Rapid Photochemical Reduction of U(VI) for the Development of New Mixed Metal Oxide Fuel Production Processes

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INTRODUCTION

Within the Advanced Fuel Cycle Programme (AFCP) work has begun on the development of new fuel cycle options needed to meet the demands of an expanded civil nuclear programme while reducing storage and disposal of spent fuels[1-4]. The aim is to develop efficient, flexible, safe processes that reduce costs and secondary wastes with added proliferation barriers.

In this context, for the recycling of U/Pu for mixed metal oxide (MOx) fuel fabrication Lancaster University has developed a rapid and clean photochemical process for the conditioning of U(VI)/Pu(IV) prior to their subsequent precipitation and calcination into homogeneous MOx fuel.

OBJECTIVES

- Develop a process for the conditioning of U(VI) to U(IV)
- Eliminate hazardous reagents such as hydrazine and H_2 gas
- Determine capability of the technology with high heavy metal loadings
- Assess effectiveness of the co-reduction of U(VI) & Pu(IV)
- Increase technology readiness level – target TRL 4

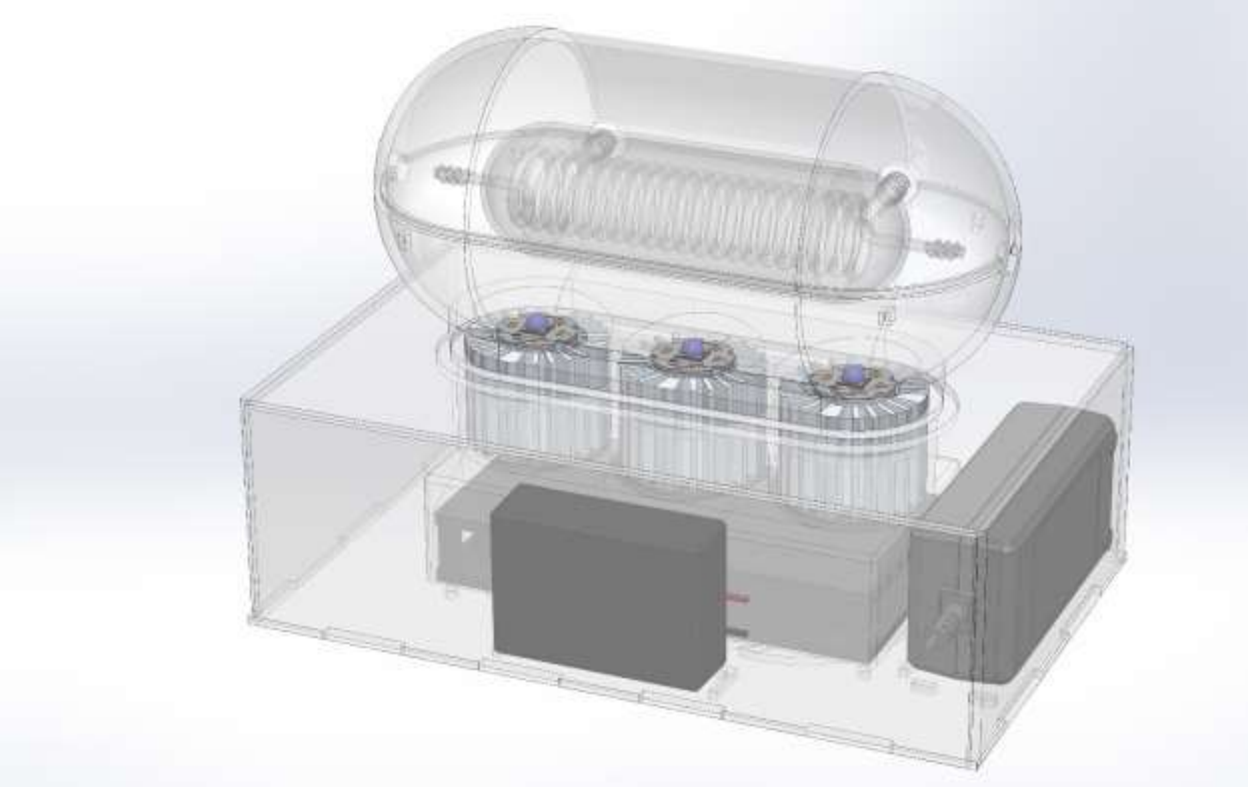
EXPERIMENTAL METHODS

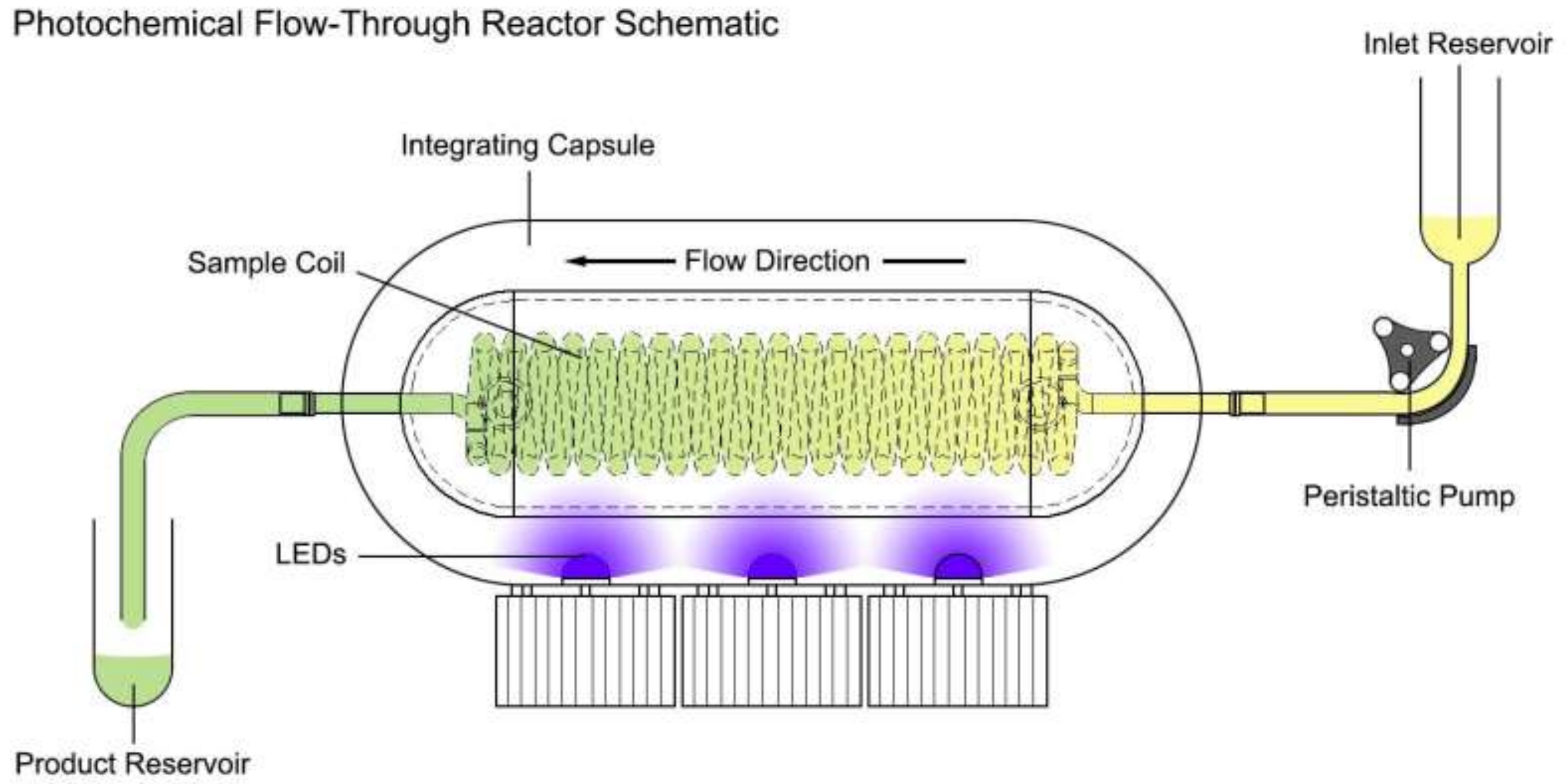
- U and U/Ce (non-active Pu surrogate) solutions in nitric acid are photoexcited by direct illumination with 405 – 410 nm light from LED arrays
- Alcohol-based reductants (isopropanol or butanol) enable the rapid chemical reduction of photoexcited species within the sample liquor
- Hydroxylammonium nitrate (HAN) is added as a nitrous acid scavenger to prevent re-oxidation by HNO_2 – stabilising the photochemically generated product
- Narrow-band LED output avoids further HNO_2 generation from photolytic degradation of HNO_3
- Illuminated residence time is conveniently controlled by solution flow rate, coolant jacket maintains a constant liquor temperature of <29°C

The direct photochemical generation of U(V) and subsequent disproportionation into U(VI) & U(IV) results in a net increase in U(IV) concentration. An α-hydroxyalkyl radical formed the same process facilitates a secondary reductive route and increases overall conversion efficiency.

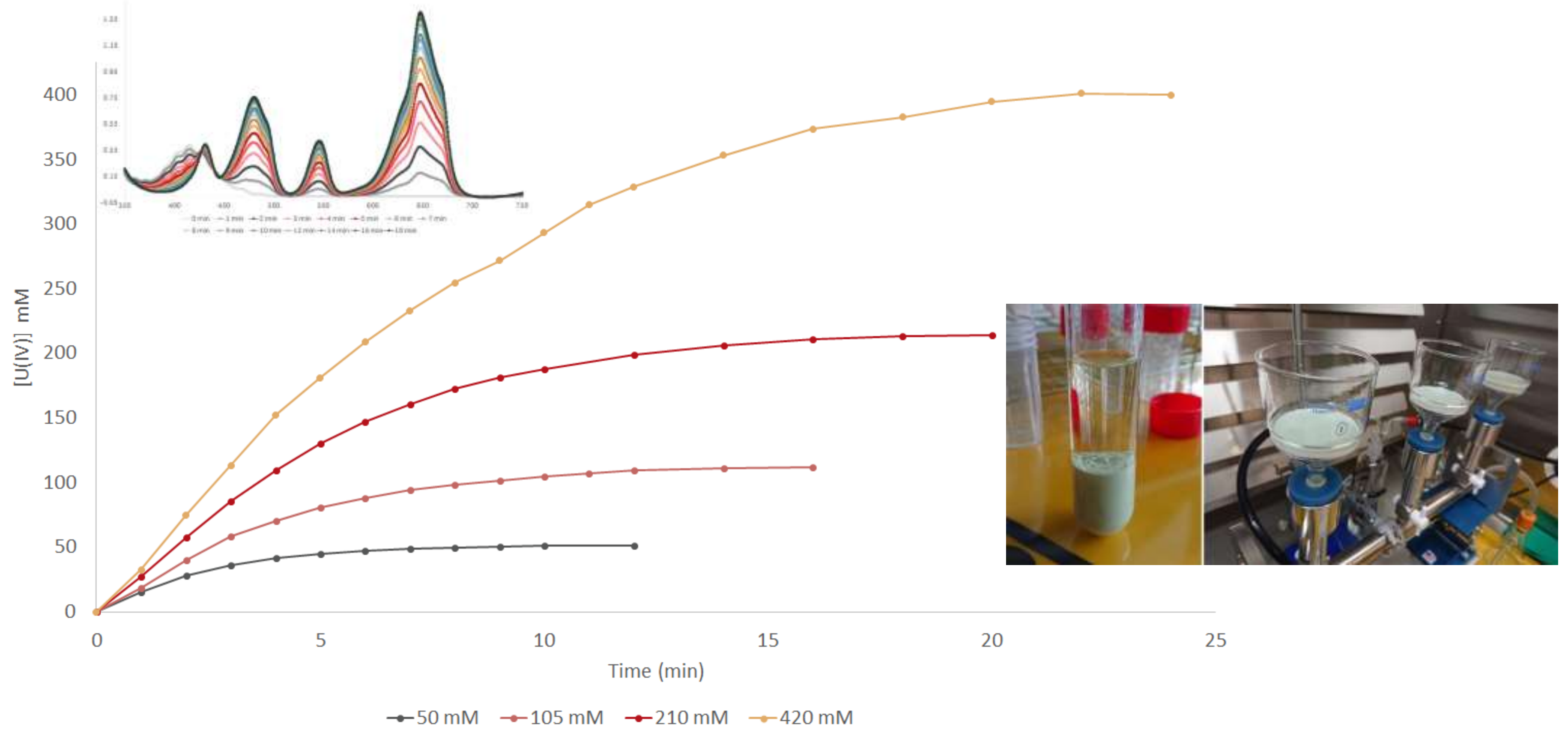
RESULTS

- 100% conversion of U and U/Ce solutions (monitored via UV-Vis spectroscopy) containing up to 100 g/l HM content is achieved within total illumination periods of 10 - 24 min
- Alcohol-based reductants show greater efficiency than hydrazine while effective thermal control allows the use of thermally sensitive reagents such as HAN
- Complete photochemical generation of stable U(IV) and U(IV)/Ce(III) products has been achieved in a hydrazine-free system
- Overall efficiency observed to be greater than the theoretical maximum for a single reductive pathway
- Photochemically generated U(IV)/Ce(III) product streams used directly in the subsequent precipitation of mixed metal oxalate powders





Photochemical Flow-Through Reactor Schematic



PHOTOCHEMICAL REACTOR

Initially developed as a lab-scale small batch reactor during AFCP Phase 1, the photochemical reactor has been re-designed with a flow-through configuration for increased efficiency and greater throughput. Key features include:

- Ultra-high output LED arrays – 12 W radiant flux, 405 – 410 nm peak output λ
- Glass reaction flow coil with increased SA : Vol and integrated coolant jacket
- Light integrating capsule with $BaSO_4$ internal coating for up to 98% diffuse reflectivity

REACTION MECHANISM

Photoexcitation	$UO_2^{2+} + h\nu \rightarrow * UO_2^{2+}$
Primary reductive route	$* UO_2^{2+} + (CH_3)_2CHOH \rightarrow * [UO_2^{2+} \cdots (CH_3)_2CHOH]$
Generation of U(V)	$* [UO_2^{2+} \cdots (CH_3)_2CHOH] \rightarrow UO_2^{+} + (CH_3)_2 \cdot COH + H^+$
U(IV) via disproportionation	$2UO_2^{+} + 4H^+ \rightarrow U^{4+} + UO_2^{2+} + 2H_2O$
Secondary reductive route	$(CH_3)_2 \cdot COH + UO_2^{2+} / UO_2^{+} \rightarrow (CH_3)_2CO + UO_2^{+} / U^{4+} + H^+$

ONGOING & FUTURE WORK

- Polar-coordinate theoretical model is being developed to determine the total amount of light absorbed and to begin quantification on quantum efficiencies
- Further refinement of reactor design for optimised conversion rates & reagent concentrations
- A duplicate photochemical reactor was tested with U and Pu in the NNL's PuMA Lab at Sellafield to demonstrate co-reduction of U(VI) and Pu(IV)

REFERENCES

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3. Taylor, R.J. and F. Livens, *Advanced Reprocessing Research and Development Needs - Position Paper, 2014, 22*
4. Nuclear Innovation and Research Advisory Board, "*UK Nuclear Innovation and Research Programme Recommendations*", *HM Government, 2016*

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Work Package 1 – Dissolution

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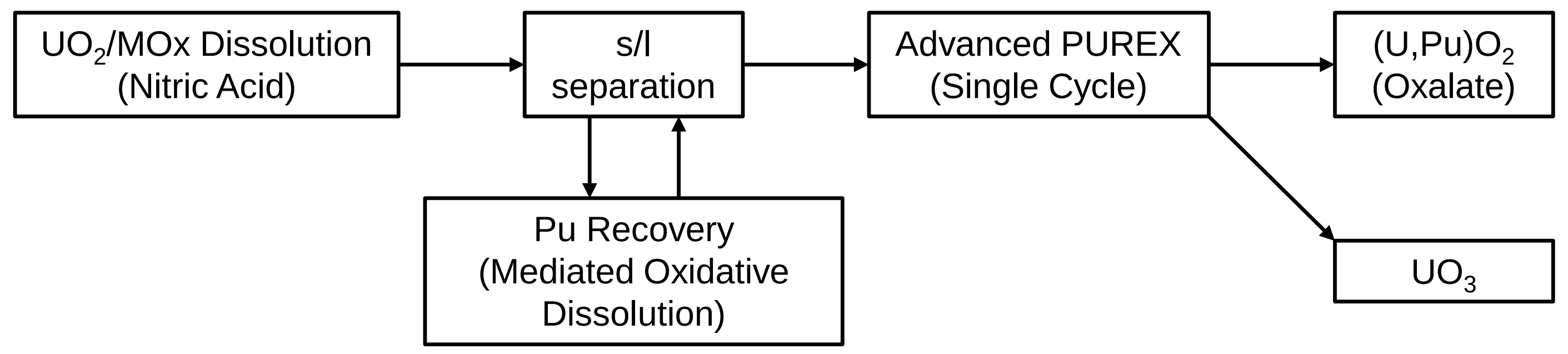
INTRODUCTION & OBJECTIVES

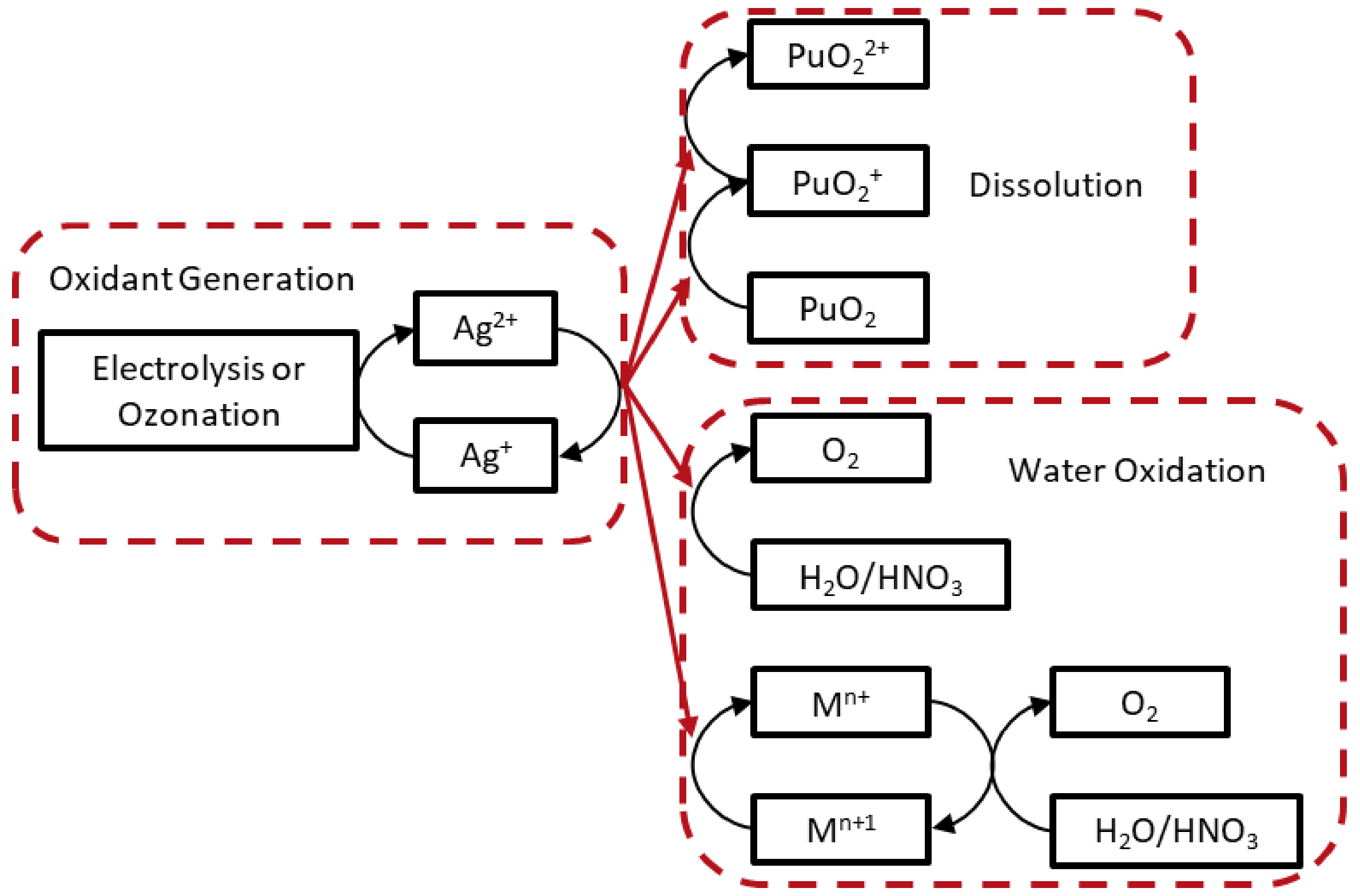
With new light water reactors and advanced reactors such as Generation IV fast reactors having the ability to more efficiently utilise recycled uranium and plutonium as mixed oxide (MOx) fuels, future options to close the fuel cycle would require advanced reprocessing capability that could deal with spent MOx fuels as well as uranic fuels, such as that shown in the overall flowsheet concept shown below.



However, an efficient dissolution of MOx fuel (first step) would be required for any future advanced reprocessing. A method for this dissolution is through the use of an electrogenerated Ag^{2+} as an advanced oxidation process (AOP) that may promote the oxidative dissolution of the spent fuel. Thus, we explored the kinetics of this new process for simulated spent MOx and simulated spent LWR fuel dissolutions.

Thus, here we present the results of experiments seeking to address the following **knowledge gaps**, and develop a mechanistic understanding of the dissolution (corrosion) process:

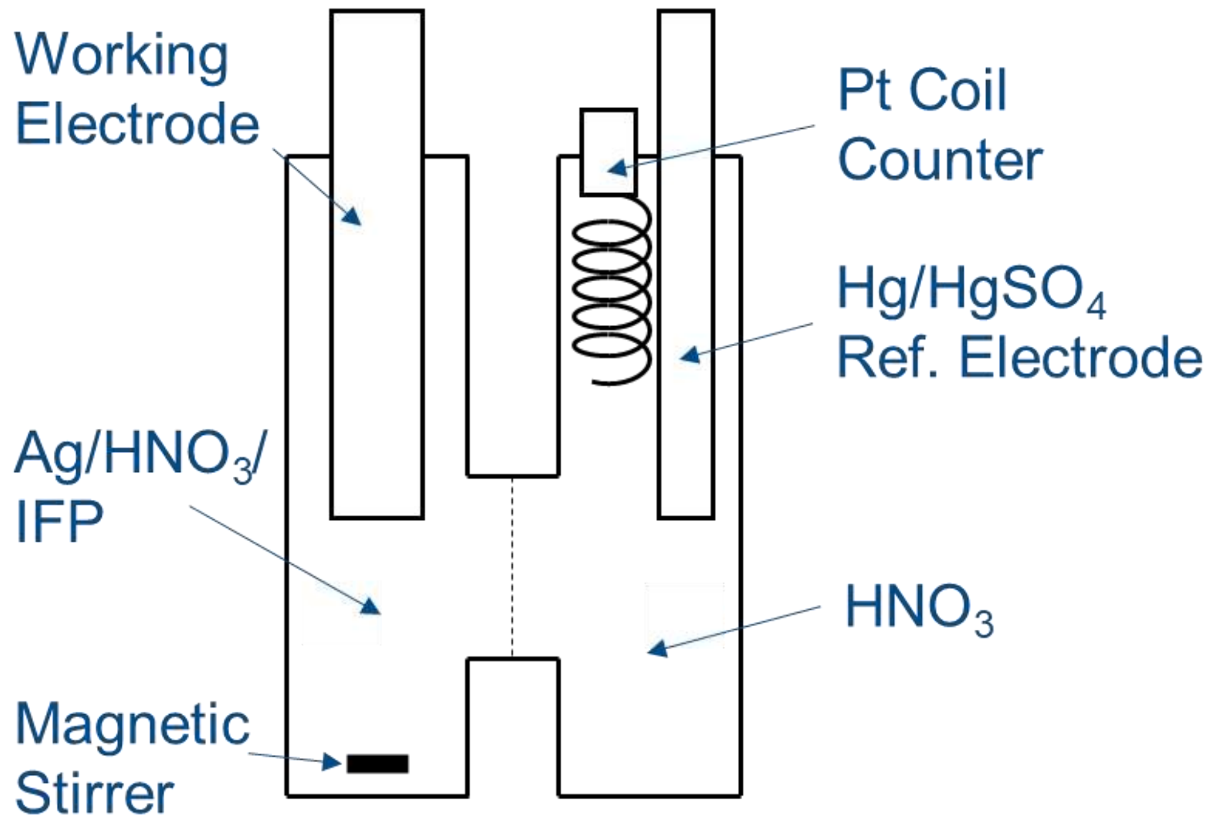
1. understanding the mechanisms of novel mediator (Ag^+/Ag^{2+}) catalysed MOx dissolution;
2. assessment of the effect of insoluble fission products (IFP) on the efficacy of the Ag^+/Ag^{2+} dissolution mediators.
3. assessment of ozonolysis to replace electrochemical silver oxidation;
4. understanding the role of nitrous acid in the dissolution of high Pu content MOx



MATERIALS & METHODS

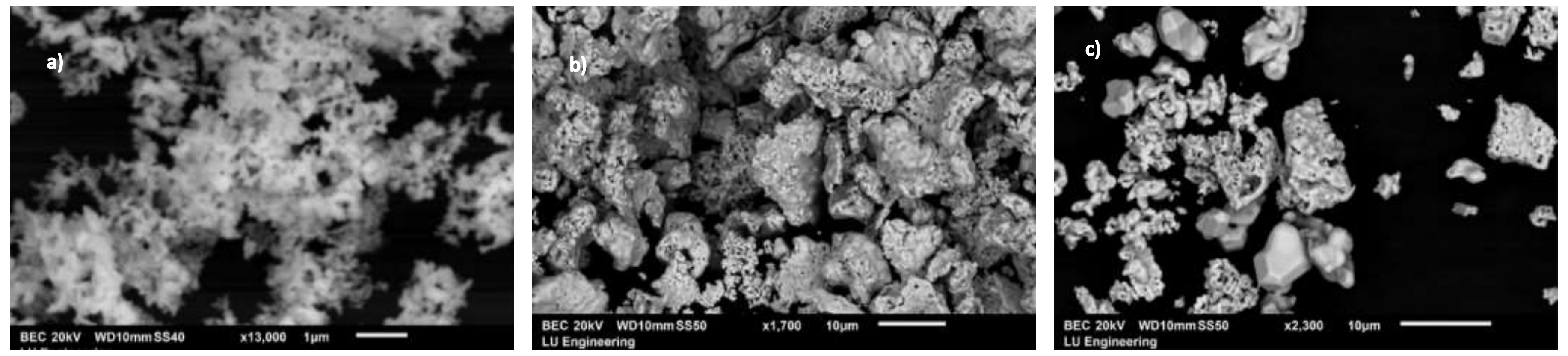
All electrochemical experiments were conducted using a WaveVortex 10 Electrode Rotator with a E6R1 ChangeDisk RRDE Tip from Pine Research. This system allowed for RRDE experiments to be conducted on a variety of materials. Experiments were conducted within an electrochemical H-cell with each side of the cell partitioned by a porous glass frit (porosity 10-20μm) in order to keep solutions separate whilst maintaining electrical continuity throughout the cell. A $Hg/HgSO_4$ reference electrode was also used. All experiments were conducted at room temperature.

H-cell and Electrode Rotator



RESULTS – Effect of IFPs on electrogeneration of Ag(II)

- Exploration of the fundamental electrochemistry of the Ag(I)/Ag(II) system has shown the electrogeneration of Ag(II) to be an EC' process (i.e. an electrochemical step, E, followed by a chemical step, C')
- kinetic rate parameters for both steps have been determined both on commonly used platinum electrodes and on boron-doped diamond (BDD).
- Baseline electrochemical characterization experiments have also been conducted as a function of headend-relevant nitric acid concentrations, in the absence and presence of IFP particles.



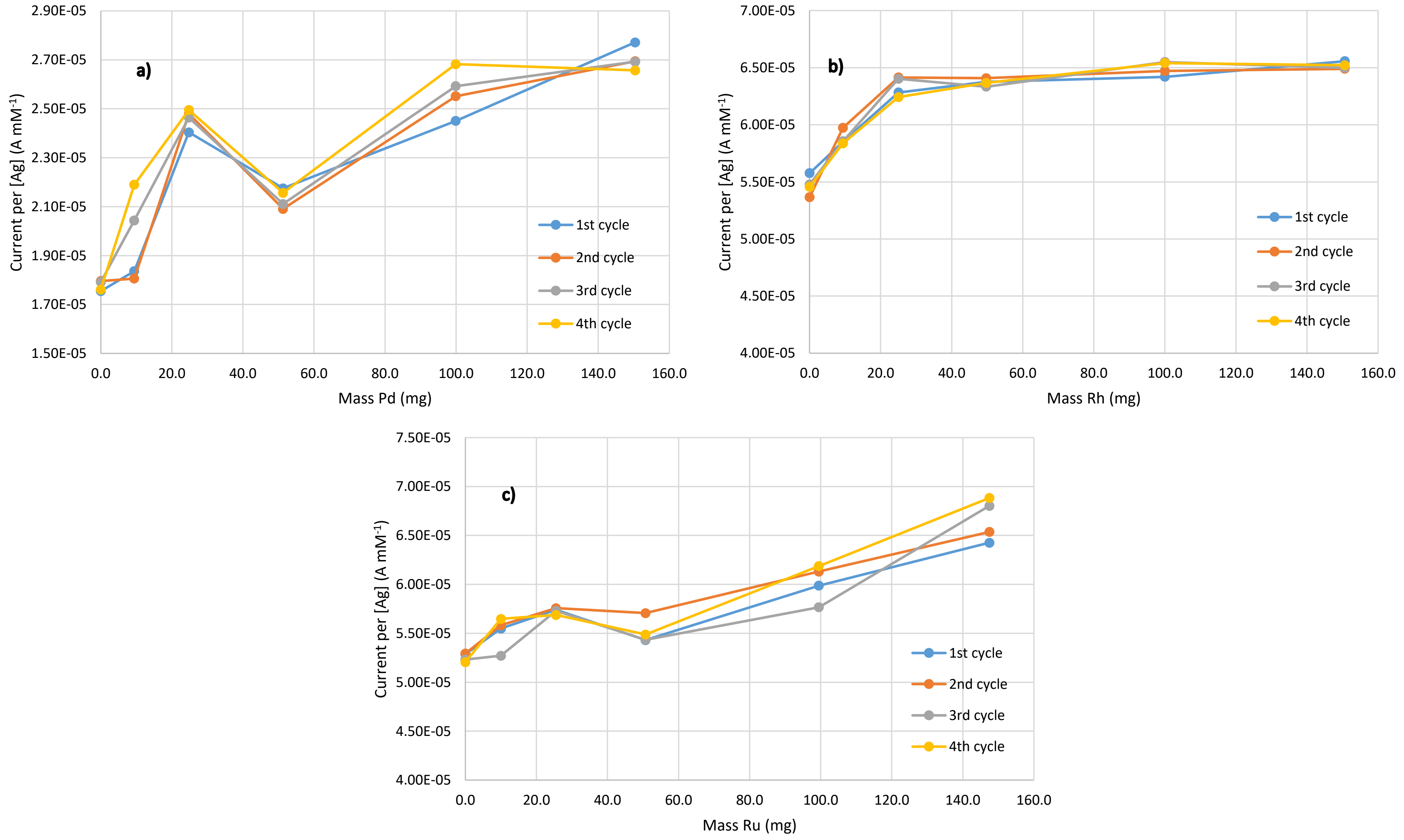
Images of a) Pd, b) Rh, and c) Ru particles used as IFP simulants.

Through the use of quantitative analytical models of the voltammetric behaviour of EC' processes derived by Nicolson and Shain, as shown in the equations below, we can see that an increase in the rate constant for the chemical step, k_f, will result in an increase in the overall current.

$$i = nFA\sqrt{aD_O}C_O^*\sqrt{\pi}\chi(at)$$

$$\chi(at) = \frac{1}{\sqrt{\pi}}\sum_{j=1}^{\infty}(-1)^{j+1}\sqrt{\left(\frac{k_f}{a}+j\right)}\exp\left[-\frac{jnF}{RT}\left(E-E_{1/2}\right)\right]$$

Therefore, by plotting [Ag] corrected current at 1.25 V *vs* mass of IFP particles added for the 1st, 2nd, 3rd, and 4th cyclic voltammogram cycles the effect of IFPs on the rate of Ag(II) generation has been successfully demonstrated that the rate parameter for the C' step increases with increasing amounts of added IFP simulant.



Plots of [Ag] corrected current at 1.25 V *vs* mass of a) Pd, b) Rh, and c) Ru particles added for the 1st, 2nd, 3rd, and 4th cyclic voltammogram cycles.

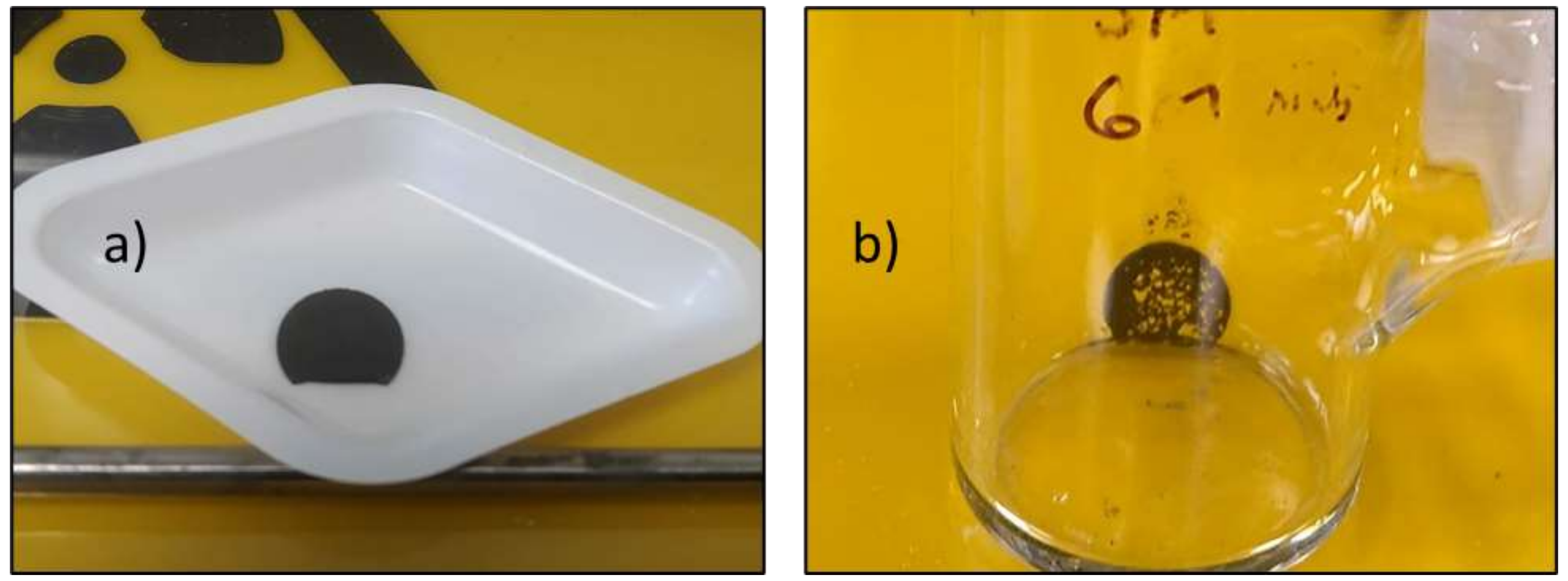
RESULTS – Dissolution of SIMFuel

Initial dissolution studies using a SIMFuel pellet simulating a UK Advanced Gas-cooled Reactor spent fuel pellet at 25 GWd/tU burnup have been conducted as part of the commissioning/testing of the dissolution rig with the aim to;

1. confirm that spent fuel dissolution could be achieved in the rig under conditions relevant to headend
2. establish baseline behaviour in support of future studies.

To maximise the possibility of inducing pellet dissolution, the commissioning test dissolution was performed at both a high nitric acid concentration and in the presence of electrogenerated Ag(II).

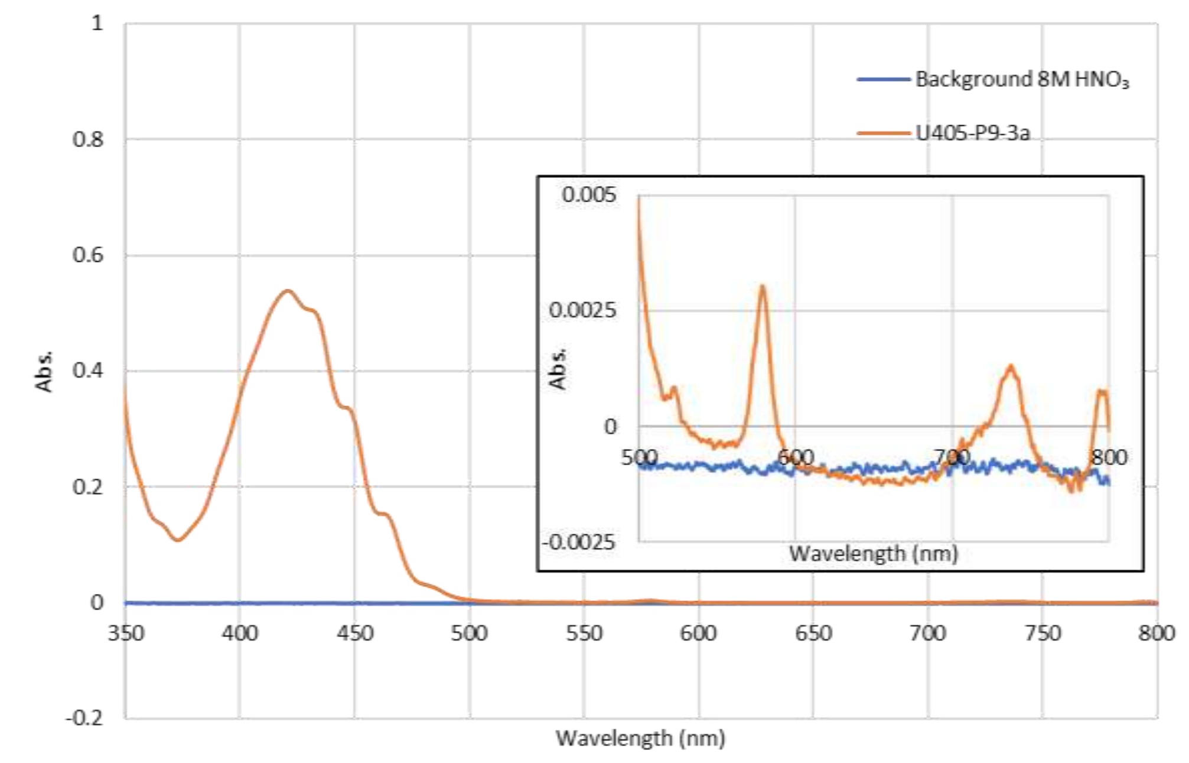
- In order to generate Ag(II) as an oxidation mediator, 1.3 V *vs* $Hg/HgSO_4$ was applied for a period of two hours at the Pt macroelectrode, which was rotated at 600 rpm to provide good mass transfer of both Ag(I) to the electrode surface for electrooxidation to Ag(II) and the so produced Ag(II) away from the electrode surface to that of the SIMFuel pellet.
- Ag(II) could be seen to be formed at the electrode surface, and the supernatant solution was seen to gradually turn a yellowy-green colour.
- Visual examination of the pellet at the end of the dissolution test revealed that it had become heavily perforated, indicating that successful dissolution has occurred.



Images of 25 GWd/tU SIMFuel both a) before and b) after dissolution study

Resulting supernatant solution from the dissolution was analysed using UV-vis spectrophotometry.

- The main component present was seen to be U(VI) based on the characteristic strong peaks between 375 and 475 nm
- Two less intense peaks seen at 580 nm and 737 nm respectively can be assigned to Nd^{3+}, the second largest component by weight present in the SIMFuel used.
- ICP-OES measurements are ongoing in order to determine whether any of the IFP elements have been dissolved.



CONCLUSIONS

An investigation into the effect of IFPs on the rate of Ag(II) generation has demonstrated that the rate parameter for the C' step increases with increasing Pd loading – and that this IFP-enhanced rate of Ag(II) reduction is proportional to the surface area of IFP particles present in solution.

An initial dissolution study has also been carried out, demonstrating efficient dissolution of a 25 GWd/tU SIMFuel pellet within the rig established at Lancaster. Further analysis of the data acquired for this dissolution is ongoing in order to determine: (i) the extent to which different components of the SIMFuel have been dissolved; and (ii) the relative contributions to that dissolution of simple nitric acid driven and Ag(II)-driven oxidative processes.

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Process modelling & simulation

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INTRODUCTION

AFCP is developing a an Advanced PUREX process based on a simplified single solvent extraction cycle with increased proliferation barriers and reduced costs and wastes.

A key gap in the development of the Advanced PUREX process is controlling the routing of technetium (Tc) to keep it away from the uranium product streams. Models for Tc in the process are essential to simulate flowsheets that can achieve this aim.

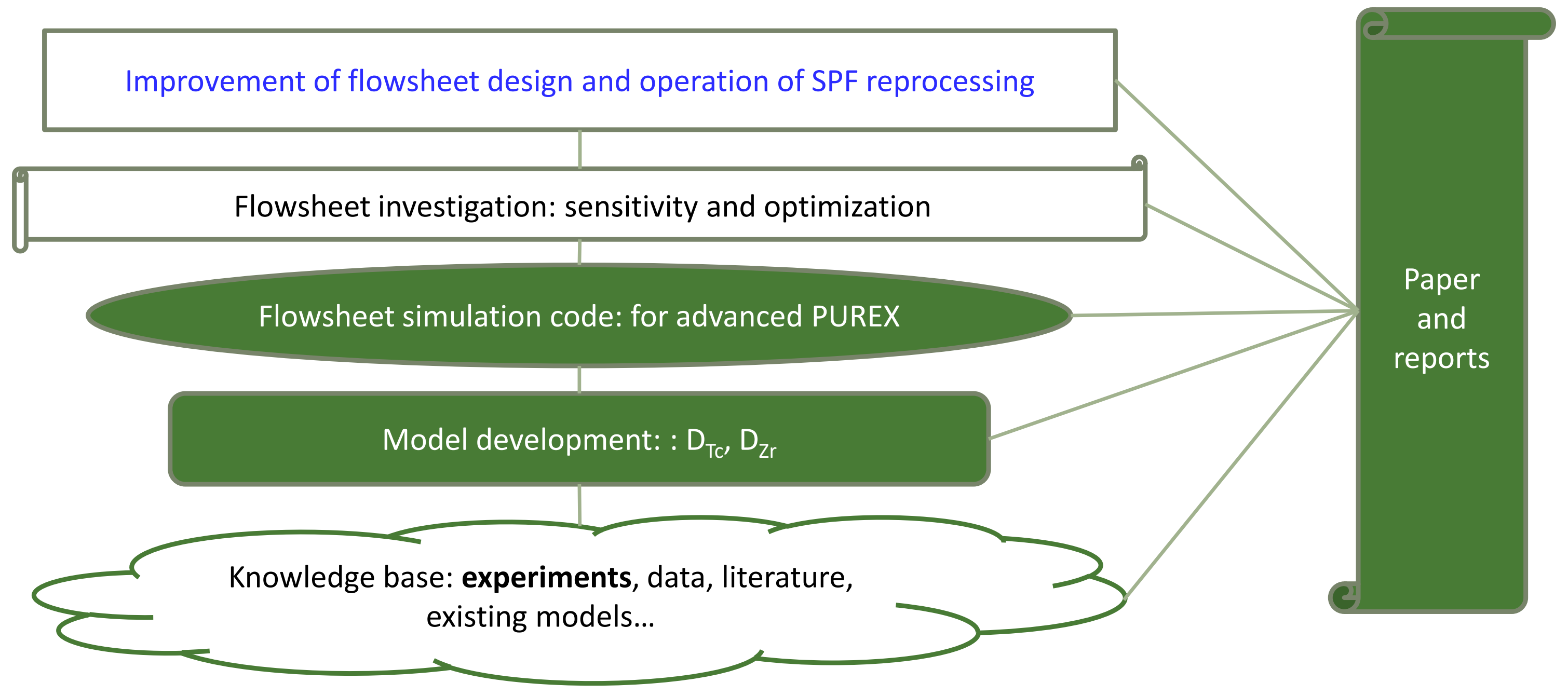
This work is developing technetium and zirconium distribution coefficient models for predicting their distribution between nitric acid solution and tri-butyl phosphate in diluent for solutions containing uranium, technetium and zirconium.

The distribution coefficient model for zirconium is based on the organic nitric acid concentration, rather than the free TBP concentration. An improved technetium distribution coefficient model is also developed. The co-extraction of technetium and zirconium or uranium is calculated by ligand exchange mechanisms. The validation results demonstrate that the distribution coefficient models developed in this work are more accurate than past models.

A flowsheet simulation code is also developed for the Advanced PUREX flowsheet with consideration of the slow conversion of inextractable forms of zirconium to extractable forms in the modelling of mass transfer rates. The code is applied to model a flowsheet tested experimentally at NNL and is validated by experimental results. Sensitivity of the flowsheet to operating parameters is investigated and optimized operating conditions identified.

OBJECTIVES

1) Develop reliable distribution coefficient model for the prediction of Tc and Zr distribution in the context of Advanced PUREX process;
2) Develop flowsheet simulation code using this distribution coefficient for the simulation of Advanced PUREX process
3) Investigate the process performance using this simulation code and provide guides to improve the performance of the process:



Improvement of flowsheet design and operation of SPF reprocessing

Flowsheet investigation: sensitivity and optimization

Flowsheet simulation code: for advanced PUREX

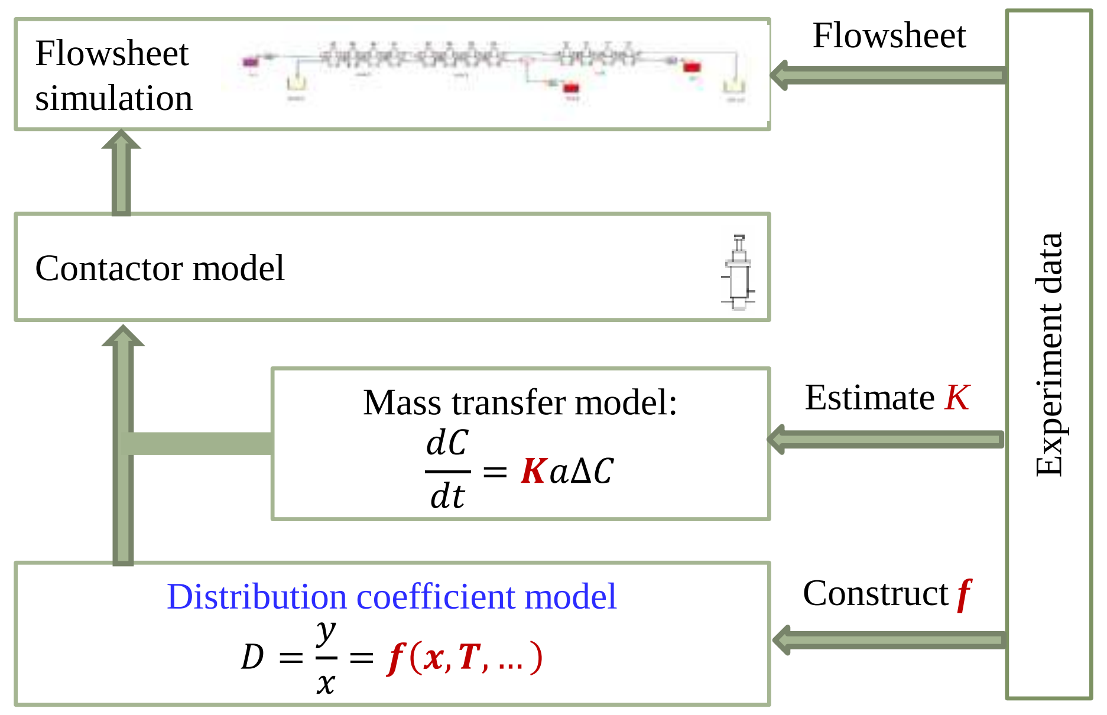
Model development: : D_{Tc}, D_{Zr}

Knowledge base: **experiments**, data, literature, existing models…

Paper and reports

MODEL DEVELOPMENT

- Distribution coefficient data set
  - Experimental distribution coefficient data from accessible literature and NNL internal reports
  - Data used to fit, validate and evaluate models
- Distribution coefficient model development
  - Model development for D_{Tc}
  - Model development for D_{Zr}
- Multistage flowsheet simulation code
  - Based on gPROMS software
  - Developed previously*, with new distribution coefficient models added
  - Mass transfer of Tc and Zr estimated from experimental data



Flowsheet simulation

Contactor model

Mass transfer model:

$$\frac{dC}{dt} = Ka\Delta C$$

Distribution coefficient model

$$D = \frac{y}{x} = f(x, T, \dots)$$

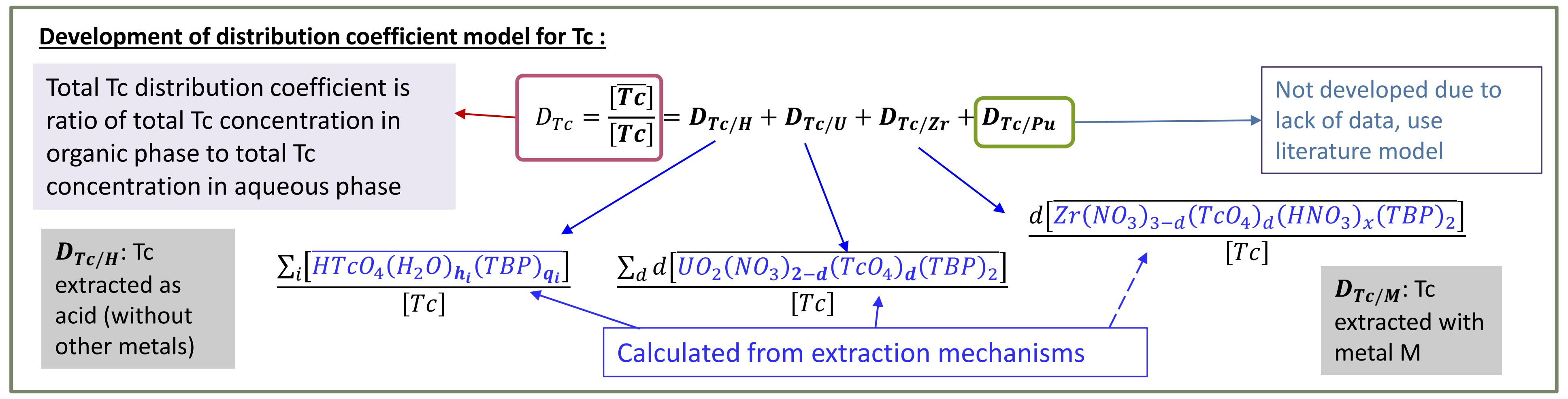
Flowsheet

Estimate K

Construct f

Experiment data

* *Chen, H. et al, Sol. Ext. & Ion Exch., 34(4), 297-321*



Development of distribution coefficient model for Tc :

Total Tc distribution coefficient is ratio of total Tc concentration in organic phase to total Tc concentration in aqueous phase

$$D_{Tc} = \frac{[\overline{Tc}]}{[Tc]} = \boldsymbol{D_{Tc/H}} + \boldsymbol{D_{Tc/U}} + \boldsymbol{D_{Tc/Zr}} + \boldsymbol{D_{Tc/Pu}}$$

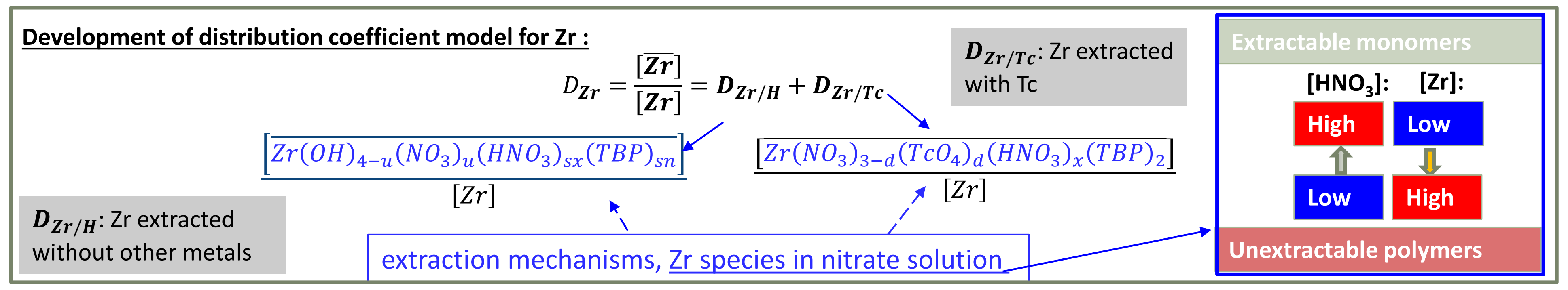
Not developed due to lack of data, use literature model

$$\frac{\sum_i [\overline{HTcO_4(H_2O)_{h_i}(TBP)_{q_i}}]}{[Tc]} \qquad \frac{\sum_d d[\overline{UO_2(NO_3)_{2-d}(TcO_4)_d(TBP)_2}]}{[Tc]} \qquad \frac{d[\overline{Zr(NO_3)_{3-d}(TcO_4)_d(HNO_3)_x(TBP)_2}]}{[Tc]}$$

$D_{Tc/H}$: Tc extracted as acid (without other metals)

Calculated from extraction mechanisms

$D_{Tc/M}$: Tc extracted with metal M



Development of distribution coefficient model for Zr :

$$D_{Zr} = \frac{[\overline{Zr}]}{[Zr]} = \boldsymbol{D_{Zr/H}} + \boldsymbol{D_{Zr/Tc}}$$

$$\frac{[\overline{Zr(OH)_{4-u}(NO_3)_u(HNO_3)_{sx}(TBP)_{sn}}]}{[Zr]} \qquad \frac{[\overline{Zr(NO_3)_{3-d}(TcO_4)_d(HNO_3)_x(TBP)_2}]}{[Zr]}$$

$D_{Zr/Tc}$: Zr extracted with Tc

$D_{Zr/H}$: Zr extracted without other metals

extraction mechanisms, Zr species in nitrate solution

Extractable monomers

[HNO_3]: **[Zr]:**

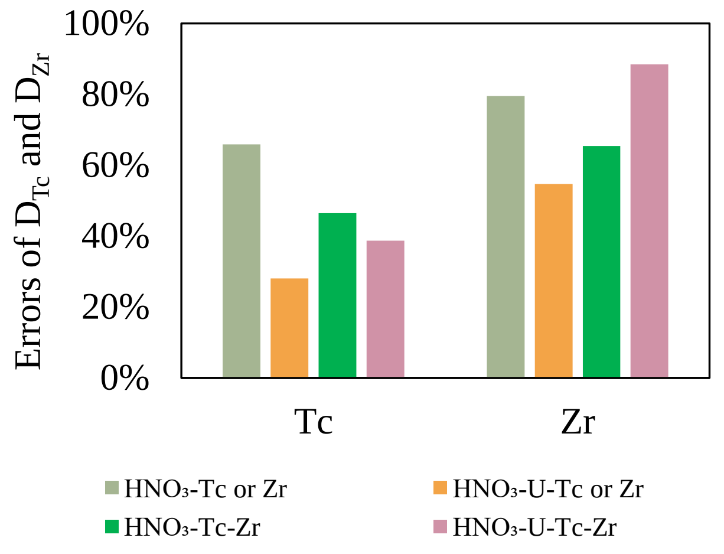
High Low

Low High

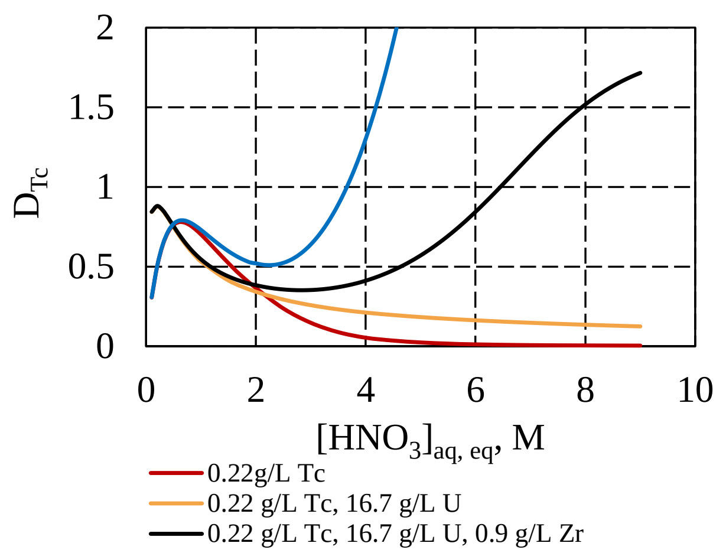
Unextractable polymers

RESULTS

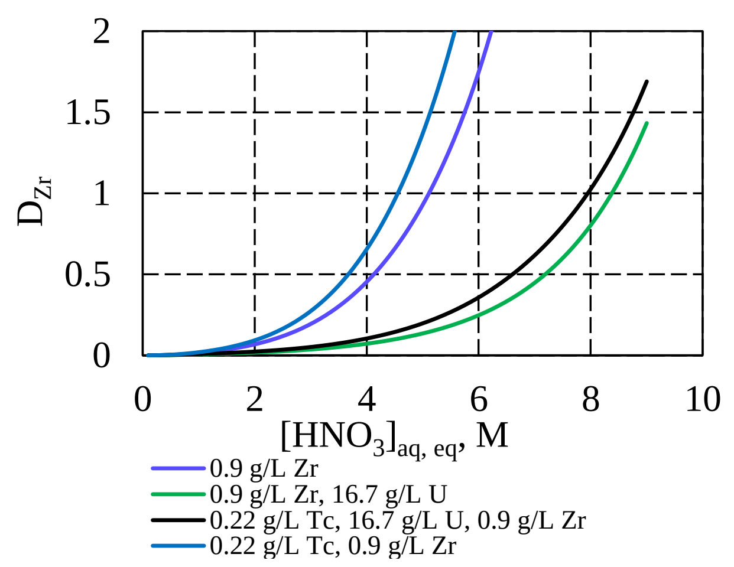
1. Distribution coefficient model for Tc and Zr extraction calculation: good prediction of Tc and Zr distribution coefficients



Over all performance of models

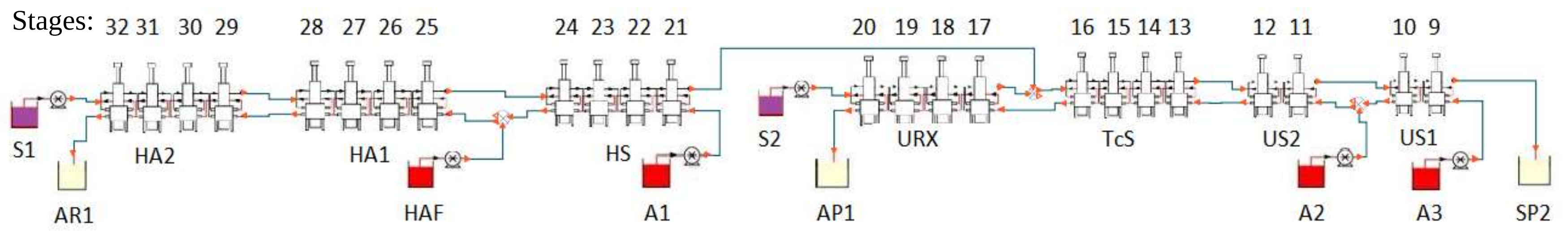


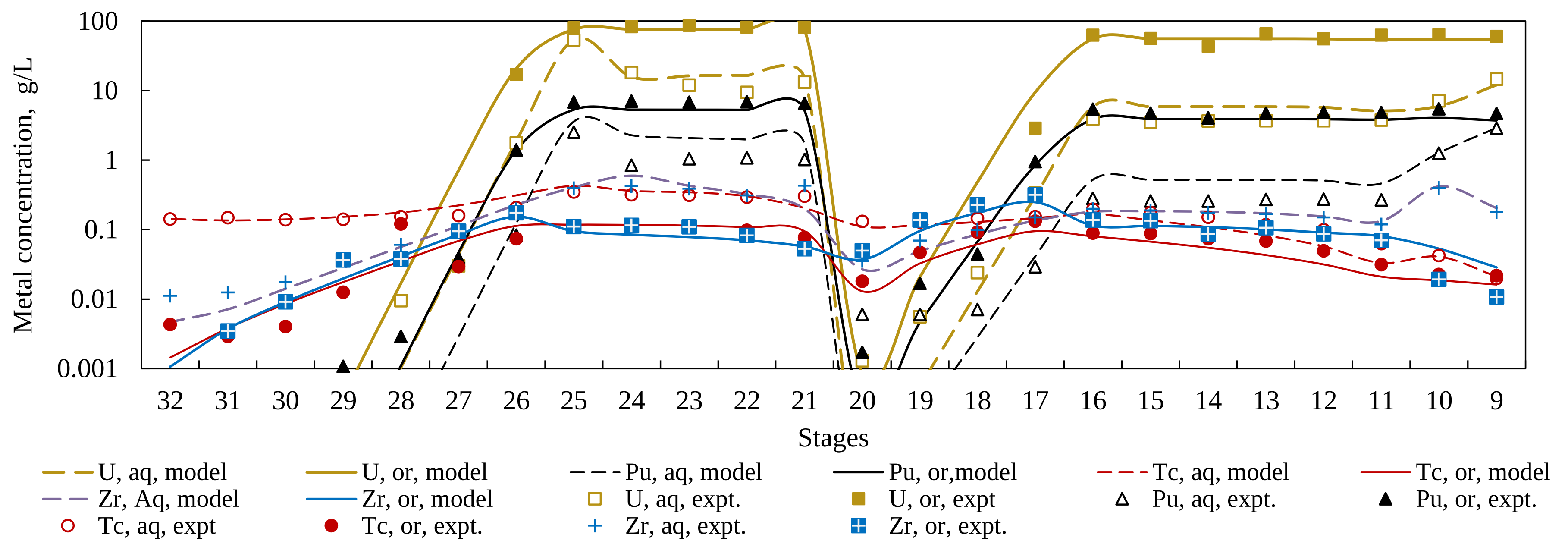
D_{Tc} predicted by model



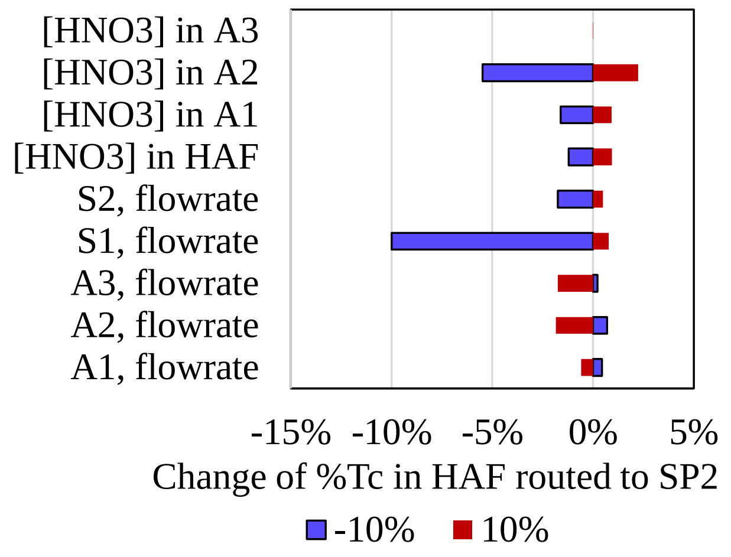
D_{Zr} predicted by model

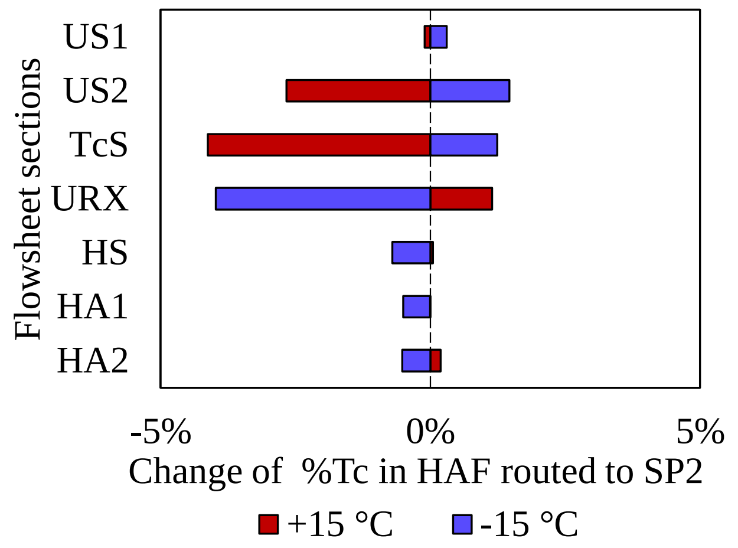
2. Flowsheet simulation of Tc and Zr extraction in an Advanced PUREX process: prediction of metals concentration profiles in an Advanced PUREX process

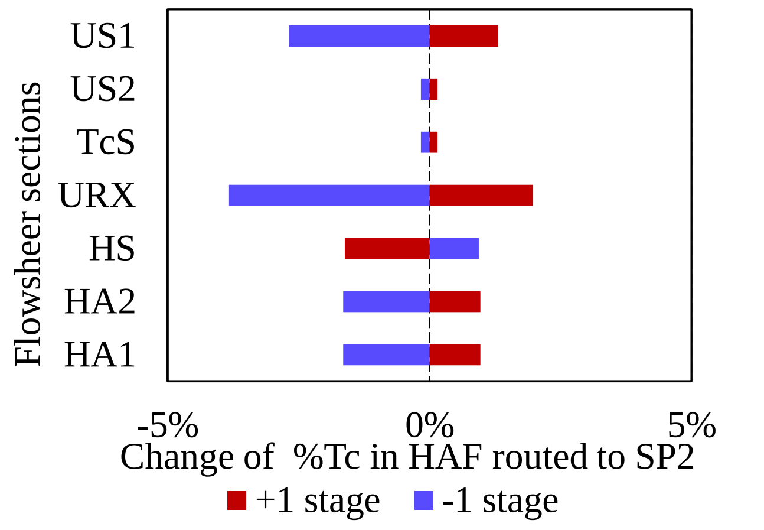




3. Study of the sensitivity of flowsheet operation conditions on Tc and Zr routing in an Advanced PUREX process







Sensitivity of flowrates and nitric acid concentrations *Sensitivity of temperatures* *Sensitivity of stage numbers*

For the base case, 96% Tc in HAF will route to SP2.

4. Optimization of operation conditions for minimization of Tc routed to SP2:

Flowrates of all feeds, nitric acid concentration in all feeds and temperature are optimized for the minimization of %Tc in HAF routed to SP2:

gPROMS OPTIMISATION

Optimisation problem	NIP3OPT_MT_2
Final optimisation status	Optimal
Objective function being minimised	plant.SP2TCREC
Objective function value	0.228027

	Base case	Optimized case
% Tc in HAF routed SP2	96%	**23%**
% Zr in HAF routed SP2	30%	**1%**
% U in HAF not routed SP2	0.00002%	**0.00002%**
% Pu in HAF not routed SP2	0.0002%	**0.0002%**

CONCLUSIONS

- Distribution coefficient models for the prediction of Tc and Zr extraction in spent nuclear fuel reprocessing are developed and validated.
- The speciation of zirconium in nitric acid solutions is complex and affects the extraction of Zr in nitric acid – TBP systems. A new method that calculates the distribution coefficient of Zr from organic nitric acid concentration is developed and shows good results.
- The effect of the conversion reaction rate of different zirconium forms in nitric acid solution to the extraction rate is also considered by fitting the mass transfer coefficients of Zr and Tc in the flowsheet simulation code. The results show this method gives good prediction of Tc and Zr profiles.
- The validated flowsheet simulation code is used for the sensitivity studies for an Advanced PUREX flowsheet and the results can be used for improving the flowsheet operation.
- An Advanced PUREX flowsheet is optimized for minimizing Tc routed to solvent product using the developed simulation code and gPROMS optimization tool. The result shows a significant reducing of Tc routed to solvent product using the optimized operation conditions comparing original base case. This result shows the value of modelling in guiding future R&D.

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Advanced Fuel Cycle Solvent Management & Treatment

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1. Introduction

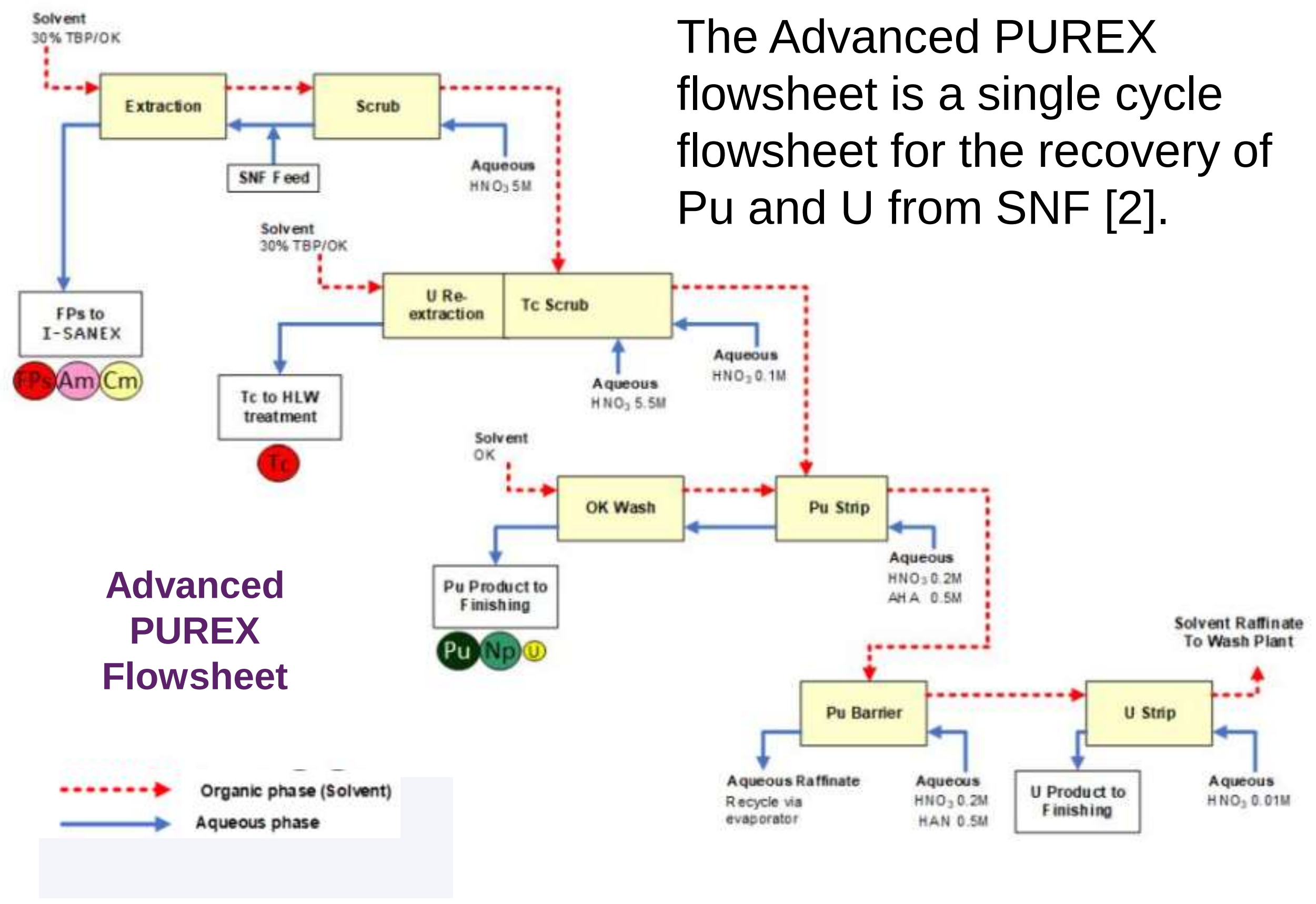
Solvents are the cornerstone to the effective recycle of Spent Nuclear Fuel (SNF) as they enable the efficient separation of valuable radionuclides so that they can be recycled for fuel manufacture and other purposes.

Solvents degrade with use which reduces their performance. Fortunately the solvents can be treated to remove degradation products and allow them to be re-used many times before they must be disposed of.

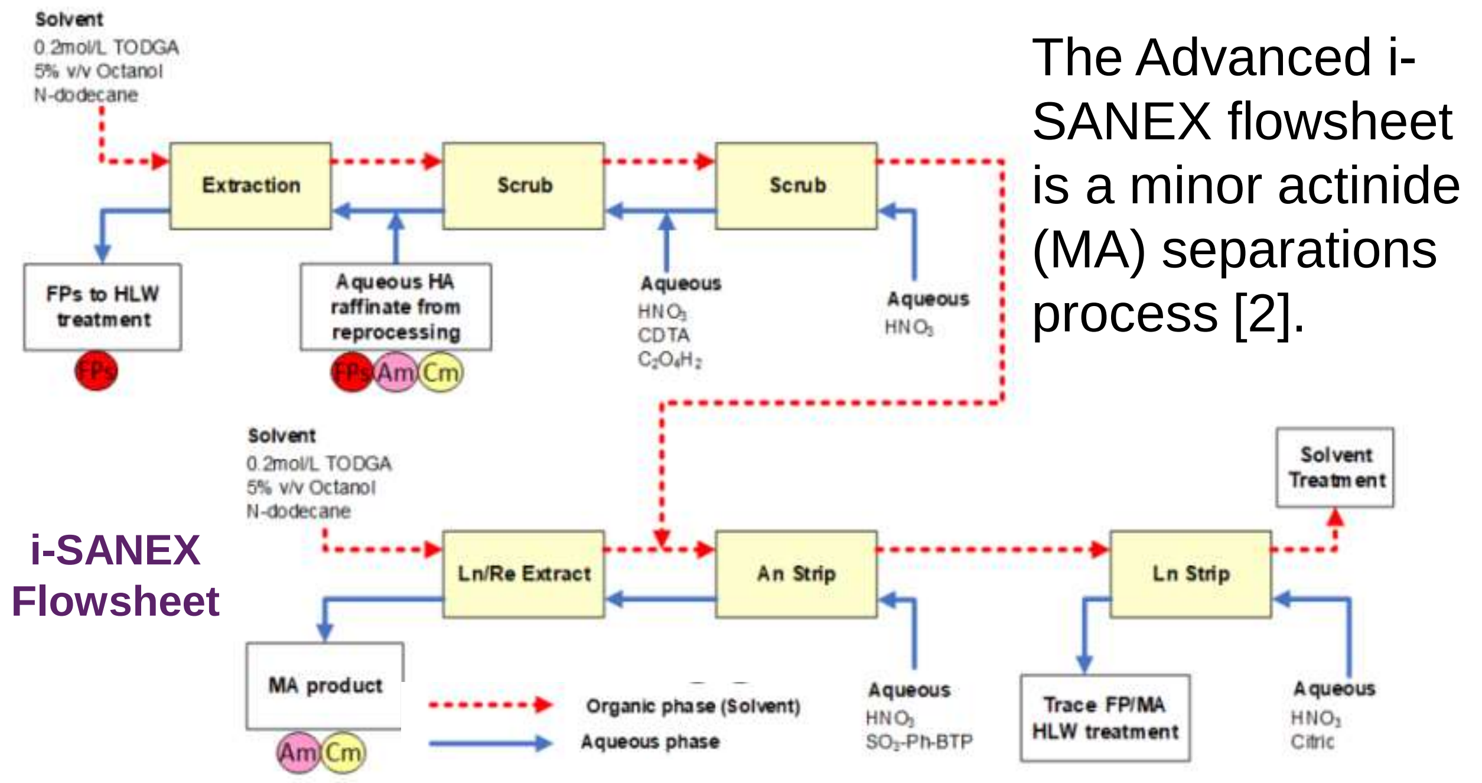
Through AFCP we are investigating the degradation of solvents used in Advanced Fuel Cycle Flowsheets with the goal to find the most cost efficient and sustainable option for their management and treatment.

2. Advanced Fuel Cycle Flow Sheets

The Advanced PUREX flowsheet is a single cycle flowsheet for the recovery of Pu and U from SNF [2].

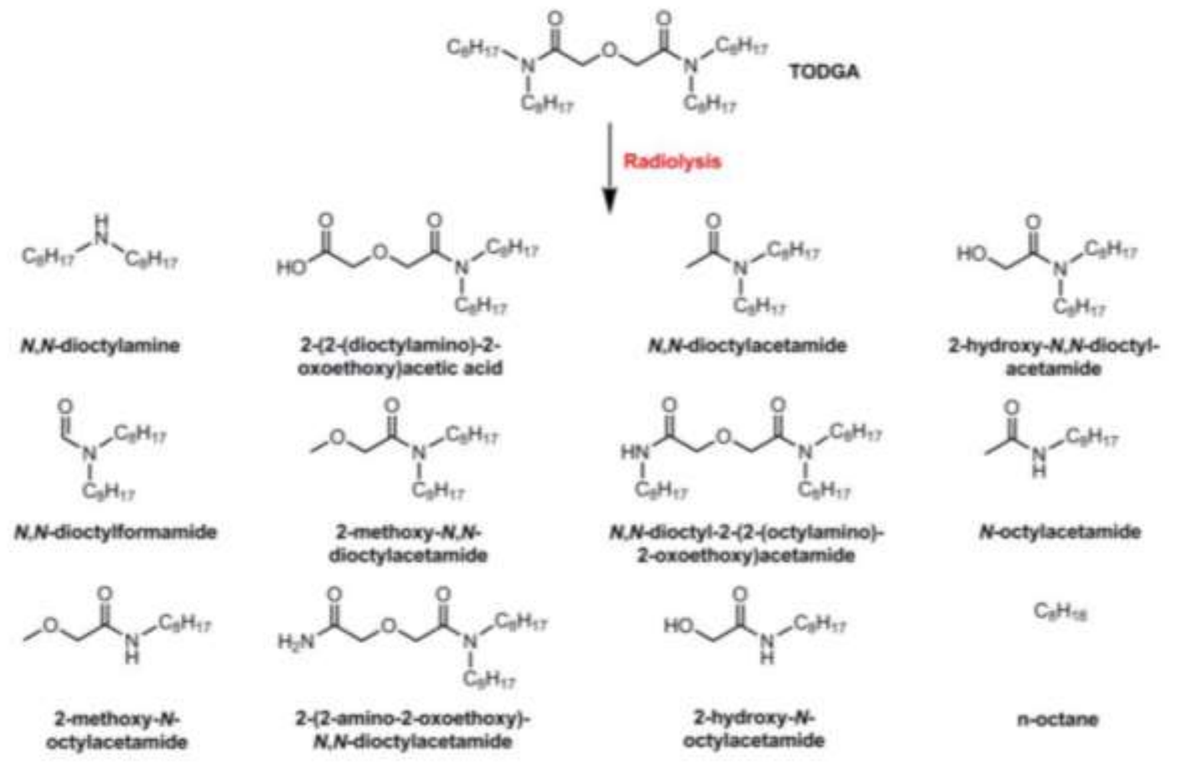


The Advanced i-SANEX flowsheet is a minor actinide (MA) separations process [2].

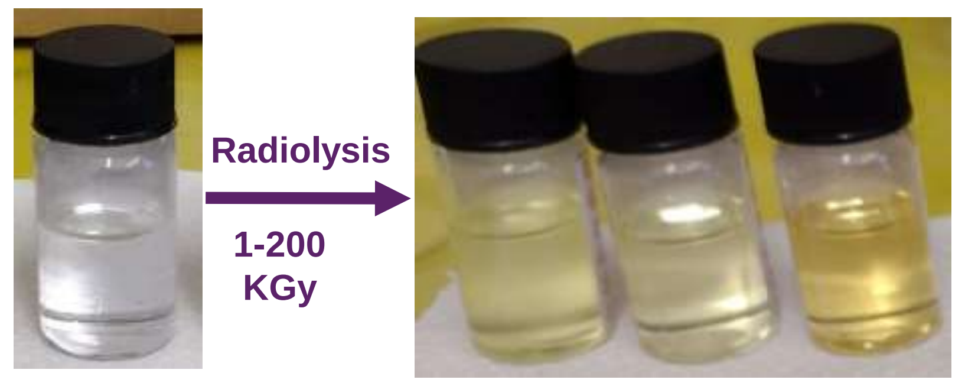


3. Solvent Degradation

Solvents can degrade by radiolytic, chemical and thermal pathways. The degradation products generated can be complex and require characterisation [3].

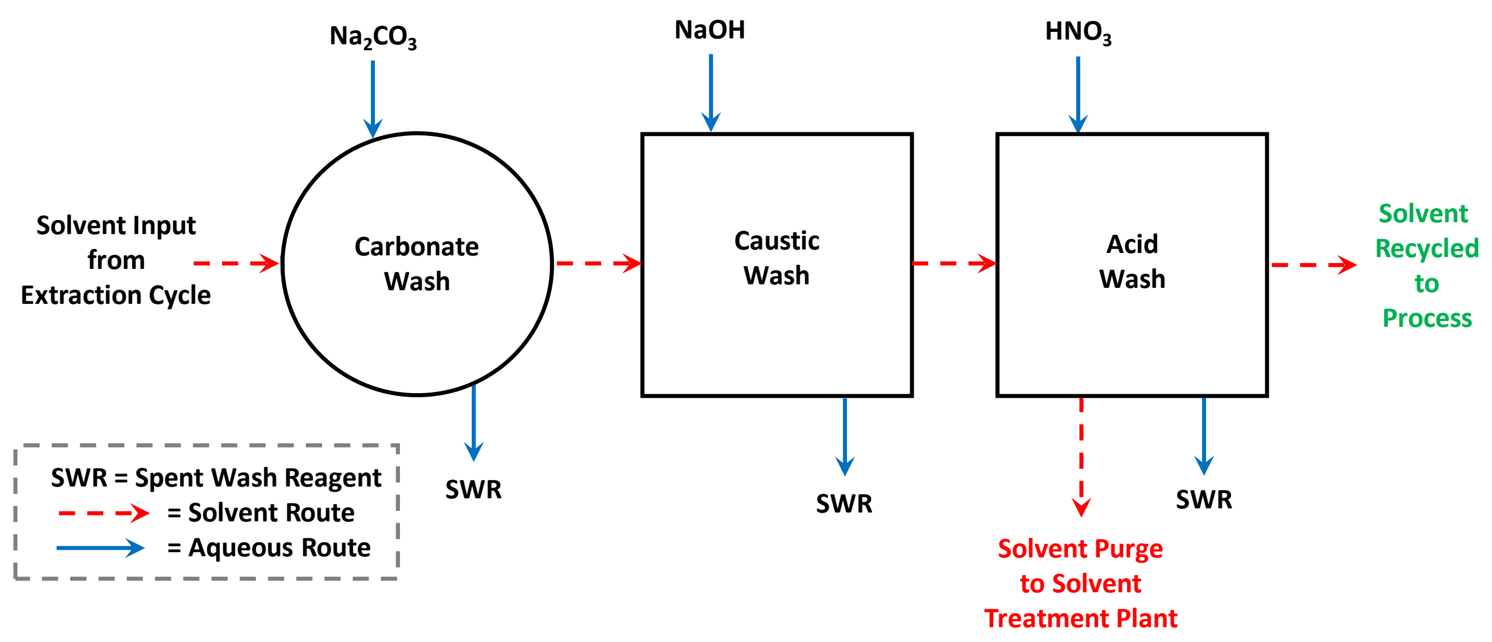


Degradation of the solvent can have a number of detrimental impacts on the spent nuclear fuel recycling process [3]. Experiments have been performed to understanding advanced fuel cycle degradation products (***below***).

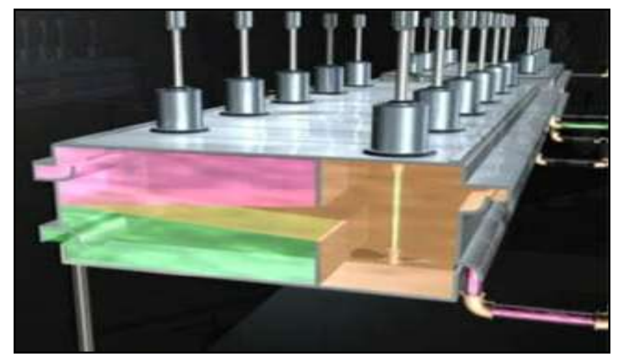


The degraded solvents (***above***) have been characterised. The information will help to develop strategies for solvent management.

4. Solvent Management



Solvent degradation products are managed within PUREX flow sheets through solvent washing (***left***). Solvent washing activities are typically undertaken within mixer/settlers (***right***). [4].



Strategies for managing PUREX solvent degradation products are well understood from decades of operational experience, however, a knowledge gap exists with respect to the management of MA separation flow sheet solvent degradation products [4].

Solvent washing experiments have been conducted using the degraded solvent materials resulting in the precipitation of solids or gel formation and difficulties with phase separation (***below***).

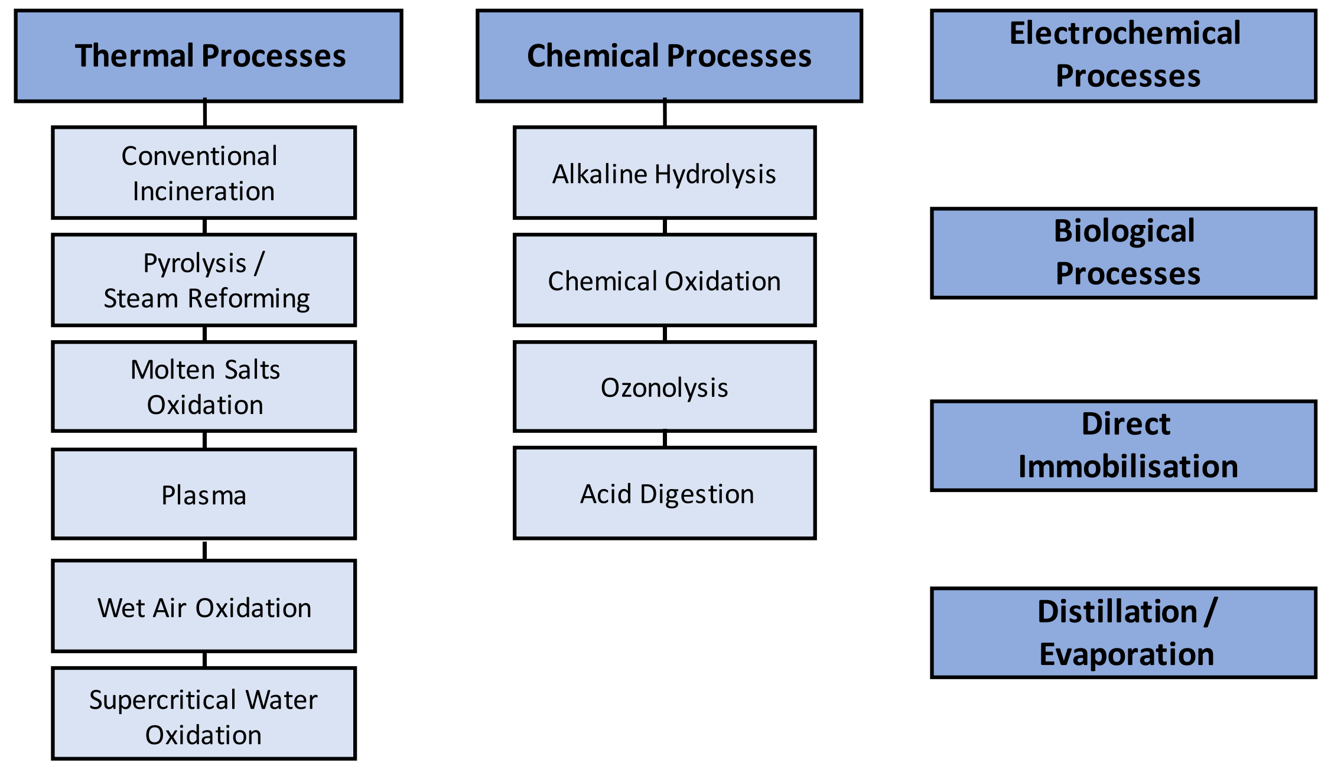
The formation of solids / gels during washing suggests that alternative approaches are likely to be required.

Solid sorbents are being investigated as an alternative approach to solvent cleaning [4]. Preliminary experiments have been undertaken at the University of Manchester to screen materials.

- Magnesium based sorbents have been identified as promising materials for the removal of PUREX solvent degradation products.
- Analytical methods have been developed to assess sorbent performance.
- Dynamic flow-cell experiments (***left***) will provide information on sorption capacity.

5. Solvent Treatment

At the end of its operational life spent solvent needs to be treated prior to disposal.
Previously employed technology is unlikely to be effective in the treatment of all advanced fuel cycle solvent systems.
A knowledge gap exists and this has been probed through a review of alternate technologies for solvent treatment [5].



Thermal Processes
- Conventional Incineration
- Pyrolysis / Steam Reforming
- Molten Salts Oxidation
- Plasma
- Wet Air Oxidation
- Supercritical Water Oxidation

Chemical Processes
- Alkaline Hydrolysis
- Chemical Oxidation
- Ozonolysis
- Acid Digestion

Electrochemical Processes

Biological Processes

Direct Immobilisation

Distillation / Evaporation

ELENDES (***left***). is an Electrochemical technology that has shown promise for the destruction of PUREX based solvent systems Working in collaboration with C-Tech Innovation Ltd. we have shown effective destruction of active solvents [6].
Complete recycle of the catalyst used in the process has been achieved using novel technology, reducing reagent consumption and waste production..
(***right***) [7].

6. Future Work

- Quantification of solvent degradation products.
- Defining the key solvent degradation products that impact on MA separation flowsheets.
- Development of effective solvent management approaches.
- Further development of the ELENDES electrochemical solvent treatment process.

7. Acknowledgements

- **This work was funded under the £46m Advanced Fuel Cycle Programme as part of the Department for Business, Energy and Industrial Strategy's (BEIS) £505m Energy Innovation Programme.**
- The authors also acknowledge financial support from the NNL S&T budget for the experimental work undertaken at the University of Manchester.
- The authors would also like to acknowledge the contributions of Duncan Coppersthwaite (NNL) / Rob Bell and John Collins (C-Tech Innovation Ltd.) in relation to ELENDES developmental work and ongoing support and Ruth Edge (UoM) for assistance with sample irradiation.

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Life Cycle Assessment to support decision-making

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Introduction: Life Cycle Assessment

LCA is an ISO standardized methodology for quantifying the environmental impacts of products or processes throughout their life cycle[1].

It has been rarely applied in the nuclear industry compared to other energy technologies.

It is widely used to support decision- and policy-making.

Objectives

1. Build on previous LCA studies of open vs closed cycles at CEA & UCL.
2. Demonstrate by example how the LCA methodology can be applied in the nuclear industry to support decisions.
3. Identify future areas of interest within advanced nuclear fuel cycles

Case study: uranyl nitrate from depleted uranium

Goal: Quantify the environmental benefits of using depleted (instead of natural) uranium for uranyl nitrate

Data: Based on previous studies[2]

System boundaries: Cradle to grave

Functional Unit: Management of 1 ton U in used nuclear fuel.

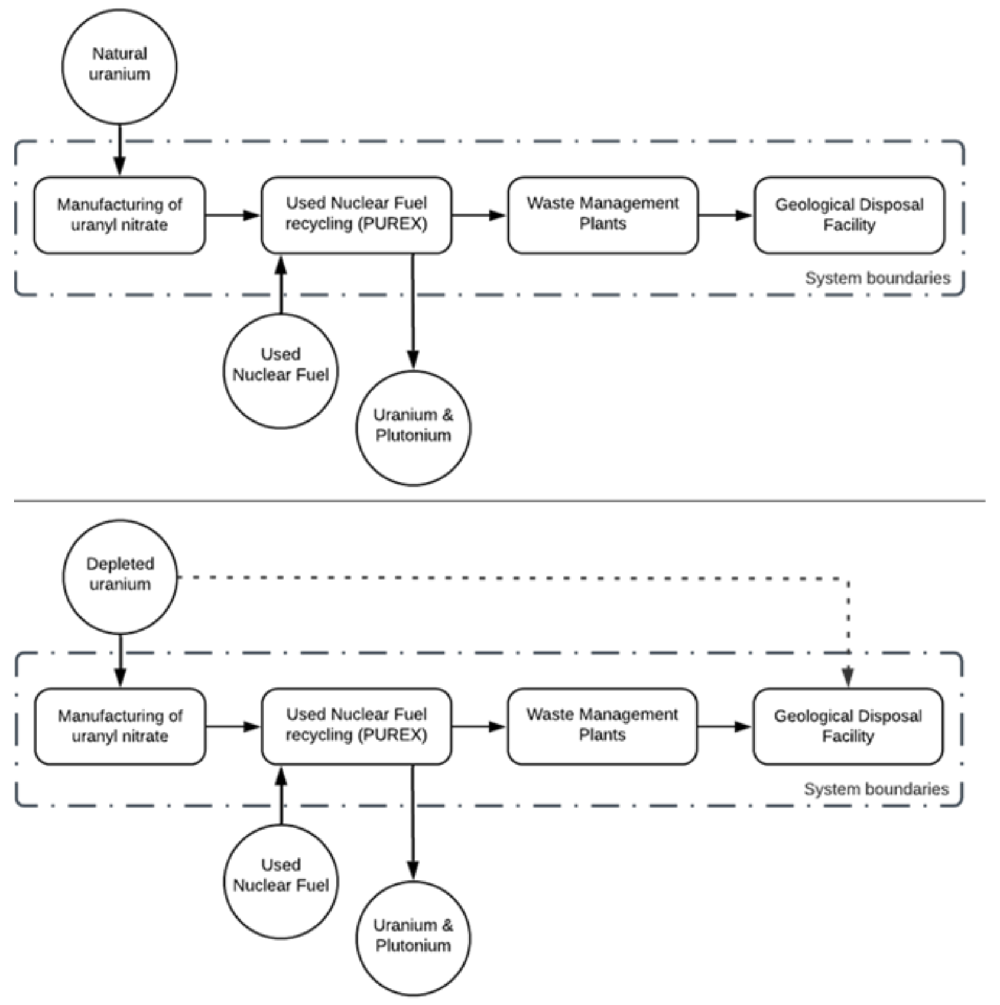
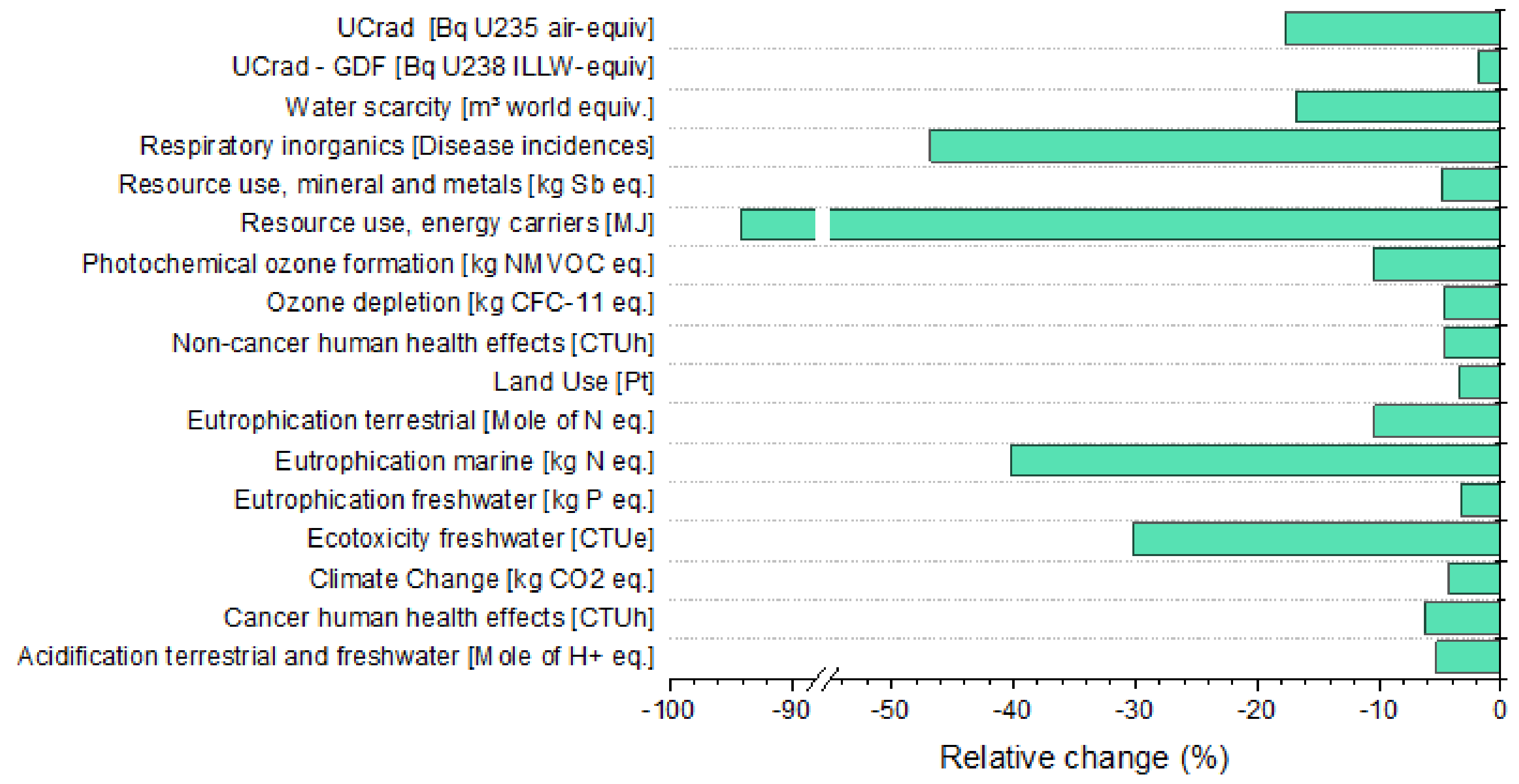


Fig1: Schematic diagrams for baseline scenario (top) and the alternative (bottom), where the depleted uranium substitute natural uranium. The dashed-line in figure (b) represent the avoided impacts due to substitution.

Results: percentage reduction in the environmental impacts of used fuel recycling



Case study: Recycling of Zircaloy™ cladding

Goal: Quantify the environmental benefits

Technology: Two-step recycling process developed in USA[3]

Data: Literature from lab-scale experiments

Key assumptions:

- Recovered and primary zirconium have same properties
- Unreacted cladding and other wastes are disposed of as ILW

Functional Unit: Amount of cladding per ton of U in used fuel

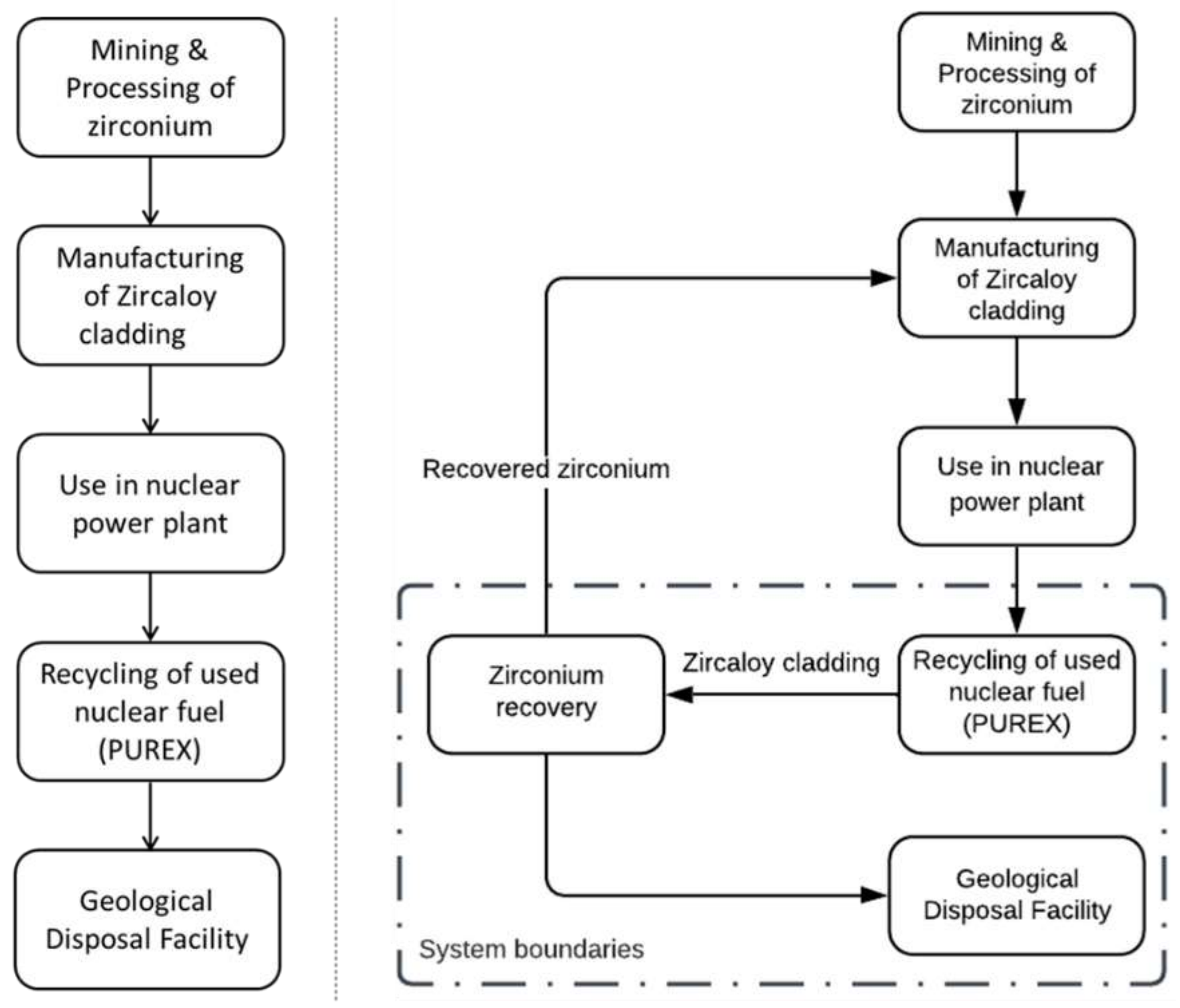
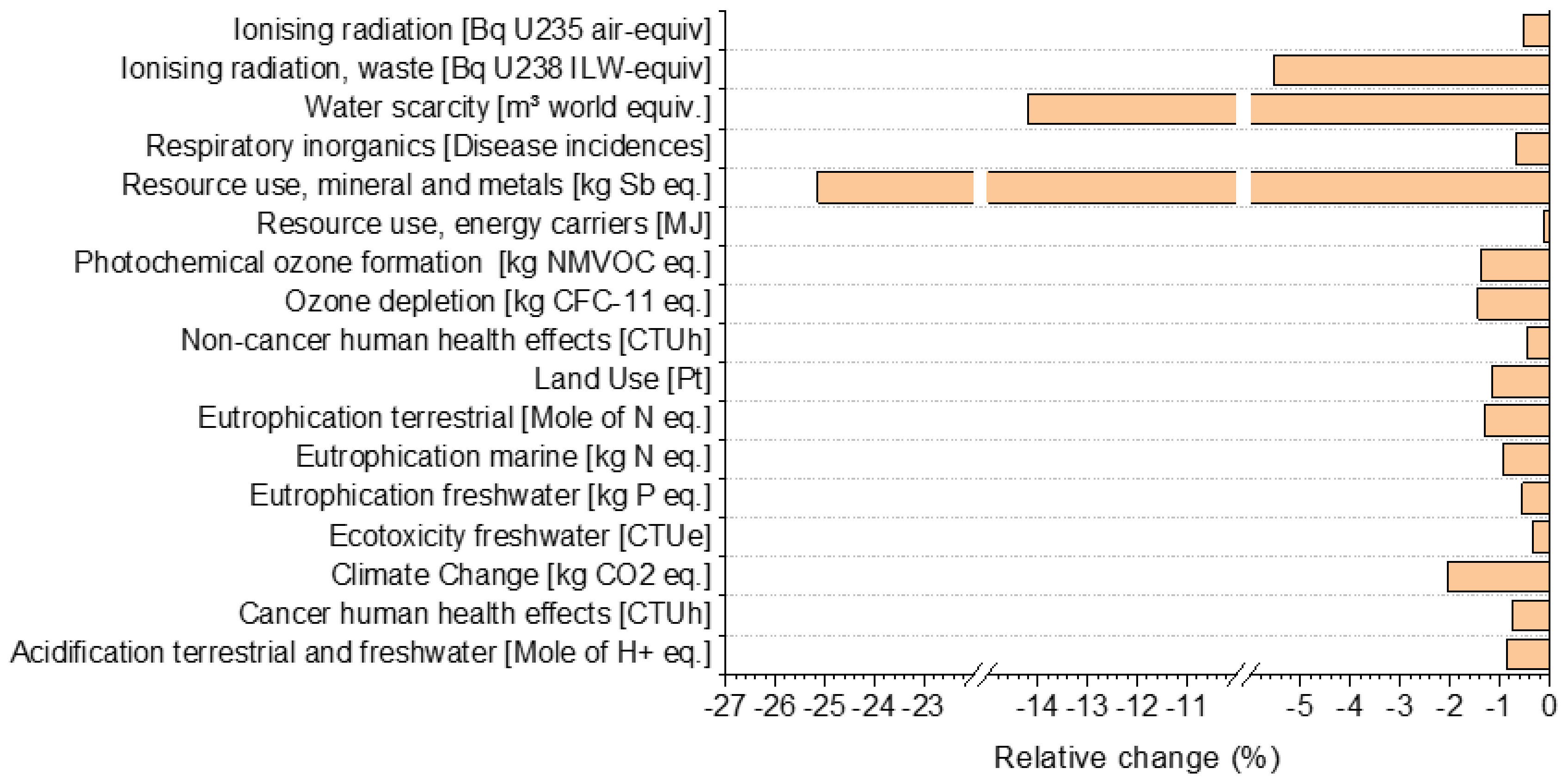


Fig. 2 - Simplified schematic diagram of the life-cycle of Zircaloy™ cladding for linear (left) and circular (right) approaches

Results: percentage reduction in the environmental impacts of used fuel recycling



Conclusions from case studies

- Circular approaches outperform traditional one across the full spectrum of environmental categories.
- Switching from linear to circular approach brings sizeable improvements in the environmental performance of recycling used nuclear fuels).
- Key benefits are linked with the avoided use of primary resources and lower volume of waste disposed (mainly for Zircaloy™ cladding recycling).

LCA Workshops: Multi Criteria Decision Analysis

Methods: MCDA criteria

Criteria	Description
Data availability	Quality of information and data available to develop LCA models, either from NNL/partners or literature
Technological Readiness Level	Current assessment of the technical maturity of the technology
Technical benefits	Improvement in process efficiency quality etc. from adopting technology
Economic benefits	Reduction in OPEX and/or CAPEX from adopting technology
Environmental benefits	Reduction in overall environmental impacts from adopting technology
Societal benefits	Other non-technical benefits e.g. non-proliferation, longevity of waste, public acceptance

Results: top ranked options after scoring, with and without weighting

Workshop	Option
1. Aqueous Wate and Recycle Process	Advanced PUREX with and without iSANEX
	Alternative solvents (e.g. CHON vs TBP)
	Removal of minor actinides to minimise GDF waste burden
	Process control: Sampling vs Online Monitoring
	Energy recovery/reduction in evaporators
	Alternative to evaporators
2. Pyro-Processing	Electro-refining with and without salt clean up
	Electro-reduction salt clean up
	Fuel production: using MSR as fuel
	Head-End: High-temperature/ Voloxidation
	Product finishing: distillation of cadmium salt
3. Coated particle fuel cycles and post-processing	AMR/ large pebble reactor
	Prismatic fuel disposal: HTGR optimised vault
	Prismatic fuel disposal: HHG vault, near surface LLW vault
	AMR/micro prismatic reactor
	Prismatic fuel disposal: Recycle

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Acknowledgments

This work was funded under the £46m Advanced Fuel Cycle Programme as part of the Department for Business, Energy and Industrial Strategy's (BEIS) £505m Energy Innovation Programme.

The Product Quality, Characterisation and Testing of Group ActiNide EXtraction (GANEX) Products.

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National Nuclear Laboratory, Central Laboratory, Sellafield, Cumbria, CA20 1PG,

Introduction

It has become an international objective to develop a new hydrometallurgical based process for advanced actinide separations with increased proliferation resistance, improved economics and reduced waste arisings.

One of the more developed advanced processes being considered is the Group Actinide EXtraction (GANEX) process.

From the investigative work, the EURO-GANEX flowsheet has been produced.

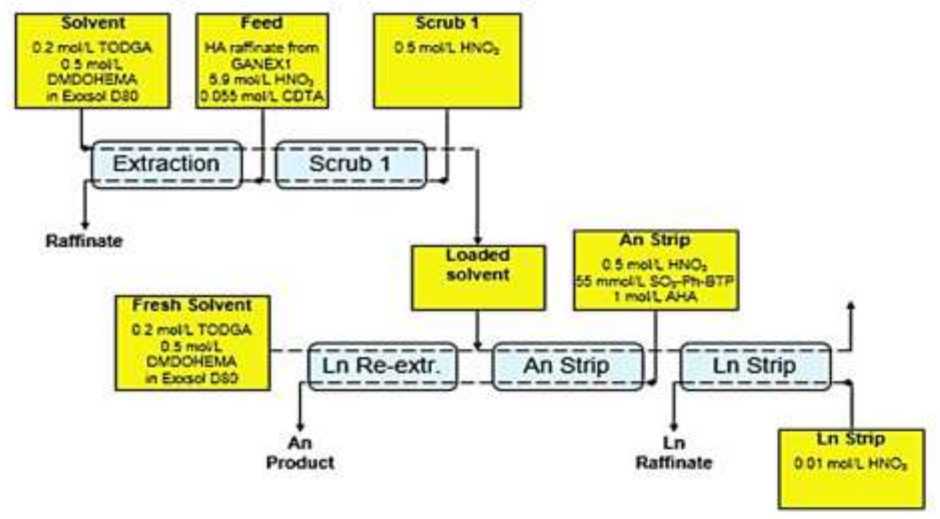


Figure 1: EURO-GANEX chemical separation flowsheet schematic[1]

Challenges:

Complexants (e.g. PTD) used during the chemical separation are carried over into the finishing process.

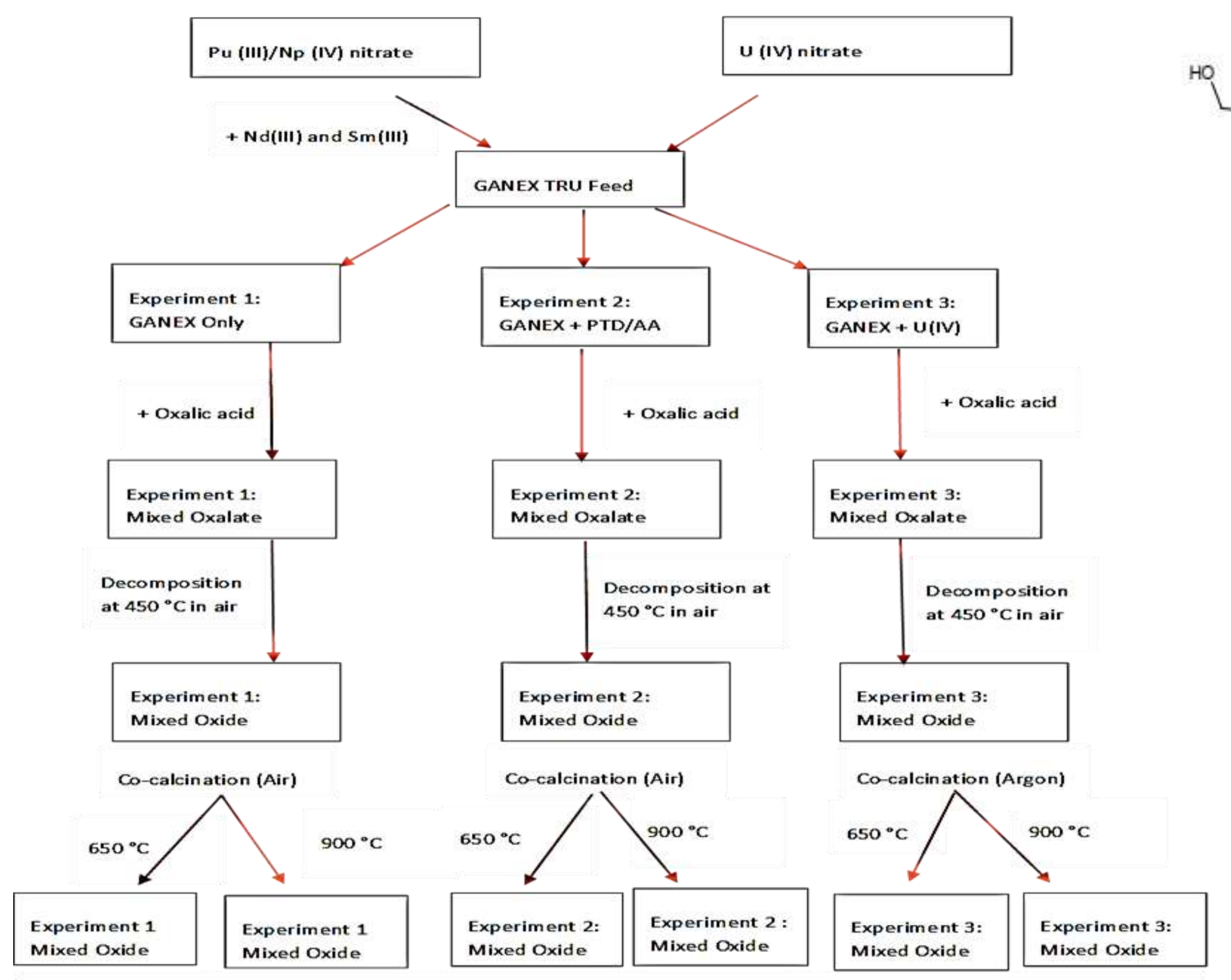
There is a risk that the complexants (or their degradation products) used to strip the Transuranic (TRU) from the solvent phase in the separation stage may perturb the oxalate co-precipitation step through competing complexation.

Objectives

As part of the GENIORS project, NNL were tasked with the finishing of a GANEX TRU product, looking at the finishing process, product quality and characterisation.

Three main objectives were set:

1. Effects of temperature and atmosphere during calcination on the characteristics of the mixed oxide products and its ability to maintain a single homogenous oxide phase during conversion.
2. The addition of the complexing ligand (PTD) and the potential degradation product, acetic acid, to determine their effect on the solubility of the metal nitrates and the quality of the oxide produced.
3. The effect of precipitation and calcination of a TRU product with U(IV).



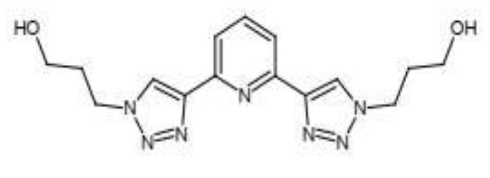


Figure 3: PyTriDiol, PTD

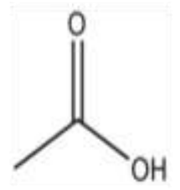


Figure 4: Acetic acid

Figure 2: Schematic of planned experiments for the finishing of a EURO-GANEX TRU products

Experimental

- Experimental work was carried out in NNL’s PuMA labs located at Central Laboratory.
- Plutonium(IV) nitrate and neptunium(V) nitrate were electrochemically conditioned in the presence of hydrazine hydrate to produce a 75 g/L Pu(III) – 2 g/L Np(IV) – 0.2 mol/L hydrazine nitrate GANEX TRU feed.
- Uranyl(VI) nitrate hexahydrate was also converted to U(IV) nitrate by electrochemical conditioning.

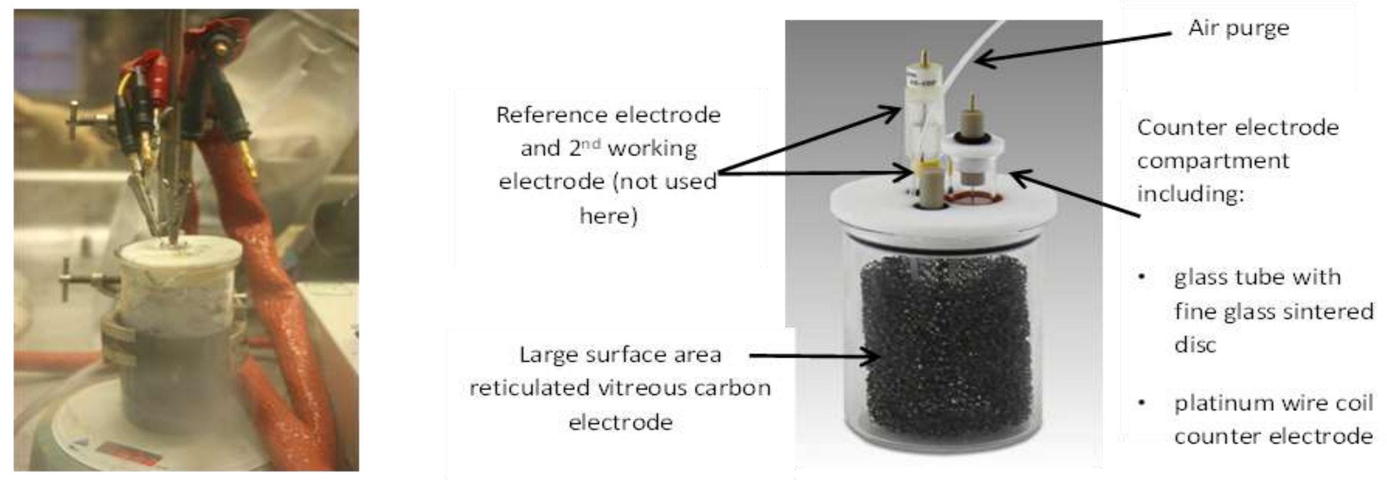


Figure 5: Electrochemical cell: (RHS) diagram of cell (LHS) set up used in glovebox to condition Pu(IV)/Np(V) nitrate.

The conditioned U(IV)/Pu(III)/Np(IV) stocks were used to prepare GANEX-TRU feed with addition of Nd(III) and Sm(III) as surrogates for Am(III) and Cm(III) respectively.

Three oxalate precipitation experiments were considered during this project:

- GANEX TRU feed
- GANEX TRU feed in the presence of PTD and acetic acid
- GANEX TRU feed co-precipitated with 66 mol/L% U(IV)

Figure 6: Batch scale oxalate co-precipitation set up (beaker contains Experiment 3: GANEX + U(IV))

Table 1: Experimental volumes used during co-precipitation of the GANEX TRU feed.

Experiment	Volume GANEX TRU Feed (mL)	Mass of PTD (g)	Volume of glacial acetic acid (17.4 mol/ L) (mL)	Volume of 0.6 mol / L oxalic acid (mL)	Total volume (mL)
1 (GANEX only)	61.2	0.0	0.0	108.3	169.5
2 (GANEX + PTD/AA)	6.12	3.1	0.5	108.3	170.1
3 (GANEX + U(IV))	30.6	0.0	0.0	108.3	138.9

Conclusions

- First test of a GANEX finishing cycle

- Successfully prepared a mixed feed of Pu(IV)/Np(V) and U(IV) with addition of Nd(III) and Sm(III).
- Excellent recovery of metal nitrates to the solid mixed oxalate during oxalate precipitation.
- Presence of PTD and acetic acid in the feed mixture had no noticeable effect on solubility of the metal nitrates in solution or resultant structure.
- FTIR analysis of oxalates confirmed a hexagonal structure for experiment 1 and 2 (TRU oxalate) and a tetragonal structure for experiment 3 (U(IV):TRU oxalate).
- XRD confirm conclusions drawn by FTIR analysis.
- TRU oxides produced a cubic MO_2 structure & U(IV).
- TRU oxalate formed a mixed phase oxide product containing MO_2 and $(U,M)_3O_8$ phases and re-oxidation of the U(IV).

- This work formed the final year research project for a BSc(Hons) degree at the University of Cumbria (L. Walton)

Acknowledgements

This work was funded under the £46m Advanced Fuel Cycle Programme as part of the Department for Business, Energy and Industrial Strategy’s (BEIS) £505m Energy Innovation Programme.

This work has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (project GENIORS, grant agreement N° 755171).

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Results

ICP-MS of Oxalate Mother Liquor (OML)

- Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was carried out on the OML to calculate the percentage recovery of metal ions in the precipitate and any losses to the OML.
- Results showed excellent recovery of the metal nitrates to the precipitate with minimal losses to the OML.
- 20% oxalic acid excess was used and likely attributes to the high recovery.

Table 2: ICP-MS results for Pu, Np and U from the Oxalate Mother Liquor

Experiment	Plutonium			Neptunium			Uranium		
	[Pu] in OML g/L	%loss to OML of Pu	% Recovery	[Np] in OML g/L	%loss to OML of Np	% Recovery	[U] in OML g/L	%loss to OML of U	% Recovery
1	0.53	0.71%	99.29%	0.05	2.61%	97.39%	0.34	<LOD	100%
2	0.43	0.58%	99.42%	0.02	1.05%	98.95%	0.20	<LOD	100%
3	0.34	1.69%	98.31%	0.01	2.10%	97.90%	1.27	1.04%	98.96%

- **Infrared Analysis -** IR spectra recorded on an Agilent Cary 630 FTIR Spectrometer with the use of a diamond Attenuated Total Reflectance (ATR) accessory.

Oxalate IR Results:

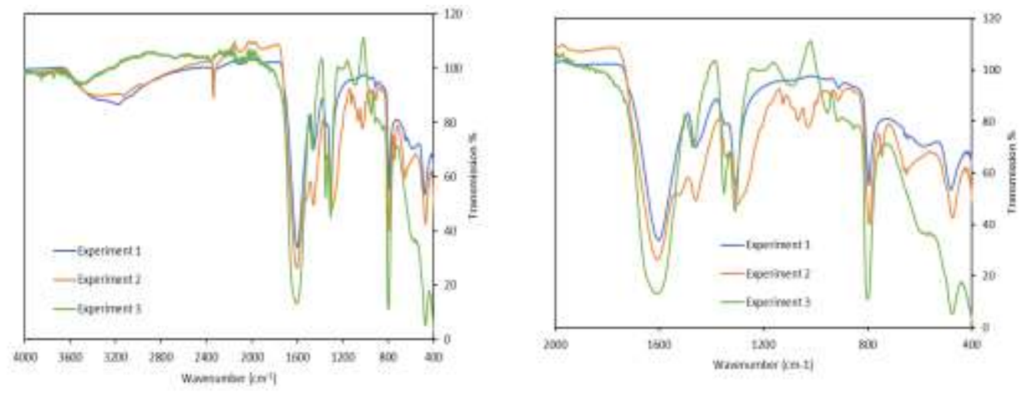

Figure 7 and 8: Infrared spectra of each oxalate solid produced from oxalate precipitation of the GANEX feeds.

- Measurements were recorded between 650 cm^{-1} and 4000 cm^{-1} in transmission mode with 4 cm^{-1} steps.
- Characteristic of oxalate compounds as indicated by the infrared bands located at 480, 795 , 1310, 1350, ~1475 and 1600 cm-1 and is in good agreement with literature reports on mixed oxalate compounds [2, 3].

Oxide IR Results

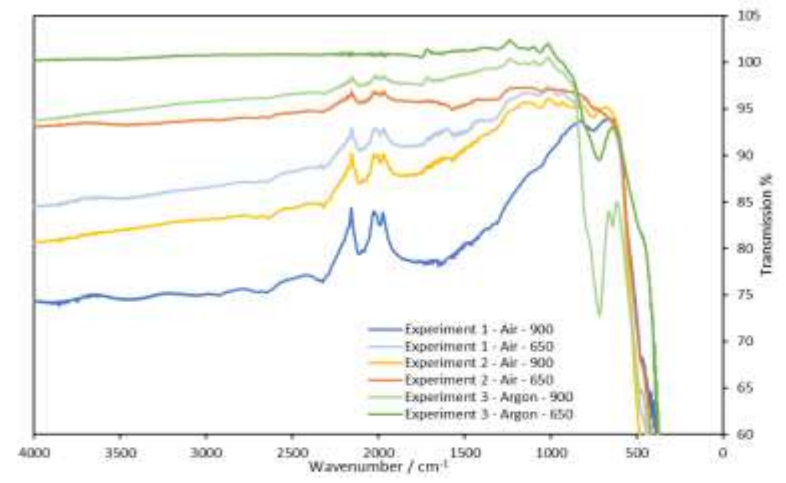

Figure 9: Infrared spectra of GANEX TRU oxides following calcination at 650 °C and 900 °C in either an air or argon atmosphere.

- Experiment 2 which included PTD and acetic acid within the oxalate shows no signs of these species left in the oxide product suggesting that if PTD was not destroyed during evaporation stages it would have no overall effect on the mixed oxide product.

- **X-RAY Diffraction Analysis -** To determine the structure of the different products.

Figure 10: From left to right: PuO_2 powder encapsulated in an epoxy resin; sample puck fixed into a plexi-glass ring; sample puck contained in a magnetic XRD sample holder on the open bench.

- NNL’s X-ray powder diffractometer is a Bruker D8 Advance open bench instrument and therefore alpha containing samples must undergo a rigorous preparation process to encapsulate the material to prevent the spread of loose alpha contamination during analysis. (Figure 10)
- Powder patterns recorded between 5 ° and 60 ° (for oxalate samples) and 25 ° and 145 ° (for oxide samples).

Oxalate XRD Results

- Results suggest Experiments 1 and 2 formed a tetragonal structure and experiment 3 had formed mainly a hexagonal structure.

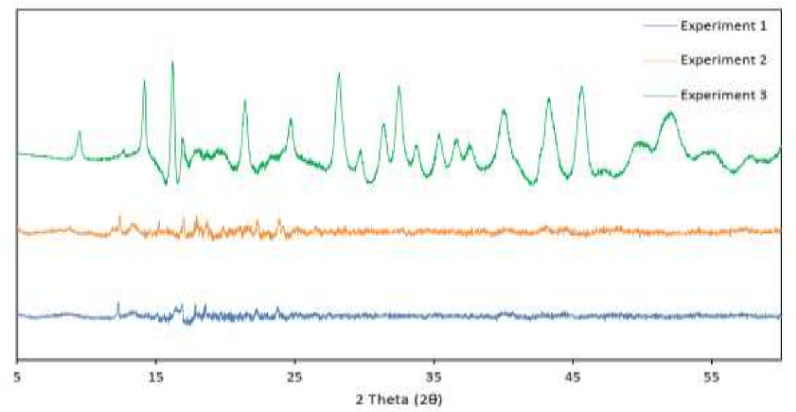

Figure 11: X-ray diffraction pattern of each mixed oxalate produced prior to calcination.

Oxide XRD Results

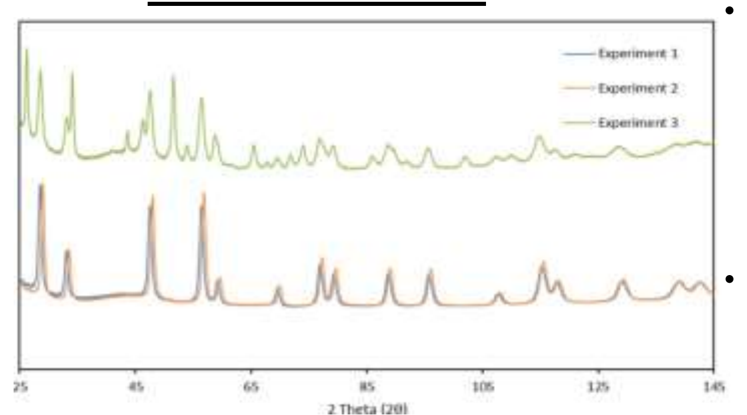

Figure 12: X-ray diffraction pattern of each mixed oxalate produced prior to calcination.

- Experiment 1 and 2 produced a cubic MO_2 structure. The presence of PTD had no effect on the structure in comparison to Experiment 2.
- Additional peaks can be seen in experiment 3, which suggest the formation of a mixed MO_2 - M_3O_8 phase.

Specific Surface Area (SSA) – Analysis of SSA carried out within the NNL High Alpha Inventory Laboratories using a modified Micromeritics Gemini VII 2390a analyser.

Table 3: Specific surface area of each oxide product.

	Experiment 1		Experiment 2		Experiment 3	
Calcination conditions	900 °C air	650 °C air	900 °C air	650 °C air	900 °C argon	650 °C argon
SSA (m^2/g)	5.01	24.36	3.70	16.79	2.78	8.74

- In agreement with literature and subsequent growth of crystallites[4], the SSA decreases considerably as calcination temperature increases from 650 ° C to 900 ° C regardless of the initial feed mixture.

Sim Plant – a Fuel Cycle Evaluation Tool

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INTRODUCTION

New reprocessing technologies have promised various advantages over current generation approaches. These include but are not limited to:

- reductions in waste production,
- reduced footprint,
- better economics,
- flexibility in the types and compositions of spent fuels they can handle,
- reduced environmental impact,
- and increased proliferation resistance.

Sim Plant is a tool being specifically developed to objectively assess whether these benefits can be realised.

METHODS

Sim Plant is a series of models written in multiple software languages covering the entire nuclear fuel recycling process, from spent fuel to the final wastes. A Sim Plant model has three parts:

1) A reprocessing flowsheet model

This is a simple, DF-based, steady state model of a given reprocessing option (tracks mass flows, isotopic compositions and volumetric flowrates).

2) An effluents management flowsheet

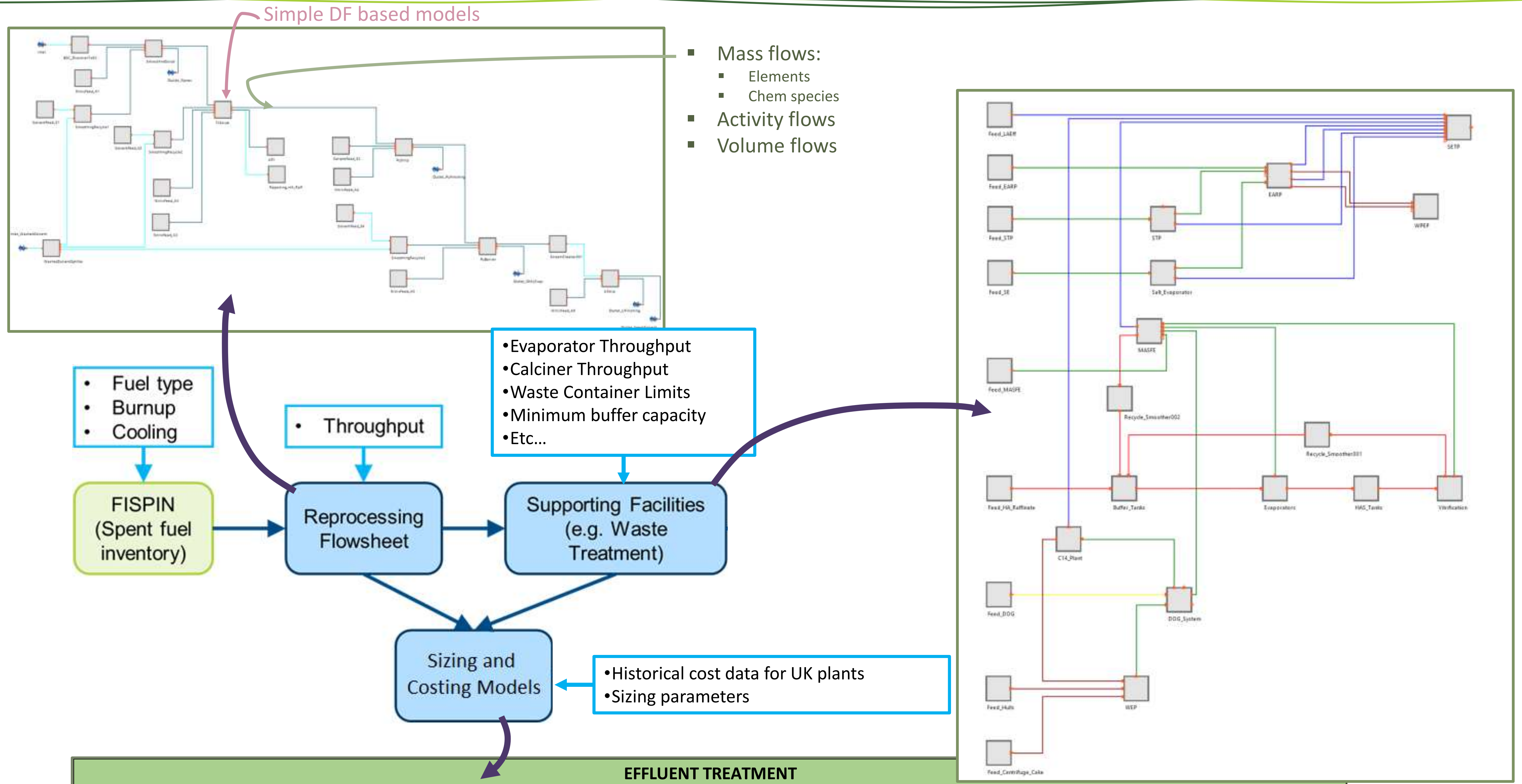
A second simple flowsheet is used to simulate the management of the effluent produced by the first flowsheet and to predict the waste arisings that result from this. Based on the aqueous effluents strategy of the Sellafield site.

3) Sizing and costing calculations

These are a series of engineering calculations which take place in an excel interface connected to the two flowsheet models.

Using these models in concert allows the user to explore the effect of changing the reprocessing flowsheet on the production of final waste forms. A user can also see the demand on waste treatment units for future reprocessing options.

What makes Sim Plant powerful is that it does not only consider the cost of a solvent extraction process – but also all of the associated plants that will be required to treat its effluents.



Simple DF based models

- Mass flows:
  - Elements
  - Chem species
- Activity flows
- Volume flows

- Fuel type
- Burnup
- Cooling

- Throughput

- Evaporator Throughput
- Calciner Throughput
- Waste Container Limits
- Minimum buffer capacity
- Etc…

FISPIN (Spent fuel inventory)

Reprocessing Flowsheet

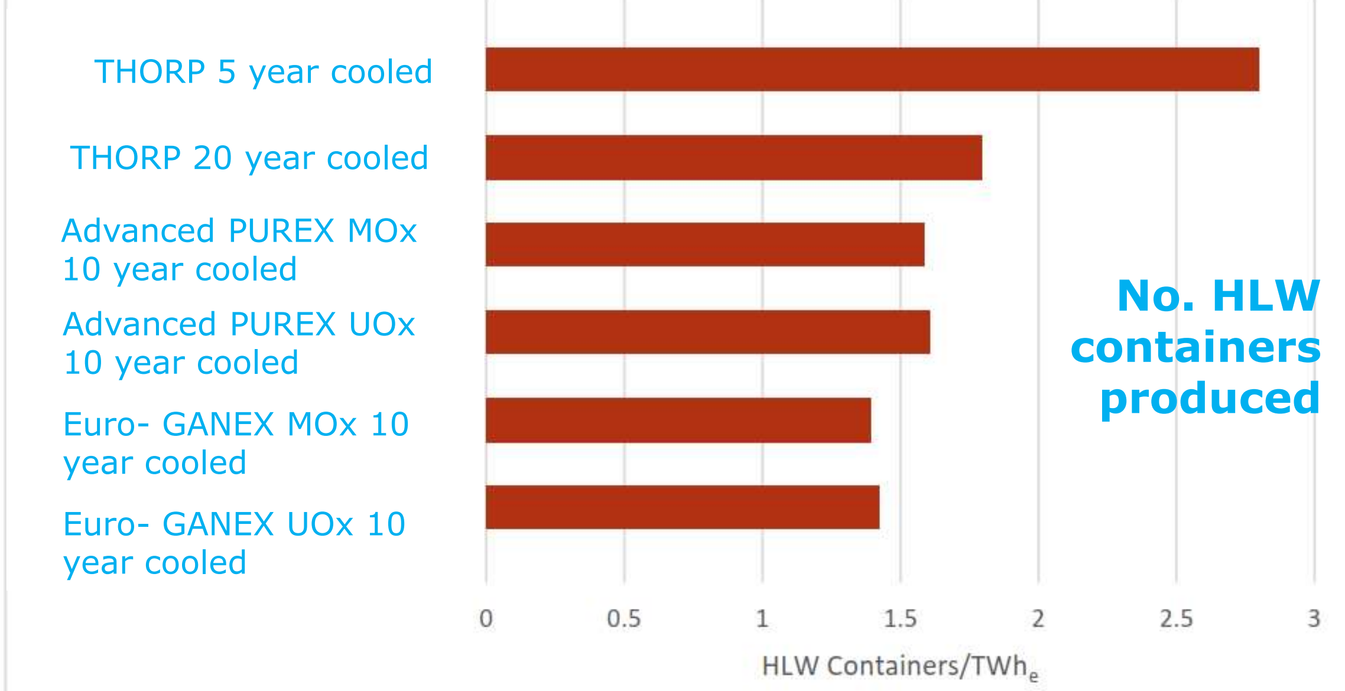
Supporting Facilities (e.g. Waste Treatment)

Sizing and Costing Models

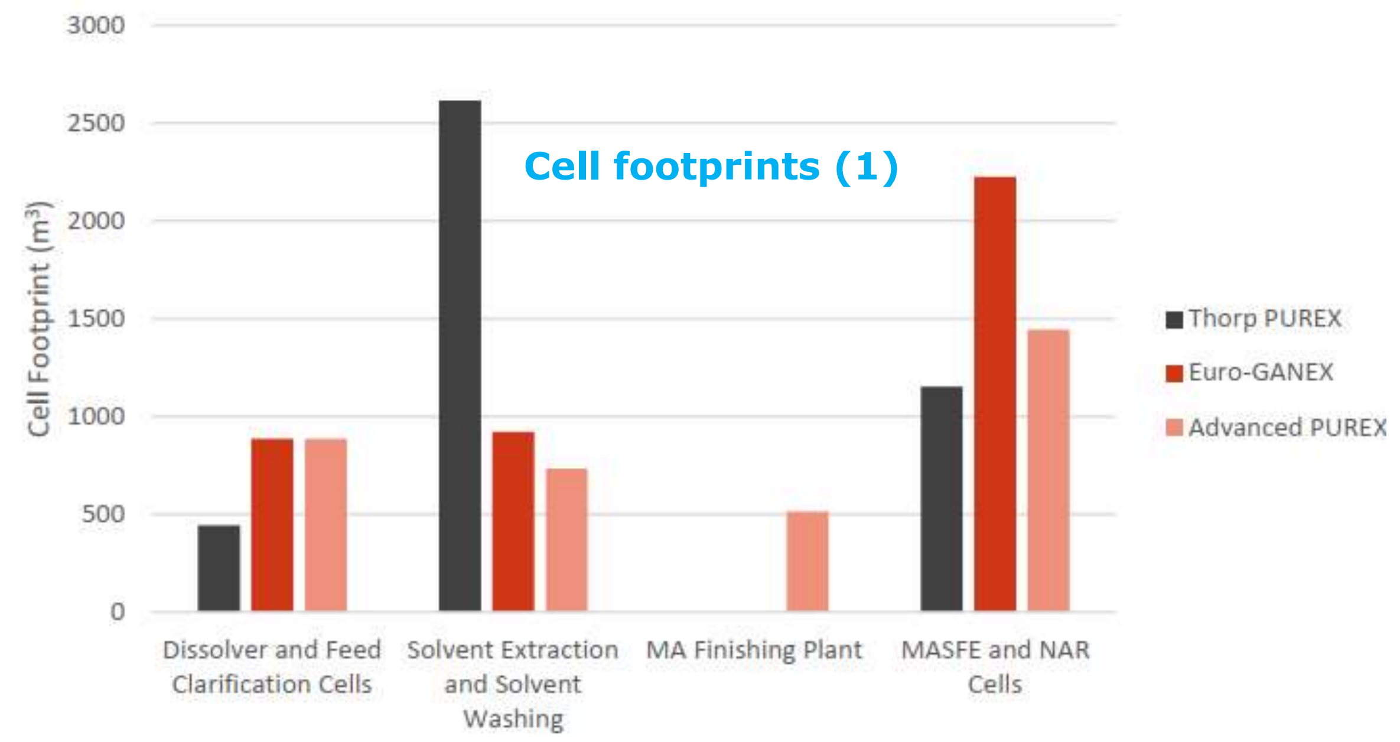
- Historical cost data for UK plants
- Sizing parameters

EFFLUENT TREATMENT

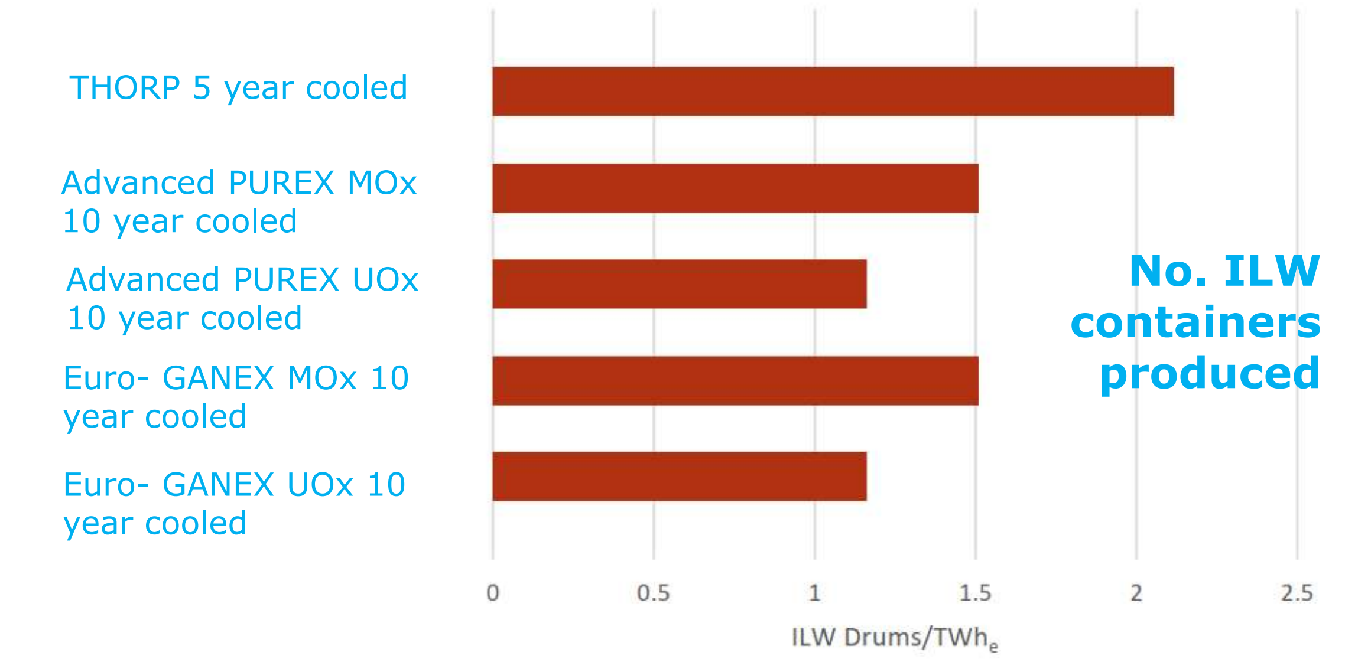
STP		WEP+WPEP Combined Plant					HALES																
							HALES Buffer Tanks		HALES Evaporators					HASTs					Vitrification Plant				
Volume	% Volume vs THORP	Footprint	Height	Volume	% Footprint vs THORP	% Volume vs THORP	Volume	% Volume vs THORP	Footprint	Height	Volume	% Footprint vs THORP	% Volume vs THORP	Footprint	Height	Volume	% Footprint vs THORP	% Volume vs THORP	Footprint	Height	Volume	% Footprint vs THORP	% Volume vs THORP
1698.677	27.40	4510	23	103730	100	100	32459.05	400.00	384	30	11520	400.00	400.00	1550.073	10.264	15909.95	190.00	190.00	2880	18	51840	120.00	120.00
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9573.961	27.40	6536	35	210400	100	100	103384.6	400.00	2088	30	62640	400.00	400.00	2553.6	20	51072	190.00	190.00	10858	40	434320	114.02	114.02
Cost :	£26,620,362				Cost :	£479,522,378	Cost :	£338,273,128				Cost :	£3,211,453,744				Cost :	£1,606,797,357				Cost :	£2,794,821,297



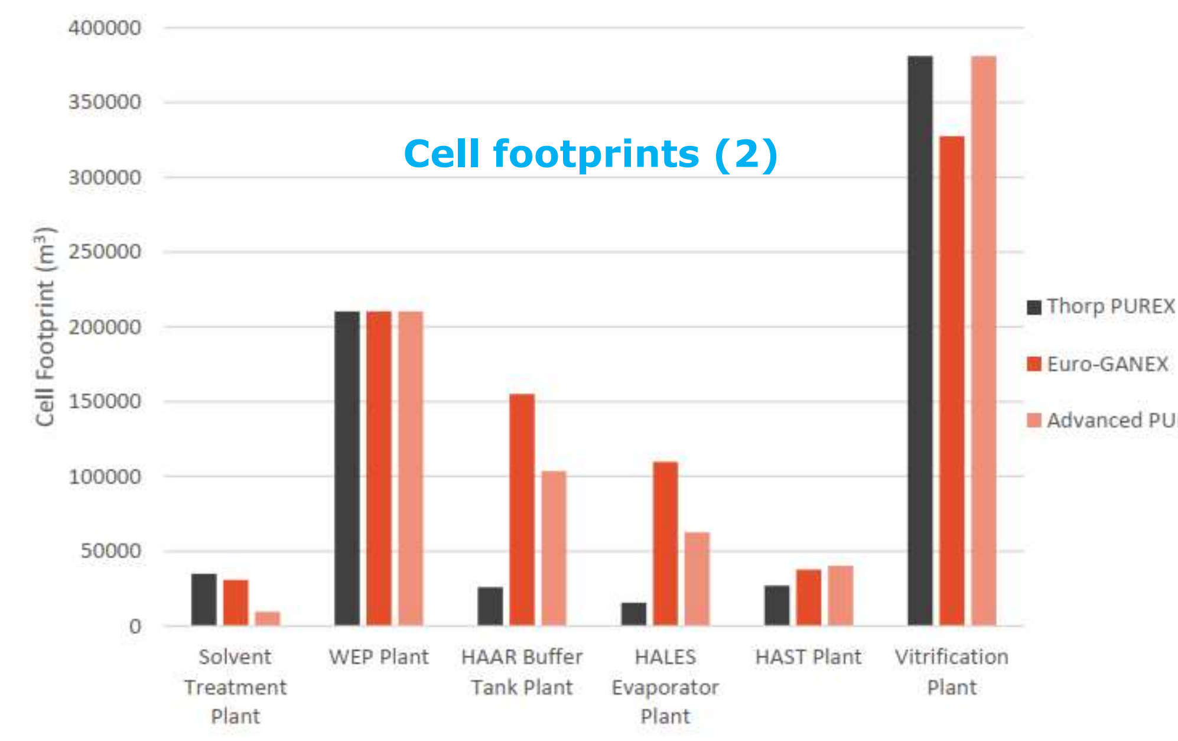
No. HLW containers produced



Cell footprints (1)



No. ILW containers produced



Cell footprints (2)

RESULTS

Using the Sim Plant tool, two next generation flowsheets were compared against the existing THORP flowsheet at the Sellafield site:

- An Advanced PUREX flowsheet incorporating the i-SANEX process;
- And the Euro-GANEX flowsheet.

From the results shown below it can be seen that both Advanced PUREX + i-SANEX and Euro-GANEX:

- Had a reduction in high-level waste (HLW) containers per TWh of electricity.
- Had a reduction in intermediate level (ILW) waste containers per TWh of electricity.
- A decreased footprint for solvent extraction (due to centrifugal contactors)
- An increased footprint in other areas

The results show that this is because of the downstream effects of the new solvent extraction processes on the Sellafield-based waste management plants.

Further R&D optimising the solvent extraction processes should rectify this issue.

Development of advanced waste treatment processes should lead to further large gains.

Without a tool like Sim Plant, which puts R&D work into an overall context, these issues might not have been identified – demonstrating the value of this approach.

THE FUTURE OF SIM PLANT

Based on the work performed to date, the next phase of Sim Plant will be to use it as a strategic tool. It is intended that in the next phase of work Sim Plant will be used to identify "Big Hitters" which can reduce the cost of next generation reprocessing. This will be achieved by:

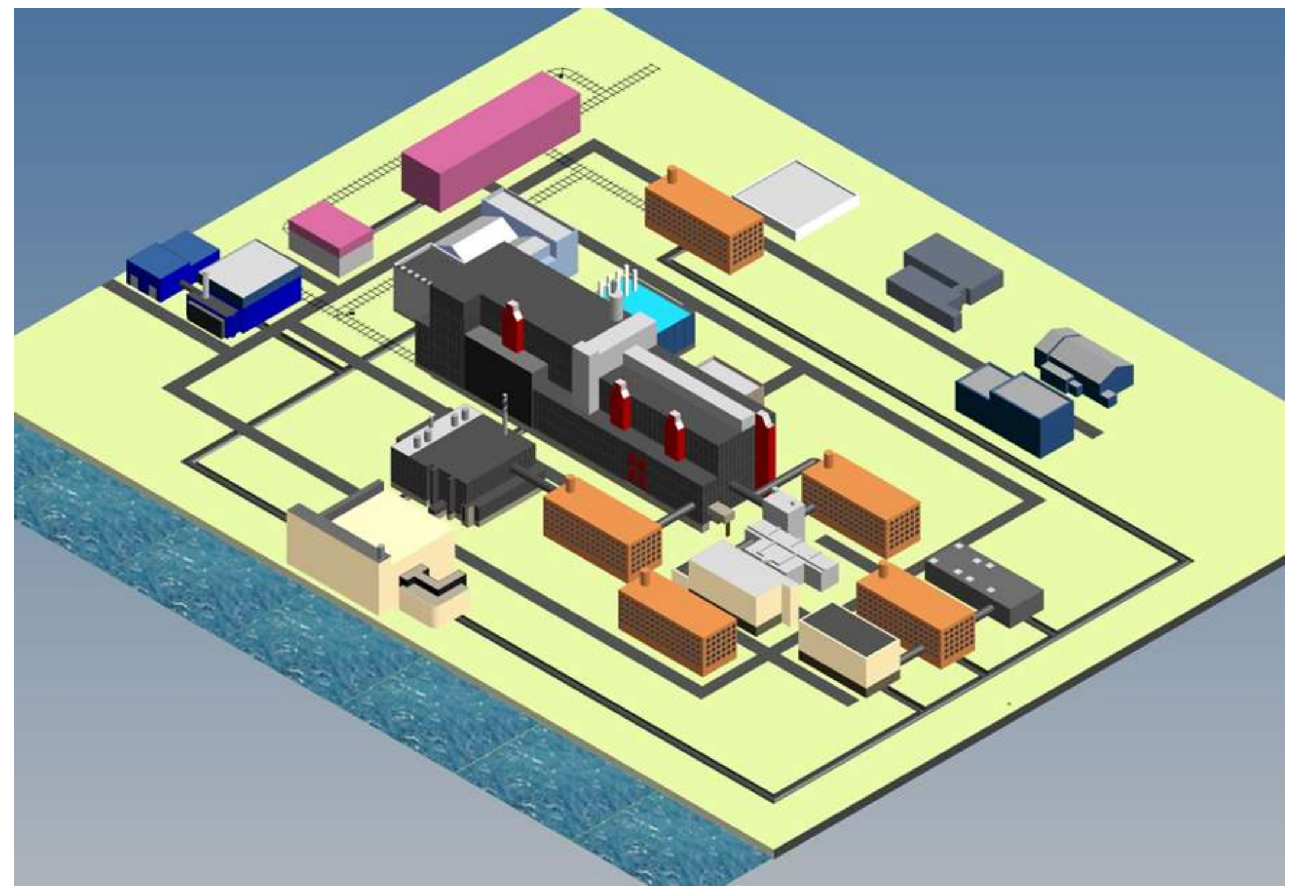
- Performing sensitivity studies with the current input parameters.
- Performing "What if?" scenarios.
- Performing comparisons of novel effluent treatments against their present day approaches.

The stream tables produced by Sim Plant also act as valuable input data for other AFCP projects and Sim Plant will continue to be developed with the needs of other projects in mind.

The long-term aim of Sim Plant is to:

- Provide a user-friendly software tool for users
- Allowing them to consider the cost/footprint of next generation recycling options.
- They would be able to select a fuel and a reprocessing flowsheet and interrogate the expected performance.

Outputs would be a 3D representation of the size and cost of the overall process (as shown on the right).



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