(V) (Srinivasen, 1974) and a series of trials at low acidity, with varying temperatures and in the presence and absence of uranium showed that a high temperature was required to give rapid conversion. A low acid feed is of course not suitable for uranium extraction and further laboratory trials were carried out to establish the temperature conditions which allowed subsequent acidification without destroying the Np(V).

4.2 Plutonium in the UP cycle first contactor

During the neptunium conditioning process, plutonium will remain as extractable Pu (IV). A simple UP1 uranium extraction contactor, whilst providing a good neptunium DF, would therefore not provide any decontamination from plutonium. Use of uranium (IV) to reduce the plutonium as in the 1B system would reduce the Np(V) to extractable (IV) and was thus ruled out.

Hydroxylamine nitrate (HAN) however was known to reduce Pu (IV) to Pu (III) and Np(VI) to Np(V) but not Np(V) to Np(IV) (Guillaume, 1984) and so the effect of a low temperature, low acid hydroxylamine scrub feed to UP1 was examined in alpha active experimental trials. It was necessary to optimise by experiment the temperature and acidity, these being required to be low to minimise disproportionation of Np(V), whilst higher acidities are ideally required for efficient uranium extraction.

4.3 Neptunium and plutonium in the UP cycle second contactor

Instead of following UP1 with the usual uranium backwash contactor, it was considered that further useful decontamination of the uranium from neptunium and plutonium could be achieved in a compound plutonium backwash and uranium re-extraction contactor (Figure 2) analogous to the 1B system of the HA cycle. Plutonium backwash is achieved by using HAN again, with a higher temperature and a low acidity optimised experimentally to give the best balance of

removal from the uranium. The first UP cycle is completed by a third contactor, UP3, providing a simple low acid backwash of the uranium (Figure 2).

4.4 Second UP cycle

The original THORP flowsheet design incorporated evaporation of the product from the first UP cycle followed by a three contactor second UP cycle, analogous to the first UP cycle but utilising uranium (IV) stabilised by hydrazine in the first contactor (UP4) to maximise plutonium DF and using HAN stabilised by hydrazine in the second contactor (UP5). A backwash contactor (UP6) completed the cycle.

5. EXPERIMENTAL VERIFICATION OF THE UP CYCLE FLOWSHEET

Initial testing of the flowsheet was carried out in the alpha-active 1/5000 scale facility at Sellafield using the expected quantities of plutonium, neptunium and technetium in the UP1 feed and a "spike" or small amount of ruthenium derived from the Magnox plant. Very good DFs were demonstrated as shown in Table 2, which compares achieved DFs with those required to meet the specification. It can be seen that for plutonium, neptunium and technetium the first UP cycle alone was more than capable of meeting the product specification and with five-year cooling of fuel before reprocessing, the ruthenium specification is also comfortably met.

TABLE 2

Decontamination factors measured in alpha active trials

| | Plutonium | Neptunium | Ruthenium | Technetium |
|---------------------------|-----------|----------------------|-------------------|------------|
| DF required across UP (1) | 232 | 190 | 37 (2) 2.3 (3) | 1 |
| DF achieved in UP cycle | >560 | >3.7x10 ³ | 18 | 10 |

(1) DF required to achieve specification

DF achieved in HA cycle

(2) One-year-cooled fuel

(3) Five-year-cooled fuel

Confirmation of these findings was provided by full testing of all cycles of the flowsheet using the Miniature Pilot Plant and actual irradiated oxide fuel.

A total of 50 days active operation was carried out in five separate trials using different samples of AGR and LWR fuel (Table 3). The results

confirmed the findings from the alpha-active trials and demonstrated that the uranium product specification could be met comfortably by a single purification cycle (Table 4). It was thus possible to delete from the THORP design the entire second UP cycle complete with the evaporator feeding it, thus reducing very significantly the size and complexity of the plant and the volume of effluent generated. The flowsheet adopted is shown in Figure 2 in simplified form.

TABLE 3

Summary of miniature pilot plant campaigns

| Run | Fuel type | Burn-up Gwd t ⁻¹ (U) | Rating MW t ⁻¹ (U) | Cooling years | Comments |
|-----|-----------|------------------------------------|----------------------------------|------------------|--|
| H1 | AGR | 28.7 | 16 | 6.2 | 100% Technetium extraction found in HA/HS |
| H2 | AGR | 28.0 | 15.8 | 3.1 | Technetium extraction confirmed |
| H3 | AGR | 29.9 | 13.6 | 3.3 | Methods of dealing with technetium tested |
| H4 | AGR | 28.12 | 14.6 | 3.7 | Flowsheet and equipment modifications tested |
| H5 | BWR | 33.4 | - | 4.9 | Final confirmation of flowsheet |

TABLE 4

Compositions of uranium product from miniature pilot plant
(corrected to basis of reference fuel, 40 Gwd/tU burn-up, five year-cooled)

| Uranium product (UP3AP) | Pu alpha Bq/g U | Np 237 Bq/g U | Tc 99 ug/g U | Ru 106 Bq/g U |
|----------------------------|--------------------|------------------|-----------------|------------------|
| Pilot plant | <2 | <1 | <1 | <200 |
| Specifi- cation | 208 | 42 | 4 | 10000 |

The original THORP flowsheet showed three aqueous waste streams containing hydrazine (from UP2, 4 and 5) which had to be destroyed before they could be evaporated. This added to the cost and complexity of the plant. Deleting the second UP cycle removed two of these streams but at this stage of

flowsheet development, the UP2 HAN feed was stabilised by hydrazine thus giving rise to hydrazine in its aqueous waste stream. A fully active trial was therefore carried out to determine whether the hydrazine was necessary to stabilise hydroxylamine in this contactor. The results showed that HAN alone was stable and gave similar DFs to the mixed reagent thus allowing hydrazine to be omitted and hence simplifying the waste disposal flowsheet.

Parallel flowsheet development work on the plutonium purification cycles showed that the original provision of two cycles in this flowsheet was also unnecessary since the product specification was met by the first of these. This allowed the second plutonium purification cycle to be deleted to leave a THORP chemical flowsheet consisting of three solvent extraction cycles only.

6. CONCLUSIONS

The chemical development work carried out for THORP has allowed a flowsheet to be adopted using three solvent extraction cycles only. This has considerably reduced the size, complexity and cost of the plant and has reduced the number of waste streams requiring treatment. Further assessment of the overall process showed that the presence of hydrazine in one waste stream had a significant effect on the waste treatment processes. Flowsheet trials showed that hydrazine could be omitted with no adverse consequences thus allowing the deletion of the hydrazine treatment processes in the wastes area.

Major contributors to these simplifications of the THORP process have been the development of an efficient uranium purification cycle using novel principles to obtain decontamination from neptunium and the ability to test the whole flowsheet under fully realistic highly active conditions, thus providing the essential confidence in the results.

The work has demonstrated the value of integrating the research and development closely with the design process so that each can influence the other, leading to an efficient process and a high degree of confidence in its performance.

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Fig 1. Thorp Chemical Separation Plant

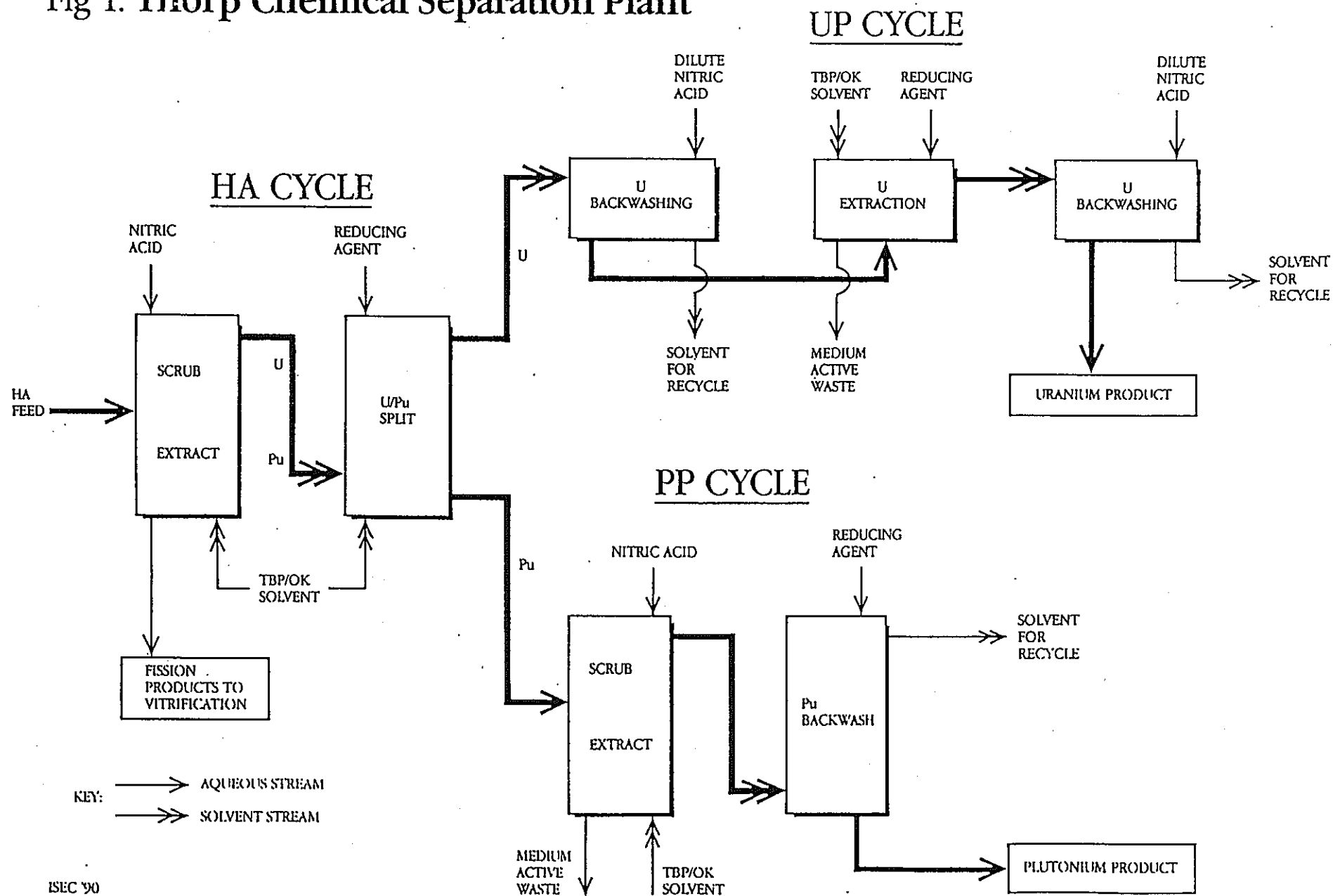


Fig 2. Thorp UP Cycle

