**Purex Process Improvements for PU and NP Control in Total
Actinide Recycle Flowsheets**

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ABSTRACT

Significant improvements are required in the Purex process to optimise it for Advanced Fuel Cycles. Two key challenges we have identified are, firstly, developing more efficient methods for U/Pu separations especially at elevated Pu concentrations and, secondly, improving recovery, control and routing of Np in a modified Purex process.

A series of Purex-like flowsheets for improved Pu separations based on hydroxamic acids and are reported. Purex-like flowsheets have been tested on a glovebox-housed 30-stage miniature centrifugal contactor train. A series of trials have been performed to demonstrate the processing of feeds with varying Pu contents ranging from 7 – 40% by weight. These flowsheets have demonstrated hydroxamic acids are excellent reagents for complexant stripping of Pu being able to achieve high decontamination factors (DF) on both the U and Pu product streams and co-recover Np with Pu. The advantages of a complexant-based approach are shown to be especially relevant when AFC scenarios are considered, where the Pu content of the fuel is expected to be significantly higher.

Recent results towards modifying the Purex process to improve recovery and control of Np in short residence time contactors are reported. Work on the development of chemical and process models to describe the complicated behaviour of Np under primary separation conditions (i.e. the HA extraction contactor) is described. To test the performance of the model a series of experiments were performed including testing of flowsheets on a fumehood housed miniature centrifugal contactor train. The flowsheet was designed to emulate the conditions of a primary separations contactor with the Np split between the U-solvent product and aqueous raffinate. In terms of Np routing the process model showed good agreement with flowsheet trial however much further work is required to fully understand this complex system.

INTRODUCTION

The UK has undertaken Purex nuclear fuel reprocessing, both in industrial deployment and research and development for many years. There are currently two reprocessing plants at Sellafield treating spent fuel from both the UK and abroad. The older of the two plants, Magnox

Reprocessing commissioned in 1965, reprocesses fuel from the UK's first generation of Magnox reactors. The more modern Thorp plant (commissioned in 1996) was designed to treat oxide fuel from both UK (for example AGR fuel) and foreign customers. The UK also operated a facility at Dounreay to process fast reactor fuel to support operation of the DFR.

Besides operation at industrial scale, in order to maintain and support UK nuclear strategy in aqueous reprocessing research is undertaken to anticipate future developments in the Nuclear Fuel Cycle and maintain a capability to respond to the challenges for fuel reprocessing technology which will emerge from 'Advanced Fuel Cycle Strategies'.

Developments in Purex technology to support current industrial operations are primarily based on maintaining and justifying safe plant operations, and achieving reductions in effluent and waste volumes, and therefore costs.

However, at a more strategic level to support Advanced Fuel Cycles other issues become important such as reducing the radiotoxicity of high-level waste, reducing uncertainties about the long-term safety of waste repositories, utilisation of the energy potential in the fissionable isotopes present in spent fuel and eliminating potential sources of weapons material (proliferation resistance).

To support the UK's requirements Nexia Solutions undertakes research on Purex process improvements. To these ends, consideration is given as to how nuclear fuel cycles might develop in the future, what scope there will be for using aqueous and Purex based fuel reprocessing as part of these 'Advanced Fuel Cycle Strategies' and what challenges they present for Purex process technology. [1]

ADVANCED FUEL CYCLE STRATEGIES

There are numerous possible Advanced Fuel Cycle (AFC) scenarios including open, and partially or fully closed variants. [2] Inevitably, these AFC scenarios give rise to numerous reprocessing options. Currently the UK has the capability to operate a partially closed fuel cycle by reprocessing and reusing plutonium in MOX fuel, although there are currently no reactors licensed to use MOX fuel in the UK. A significant mass of civil Pu has been accumulated through reprocessing operations in the UK and it is reasonable to consider that one option is to reuse this Pu in a next generation of LWR reactors.

Beyond this the likely path for recycle options is less clear, although it is possible that the two major challenges would be modifying the Purex process to be compatible with the recycle of Minor Actinides (Np, Am, Cm) and designing aqueous flowsheets with the ability to handle very high burn-up fuels with much greater Pu content.

A desire to minimise the longterm radiotoxicity of spent nuclear fuel would require the recycle of the Trans Uranic (TRU) elements, as after 300 years the radiotoxicity of fuel is effectively due to the presence of Pu and the MAs. Assuming hydrometallurgical processing continues to be the

technology of choice in the foreseeable future at the industrial scale for the treatment of spent nuclear fuel then, it is generally accepted that some form of modified Purex process would be utilized to recover U, Np and Pu and that this would be integrated with a process for the recovery of the minor actinides, Am and Cm.

Such a fuel cycle would necessitate the use of reactors with fast neutron fissioning, with the minor actinides separated and returned in the form of targets or mixed fuels e.g. co-processeded U/Np/Pu fuels. A schematic of how this fuel cycle may evolve is shown in Figure 1.
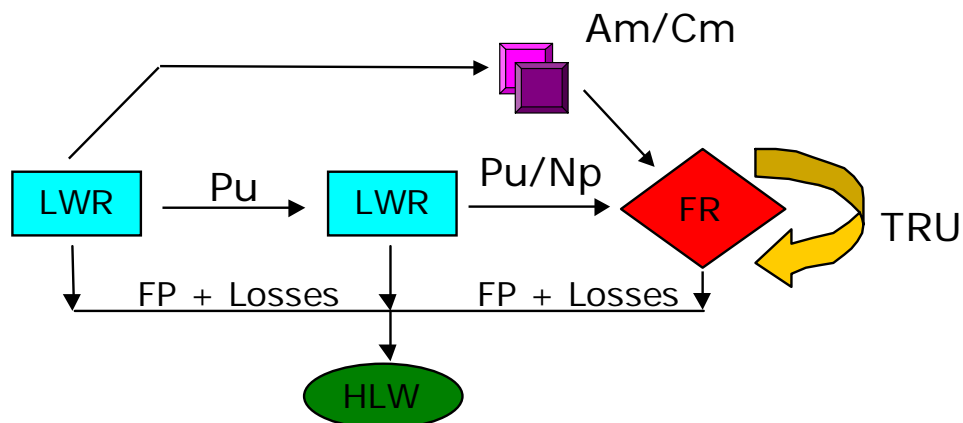
Fig. 1. Possible advanced fuel cycle scenario showing evolution from LWR through MOX to fast reactors

WORK PROGRAMME

Significant improvements are required in the Purex process to optimise it for Advanced Fuel Cycles. These improvements are focused on minimising environmental impact e.g. effluent and waste arisings and maximising the safety and security of processes, and thereby minimising spent nuclear fuel processing costs. To these ends, our own research efforts have been directed towards:

- Developing more efficient methods for U/Pu separations;[6, 7]
- Improving recovery, control and routing of Np in a modified Purex process; [1, 9]
- Equipment and flowsheet testing of short residence time solvent extraction equipment, namely centrifugal contactors; [3,4]
- Continuous improvement and development of solvent extraction process models; [5]
- Developing single cycle flowsheets. [5]

This work described herein will detail results of the development of Purex-like flowsheets for improved Pu separations based on hydroxamic acids. Hydroxamic acids have been proposed as salt-free reagents for the complexant stripping of Pu from U-loaded solvent cf. reductive stripping with hydroxylamine. Recent results on modifying the Purex process to improve recovery and control of Np in short residence time contactors are also presented.

PLUTONIUM CONTROL IN ADVANCED FLOWSHEETS

In Purex plants plutonium is conditioned to the tetravalent state in nitric acid and co-extracted with U in the primary separation cycle. It is then separated from U in a second bank of contactors by reductive back washing from the solvent. Early processes developed for U/Pu separations whilst effective in giving U and Pu products with very high specifications in terms of decontamination factors often used salt-bearing reducing agents, e.g. ferrous sulphamate, to achieve the reduction of Pu(IV) to the almost inextractable Pu(III) state. A significant advancement in U/Pu separations was the adoption of a salt-free flowsheet based on U(IV) stabilised with hydrazine, and it is this technology which is used in modern reprocessing plants. The reduction of Pu(IV) by U(IV) is both strongly thermodynamically favoured, rapid even at quite high acidity and adds no salt waste to the Pu stream.

However, the reference fuel for a Purex process using U(IV) for U/Pu splitting is typically an oxide fuel with one or less percent by mass Pu (post-irradiation). It is anticipated that fuels reprocessed for AFC scenarios would contain much higher Pu contents, possibly tens of percent, especially if a policy of Pu breeding is adopted. There are significant drawbacks with the use of U(IV)/hydrazine, and many of these are exacerbated with increased Pu content of the fuel. For higher Pu content feeds ($> 5\%$) then the mass of U(IV) required quickly becomes a significant if not majority proportion of the total mass of the U product – which in process terms is clearly unacceptable. In addition use of U(IV) results in isotopic dilution of enriched U. [Further issues on the stability and control of such a flowsheet would arise due to the lower distribution of U(IV) which results in a trade off of DF U vs. DF Pu. The consumption of hydrazine through catalytic cycles with Tc – which puts significant constraints on operation of the process – would also be expected to be significantly enhanced.

Although under many AFC scenarios it is probable that to some extent the U and Pu could be co-processed with a significant fraction of U accompanying the Pu product, and eventually for very high Pu content fuels a U/Pu separations step may be abandoned altogether. This withstanding, if during fuel cycle evolution maximum use is made of a country's existing plant infrastructure a requirement to maintain higher-than-needed specification on products may persist. For example, excess U may require decontamination so that it can be handled, stored and eventually disposed of as a low alpha-bearing stream.

To achieve efficient U/Pu separations in AFC flowsheets one option is to replace the reductive stripping of Pu by complexation: Pu(IV) is selectively complexed by a hydrophilic ligand and stripped in to the aqueous phase. The advantages of complexation include fast kinetics, relative temperature insensitivity compared to redox reactions and no reoxidation of Pu(III), hence no need for a stabiliser and likely improved criticality control.

Hydroxamic acids (e.g. AHA, Acetohydroxamic acid) are small, organic ligands that selectively complex tetravalent [e.g. Np(IV), Pu(IV)] over hexavalent actinides [U(VI)] in nitric acid. The resultant complexes are hydrophilic allowing the selective back-extraction of tetravalent actinides from uranium-loaded solvent. [6]

To support flowsheet development, distribution data for the Pu:AHA system as a function of a series of process parameters e.g. acidity, Pu:AHA ratio, Pu-loading, U-loading, has been collected at macro and trace Pu levels. [7] The data show that Pu is effectively retained in the aqueous phase by the complexant acetohydroxamic acid (AHA); for example, data as a function of acidity show that D is less than or equal to 0.05 at 1M HNO_3.

To determine the effectiveness of hydroxamic acids at separating Pu from U under conditions relevant to AFCs a series of alpha-active flowsheet trials have been performed on a glovebox-housed centrifugal contactor rig using U/Pu/Tc-active simulant solutions. [8] In all three trials were performed at 7, 20 and 40% wt Pu by mass. The testing of three trials allowed to us optimise the flowsheet in terms of process parameters such as acidity, number of SX stages, product volumes and decontamination factors of products (U, Pu). A schematic of the generic flowsheet tested in shown in Figure 2. Results for the three trials in terms of feeds, products and decontamination factors (DFs) are given in Table 1
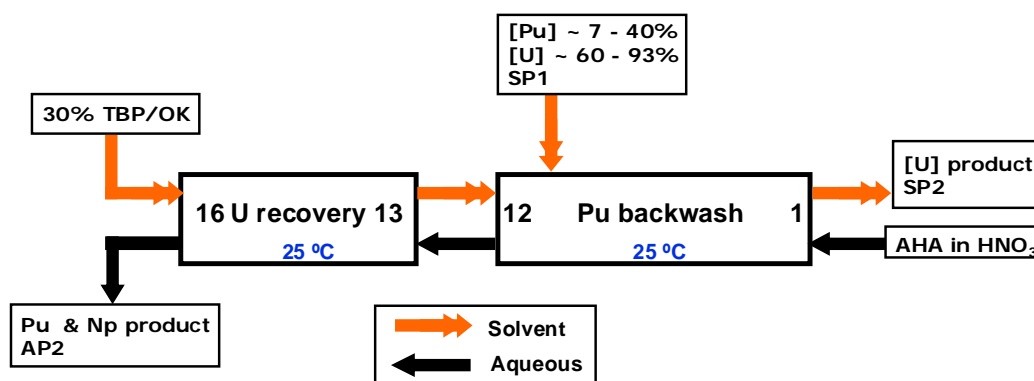

Fig. 2. Experimental testing of U/Pu separations flowsheets

A first flowsheet trial was successfully undertaken on an initial feed of 7% Pu by mass heavy metal using a glovebox-housed 24-stage centrifugal contactor rig. The U product showed a DF Pu of 1500, the Pu product a DF U of 1.3E5 and Tc was routed with the U product, see Table 1. A second trial was undertaken on an initial feed of 21% Pu by mass heavy metal which demonstrated that, a high specification can be achieved on both the U and Pu streams, even with such a large mass of Pu present. Based on the final two samples of flowsheet operation, the DFs obtained for Pu in U and U in Pu product streams were >64000 and >5000 respectively.

In order to further extend the evaluation of the performance of AHA in separating Pu from U-loaded solvent, a third flowsheet trial was run with a feed containing 40% Pu by mass heavy metal. The flowsheet conditions were modified from the previous trials to take account of the high 40% Pu content of the feed and to optimise the DF for Pu in the U product. Optimisation of the backwash conditions gave a Pu in U DF of 1.45×10^6. This was achieved at the expense of the U in Pu product DF which was 360. The higher Pu loading of the flowsheet influenced Tc routing with approximately 60% of Tc extracted in the 'HA/HS contactor' and then split 50:50 between the U and Pu products in the split contactor.

It is apparent that the optimisation of the flowsheet parameters has improved the Pu DF from a modest 1000 in the first trial to in-excess of 1.45×10^6 in the final trial, despite an almost six-fold increase in the Pu content of the feed. The main parameters responsible for the improved performance are:

- An increase in the number of strip stages;
- Reduction in aqueous acidity;
- Reduction in S/A ratio;
- Improved analysis of Pu in U.

However, it is apparent that the optimisation of the strip conditions enhances the backwashing of uranium from the solvent, increasing the re-cycle of uranium within the split cascade and resulting in higher levels of uranium in the Pu product. A reduction in the U DF, from 1.35×10^5 in the first trial to 360 in the final trial was observed.

Table I. Flowsheet Trial Parameters and Performance for a Series of Pu Stripping Trials

Flowsheet Conditions		PuX01	PuX02	PuX03
S/A ratio	PuS	5.6	2.9	1.5
	URX	0.9	0.5	0.5
Strip Feed	[HNO$_3$] / M	0.5	0.2	0.2
	[AHA] / M	0.5	0.5	0.5
	AHA : Pu(IV)	4.2:1	3.3:1	4.4:1
SP2	[Pu] mg/l	3	0.2	0.0125
	[U] g/l	70	49	28
AP2	[Pu] g/l	29	38	27
	[U] mg/l	3	25	115
DF	Pu DF	1000	60000	1.45×10^6
	U DF	130000	5500	360

In summary, these U/Pu separation trials have demonstrated that an aqueous processing flowsheet, based upon an AHA split, is capable of achieving high product specifications for both U and Pu products, even for Pu feeds up to 40% (w/w). The performance is comparable with the requirements for advanced flowsheets.

NEPTUNIUM CONTROL IN ADVANCED FLOWSHEETS

The control of Np is an important issue in the reprocessing of spent nuclear fuel using the PUREX process. With respect to Sellafield reprocessing operations and the U product, Np is considered a contaminant and decontamination factors (DFs) of over 1000 are required and achieved on the reprocessed U in the Purex Chemical Separation plants of Magnox and Thorp.

Depending upon the prevailing conditions Np may be present in any of three oxidation states, Np(IV), Np(V) and Np(VI), making the control of Np routing difficult [9]. In the 1st solvent extraction cycle of the PUREX process any Np(V) present will be rejected to the aqueous raffinate and hence to the High Level Waste (HLW). In contrast any Np(IV) or Np(VI) present

will extract into the solvent stream and continue through the process with the extracted U(VI) and Pu(IV)

However, these three oxidation states of Np are easily interconvertible under Purex process conditions – the equilibrium position being highly dependent upon a number of process parameters and species, including acidity, nitrous acid (and scavengers), uranium loading and temperature. In processes where it is intended that Np is directed to the HLW, it is necessary to maintain Np as inextractable Np(V) to avoid the need for further decontamination of the U or Pu products from Np. However, in scenarios where it is desired to leave the raffinate free from all transuranic species – which are the predominant long-lived alpha emitters - then it is necessary to extract the Np in the first solvent extraction cycle. In these scenarios the Np oxidation state needs to be maintained as Np(VI) or, less probably, Np(IV).

Chemical methods of controlling the Np oxidation state which exploit the effects of nitric acid, nitrous acid and temperature are most attractive in the PUREX process as they add no new reagents or salts to the process streams. However, in mixed phase systems, it is more difficult to gain complete control over Np oxidation states in this way. In particular the oxidation of Np(V) to Np(VI) by nitric acid is catalysed by nitrous acid, yet at higher concentrations nitrous acid can act as a reductant for Np(VI). The situation is further complicated by the extraction of nitrous acid and Np(VI) into the solvent.

In order to develop a flowsheet to achieve complete extraction of Np in the primary separation (HA/HS) cycle a thorough understanding of the process chemistry is required. We have been developing a process model to describe the oxidation and extraction behaviour of Np under Purex conditions. The process model includes appropriate algorithms for actinide/acid distribution were possible chemical reaction kinetics relevant to the oxidation and reduction of Np.

A series of aqueous only (HNO_3) and two-phase (HNO_3 / 30% TBP/OK) batch experiments were carried out in order to check the validity of the kinetic equations used in the process model to describe the HNO_2 catalysed oxidation of Np(V) by HNO_3. The oxidation of Np(V) in a two-phase system in the presence of U was successfully modelled. These two-phase experiments were particularly illustrative in showing which process parameters increased/decreased Np extraction.

These experiments determined that a number of key parameters were important in defining the rate of Np oxidation:
- Acidity
- Nitrous Concentration
- U concentration
- Temperature

Results for Np oxidation in the presence of U are given in Figure 3. U-loading of the solvent initially increases the rate of Np(V) oxidation; however, above levels of about 30 g/L in the

solvent phase no further enhancement was observed. This is expected as nitrous acid extraction is particularly sensitive to metal loading – being strongly suppressed.

A good description of Np oxidation for a two-phase system in the presence of U was obtained using the process model. This is particularly important, as it is predicted that significant Np oxidation is occurs around the feed stage where significant U concentrations are present. In terms of modelling the effects of U on Np(V) oxidation, key factors to understand, for example, are the nitrous catalysed Np(V) oxidation reaction and the nitrous distribution algorithm in the presence of U at variable temperature.
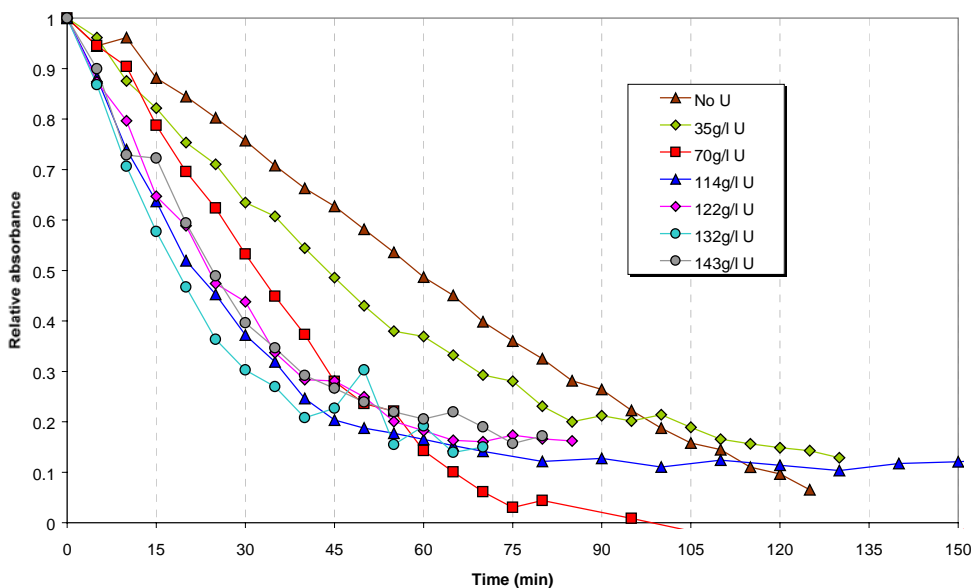

Fig. 3. Two-phase experiments (103.5mg/l Np; 0 to 143g/l U; 4M HNO_3; 1E-3 M HNO_2; S:A = 2; Room Temperature)

In terms of building a process model to understand Np oxidation in a two-phase system we need to understand:
i)   The conditions where fast oxidation occurs [fast meaning significant Np(V) oxidation achieved in minutes];
ii)   And the conditions where slow (or minimal) oxidation occurs [slow meaning tens of minutes]

To further test the performance of the model a U/Np active miniature centrifugal contactor flowsheet trial, designed to emulate a typical extract/scrub section in a modern Purex plant was undertaken. The flowsheet tested used centrifugal contactors and was Pu free. The objective of this first extraction trial was to assess the ability of the model to predict the routing of Np in a system of limited complexity from a chemical and hydrodynamic point of view. It was felt that performing a flowsheet trial designed to split Np between the solvent product and aqueous raffinate was the best option to test our understanding i.e. the strength of our model. A schematic of the flowsheet tested is shown in Figure 4.
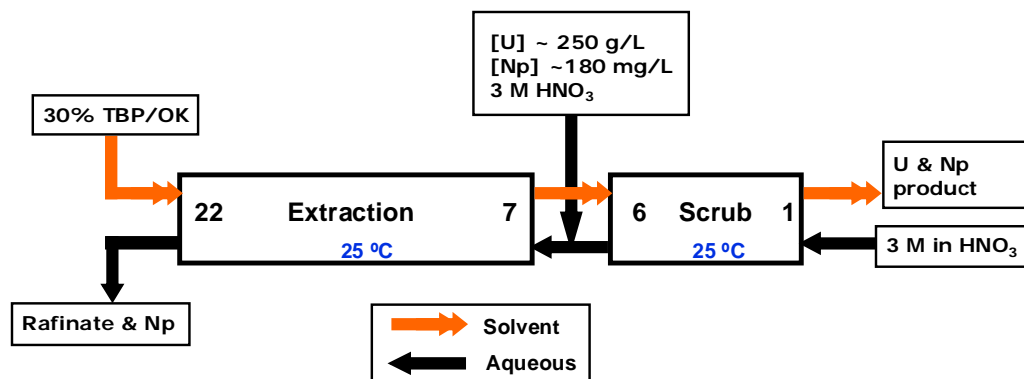
Fig. 4. Experimental testing of Np extraction flowsheet

Details of the experimental set-up and methodology are given in this section below. For the trial run a Np DF of 3, which corresponds to 34% of the Np being extracted, was achieved for the flowsheet operating at steady-state. Predicted and experimental performances for flowsheet steady state were in good agreement for U and acid and reasonable agreement was found for Np profiles. This demonstrates that the model provides an adequate of Np behaviour in a counter-current solvent extraction system.

Although reasonable agreement for Np profiles was obtained, some significant discrepancies were observed. For example, our process model under-predicts organic phase Np concentrations around the feed stage. [A similar, but less significant observation was made for the U solvent profiles, suggesting further optimisation of the hydrodynamic model around the feed stage is requried.] Secondly, the model underestimates the Np recycle in the HS scrub. The reasons for this could be that the rates of Np(VI) reduction reactions are underestimated, or the distribution of Np(VI) is over-predicted by our distribution algorithms.

We are continuing our work on improving the process model concentrating on such areas as the Np reaction kinetics and distribution algorithms for key species such as Np(VI) and nitrous acid. Further flowsheet trials will be performed to test our understanding with a view to developing a flowsheet for complete Np extraction in the primary contactor.

EXPERTIMENTAL METHDOLOGY

Centrifugal contactor rigs of up to 30 stages (1 cm annular centrifugal contactors), arranged in blocks of 2 or 4, housed in either a glovebox or fumehood, were used for the flowsheet trials. Syringe o piston pumps were used for feeds. In-line UV/vis and UV/vis/nIR spectrophotometers coupled to diptips or flowthrough cells were used to monitor concentration and speciation of specific components in various streams. Careful start-up procedures were used when running up the rig at the start of the trial and spectrophotometry used to monitor the approach to steady state

of the key species. During runs the temperature and rotor speeds of the contactors, and flowrates of all product/raffinate streams were measured.

As well as on-line spectrophotometric analysis, metals (Tc, U, Np and Pu) were analysed by a number of other methods, depending on their concentrations, concentrations of interfering species and sample matrices present. In some cases chemical separations were required prior to analysis. The methods employed include:

- Off-line spectrophotometry
- Titrations
- Liquid fluorimetry
- Inductively-coupled plasma mass spectrometry
- X Ray fluorescence
- Alpha spectrometry
- Gamma and low energy photon spectroscopy
- Liquid scintillation counting
- Thermal ionisation mass spectrometry

Titrimetric methods included analyses for acidity in both aqueous and solvent phases using acid-base titrations in the presence of KF (to complex hydrolysable ions) and a potentiometric method in the presence of $MgSO_4$.

Feeds were prepared immediately prior to the trials using standard methods. 30% TBP/Exxsol D80 was prepared and washed to ensure the absence of any degradation products, using standard solvent wash procedures. Np was conditioned to the appropriate oxidation state electrochemically and the purity checked spectrophotometrically.

CONCLUSIONS

Two key challenges in the optimisation of Purex process for AFCs are being we have identified are, firstly, developing more efficient methods for U/Pu separations especially at elevated Pu concentrations and, secondly, improving recovery, control and routing of Np in a modified Purex process.

A series of flowsheets for improved Pu separations based on hydroxamic acids have been tested and hydroxamic acids are excellent reagents for complexant stripping of Pu being able to achieve high decontamination factors (DF) on both the U and Pu product streams and co-recover Np with Pu. The advantages of a complexant-based approach are especially relevant when AFC scenarios are considered, where the Pu content of the fuel is expected to be significantly higher.

A chemical and process model to describe the complicated behaviour of Np under primary separation conditions (i.e. the HA extraction contactor) has been developed. The performance of the model has been tested against a series of two-phase experiments a flowsheet test on a fumehood housed miniature centrifugal contactor train. In terms of Np routing the process model

showed good agreement with flowsheet trial; however much further work is required to fully understand this complex system.

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