Supporting and Improving Sellafield Purex Operations: Recent Work on Reductive Plutonium-Uranium Separations Using Ferrous Sulphamate and Hydroxylamine

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ABSTRACT

The separation of plutonium in spent fuel processing through reductive stripping is a very well established technology. Although a very effective reagent for reductive stripping of Pu, Ferrous Sulphamate (FeSM) adds significantly to non-evaporable salt-bearing effluent, a situation exacerbated due to its superstoichiometric consumption in the process.

The process chemistry which leads to excessive ferrous consumption – commonly termed the 'box effect' – is a complex interplay of chemical reactions and mass transfer. We have developed a chemical model to describe the 'box effect' and incorporated it within powerful solvent extraction process models to describe and replicate the process in a counter-current mixer-settler battery at plant and laboratory scale. The chemical and process models have been validated against lab-scale experimental and plant operational data and can, therefore, be used to help justify flowsheet changes and examine a range of maloperation scenarios to support continued operation of the plant.

A programme of work to *partially* replace the FeSM feed with hydroxylamine (HAN) and thereby reduce waste arisings is well advanced. Laboratory and modelling work has furthered our understanding of the complex process chemistry of the Pu/Fe/HAN system, and flowsheet testing has shown that Fe/HAN reductive stripping can be as efficient as FeSM only stripping. Flowsheet trials on a glovebox-housed miniature mixer-settler rig have been undertaken to validate process models of a U/Pu split contactor operating under FeSM only, mixed FeSM/HAN conditions and maloperation conditions.

INTRODUCTION

The separation of plutonium in spent fuel processing through reductive stripping of Pu(IV) from a U-loaded TBP solvent phase is a very well established technology and a key step in the Purex Process. The Magnox Reprocessing plant at Sellafield uses ferrous sulphamate (FeSM) to reductively strip and separate plutonium. The plant, operated by British Nuclear Group, has been successfully reprocessing fuel from the UK's first generation of reactors for over forty years.

Although a very effective reagent for reductive stripping of Pu, FeSM adds significantly to the plant's non-evaporable salt-bearing effluent. Moreover, due to Pu reoxidation reactions catalysed by nitrous acid which occurs in the solvent extraction process, quantities of FeSM much greater than the stoichiometric requirement are used which further adds to the effluent volumes and reprocessing costs. The current treatment for this iron-bearing effluent stream is precipitation as an iron floc, which after dewatering is encapsulated in cement. Over years of operation the quantity of FeSM used in Magnox Reprocessing has been reduced through incremental changes to the plant's flowsheet. This has been supported through programmes of work that aim to continuously extend understanding of the separations process.

PLUTONIUM-URANIUM SEPARATIONS USING FERROUS SULPHAMATE

The separation of Pu from U is achieved using ferrous sulphamate to reduce Pu(IV) to 'inextractable' Pu(III) and thereby backwash Pu from the solvent (20% Tributylphosphate/Odorless Kerosene [TBP/OK]) phase. A schematic of this 18-stage mixer-settler contactor, currently operational is shown in Figure 1 below.
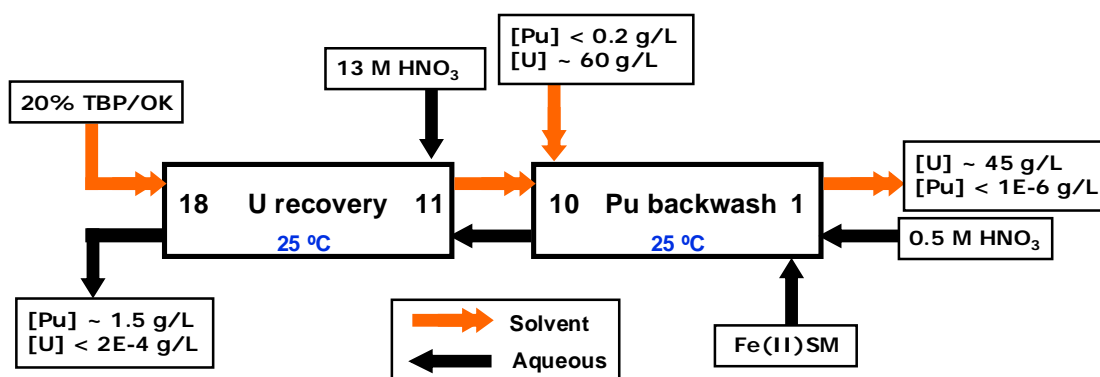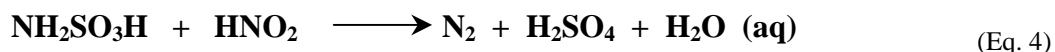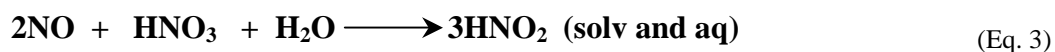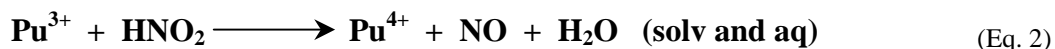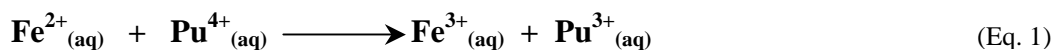

Fig. 1. The U/Pu split contactor in the Magnox reprocessing plant

Unfortunately, due to the oxidative properties of nitric acid the process chemistry of the PS4 contactor, the reductive stripping of Pu is far from simple. Through an autocatalytic mechanism nitrous acid reoxidizes Pu(III) to Pu(IV). This reaction proceeds both in the aqueous and organic phases and to minimise its effect a nitrous acid scavenger is added. In practice the reducing agent is ferrous(II) and the nitrous scavenger is sulphamate; the relevant reactions are summarised below.

$$Fe^{2+}_{(aq)} + Pu^{4+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + Pu^{3+}_{(aq)} \qquad \text{(Eq. 1)}$$

$$Pu^{3+} + HNO_2 \longrightarrow Pu^{4+} + NO + H_2O \quad \text{(solv and aq)} \qquad \text{(Eq. 2)}$$

$$2NO + HNO_3 + H_2O \longrightarrow 3HNO_2 \quad \text{(solv and aq)} \qquad \text{(Eq. 3)}$$

$$NH_2SO_3H + HNO_2 \longrightarrow N_2 + H_2SO_4 + H_2O \quad \text{(aq)} \qquad \text{(Eq. 4)}$$

Sulphamate is insoluble in the solvent phase and its ability to scavenge nitrous is therefore limited to the aqueous phase. Consequently, Pu(III) re-oxidation, whilst effectively inhibited in the aqueous phase, is allowed to continue in the solvent phase generating Pu(IV) which is once again reduced by ferrous. This leads to recycle of Pu between aqueous and solvent phases and excessive consumption of the reductant, in this case ferrous ion.[1]

The reoxidation of Pu(III) in the solvent phase results in the greater-than-expected consumption of reductant across the U/Pu split contactor. Therefore, ferrous sulphamate is added in great excess and the plant flowsheet is designed to operate such that the aqueous Pu product exiting the mixer-settler battery exhibits typical Fe(II)/(III) ratios of 5:1.

OUTLINE OF WORK PROGRAMME

This excess usage of ferrous sulphamate observed on the plant contributes greatly to the salt waste volumes handled downstream. Therefore, over the years work has been undertaken to further our understanding of ferrous consumption in the plant and optimise the flowsheet to reduce iron-bearing wastes. To support improvements to the U/Pu split contactor operation to minimise iron-bearing waste and to continually develop and support the plant safety case, which underpins operation, a programme of work is being undertaken.
The programme of work includes the following work streams:
- The development of a process model of the Magnox Reprocessing U/Pu split contactor under current operating conditions including all relevant chemical species distribution (i.e. distribution algorithms), chemical kinetic data.
- Validation of the process model against available plant data for variable throughput and operating conditions, and validation through flowsheet testing using a lab-scale mixer-settler rig housed in a glovebox.
- Determining the technical feasibility of partially replacing the ferrous sulphamate feed with hydroxylamine nitrate to reduce iron-bearing wastes
- Extending and developing the process model to understand and design flowsheets with mixed ferrous sulphamate/hydroxylamine feeds
- Validation of the 'new' mixed ferrous sulphamate/hydroxylamine flowsheets through testing on a lab-scale mixer-settler rig
- Exploring the response of the flowsheet through modelling and experimental work to the many and varied possible maloperation conditions to support extending the plant safety case to operate under mixed Fe/HAN conditions.

PROCESS MODELLING OF THE U/Pu SPLIT CONTACTOR

The process chemistry which leads to the excess ferrous consumption – commonly termed the 'box effect' - is a complex interplay of chemical species and reactions including $Fe^{II,III}/Pu^{IV,III}/Np^{VI,V,IV}/HNO_3/HNO_2$/sulphamate in both aqueous and solvent phases and the mass transfer of species across the solvent/ aqueous interface, and is exacerbated by the long residence times observed in the plant's mixer-settlers.

A key part of our work has been the development of a chemical model to describe the 'box effect' which illustrates the competition between Pu(III) extraction and nitrous acid backwashing

that lies at the heart of the excess ferrous consumption. This chemical model of the 'box effect' has been incorporated within powerful solvent extraction process models to describe and replicate the process in a counter-current mixer-settler battery at plant and laboratory scale.

A review of available in-house and external data was undertaken to provide a comprehensive listing of available chemical kinetic data for the aqueous and solvent phase reactions. Reactions of particular importance with respect to construction of a process model include:

- Pu(IV) reduction by Fe(II) (aq)
- Pu(III) oxidation by HNO_2 (aq, solvent)
- HNO_2 scavenging by sulphamic acid (aq)

The model includes a large number of other reactions which, whilst not necessarily of major importance for modelling of the contactor under normal operating conditions, may become significant when maloperation scenarios are considered. Included among these are reactions such as Pu(IV) disproportionation, which are only significant at low acidity. The model also included appropriate Np and Tc redox chemistry [e.g. Np(V) reduction by Fe(II)], where possible and relevant, to allow predictions on the routings of these contaminants. In each case the known rate equation(s) for the reaction was reviewed and recommendations on the use and limitations of each rate equation for use in process models were provided.

VALIDATION OF U/Pu SPLIT PROCESS MODEL AGAINST PLANT DATA AND LAB-SCALE RIG

Models of both the plant and the experimental rig have been developed. These are essentially the same model, with different parameter settings to account for the differences between the rig and the plant. Some of these parameters such as the sizes of vessels are easy to determine, but others, notably the stage efficiency, must be confirmed as part of the model validation process. This is because the 'box effect' mechanism which determines overall Fe(II) use is highly sensitive to the stage efficiency chosen as can be seen from Figure 2.

At low stage efficiencies the box effect is constrained by the rate of mass transfer of Pu(III) into the solvent. Although almost all the Pu(III) occurring in the solvent is oxidised by HNO_2, the limited supply of Pu(III) prevents large scale oxidation of plutonium. At very high stage efficiencies, there is the capability to supply plenty of Pu(III) to the solvent phase, but the scope for oxidation of this by reaction with nitrous is limited by the efficient backwash of HNO_2 to the aqueous phase where it is scavenged. The overall oxidation of Pu(III) in the solvent is therefore the result of a balance between rates of extraction of Pu(III), backwash of HNO_2 and the kinetics of the oxidation reaction.
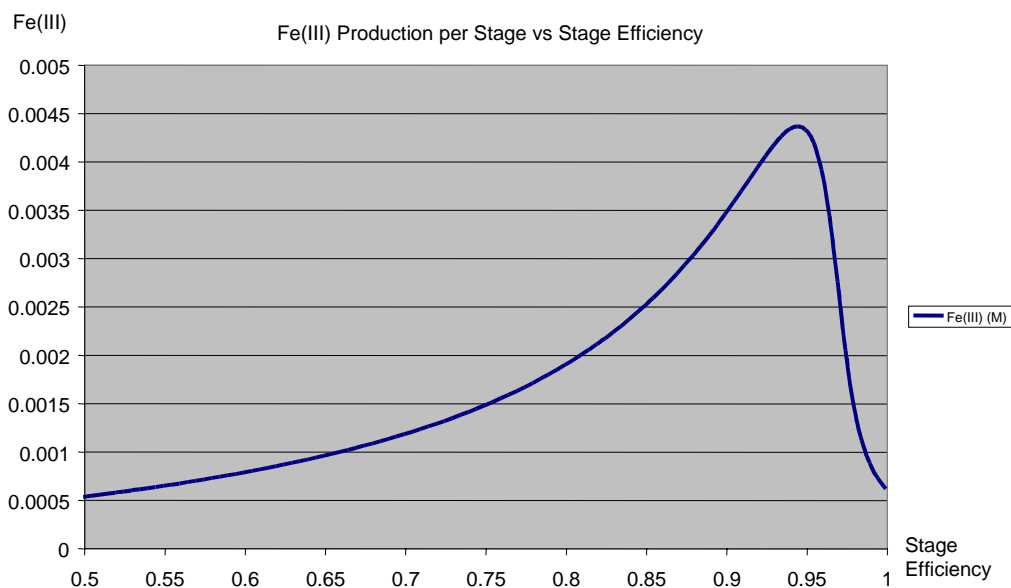
Fig. 2. Variation of Fe(II) consumption with stage efficiency for a typical contactor stage

Although the large dependency of iron use on stage efficiency makes it one of the most important sensitivities to understand, it is still necessary to have a clear understanding of the other significant sensitivities in the process.   In accordance with this a major part of the model development is concentrated on understanding how model outputs such as species profiles (e.g. Pu, U, HNO_3), product Decontamination Factors (DFs) and ferrous consumption vary with process parameters. Exploring the sensitivity of the model and comparing it to plant and lab-scale operations improves our understanding of the key process parameters and aids identification of the parameters which are important in terms of reducing ferrous consumption in the contactor. The understanding of these sensitivities is essential when it comes to the interpretation of rig results as they would apply to the plant. Apart from stage efficiency the process parameters considered in sensitivity studies included:

♦ Temperature of the contactor and feeds
♦ Ferrous Sulphamate feed (flow and concentration)
♦ Stage Efficiency
♦ Strip Acid (flow and concentration)
♦ Split Acid feed flow
♦ Kinetics of 'key' reactions

Although important, none of these parameters were as significant as the stage efficiency in determining overall Fe(II) consumption.

The plant model was tested against archive plant data, and the rig model was tested against an experimental trial undertaken on a glovebox-housed mixer-settler rig. A typical period of plant operation is shown in Figure 3 below. It is seen that, having determined suitable parameters for the plant, the variability of the iron consumption is well predicted by the model, but that there is a constant offset. This is believed to be due to a number of factors which were not included in

this model run, including the presence of small quantities of HNO_2 in the main process feed and Fe(III) in the ferrous feed.
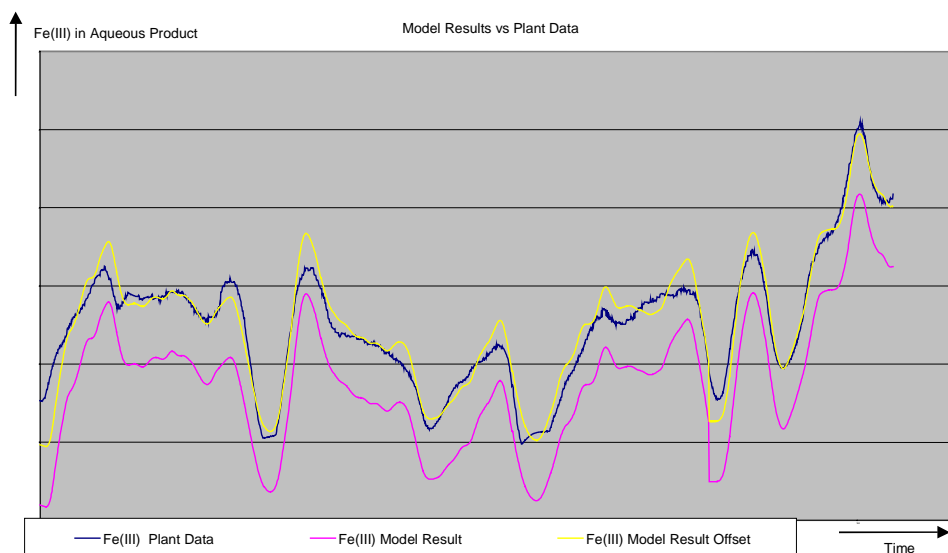

Fig. 3. Comparison of model results with plant data from the Magnox Reprocessing Plant

A scaled-down version of the plant operational flowsheet was tested on a lab-scale rig using miniature mixer-settlers. It was not possible on this small scale rig to scale both flow rates and residence times in line with plant. The flow-rates were scaled to the plant flows but this has the effect that the residence times in the mixer-settler rig are much shorter than those on plant. This was expected to have an effect on the "box effect" observed in the rig and possibly chemical kinetics, both of which are directly related to residence time in the contactor. [Note that mixer volumes were 1.8 ml and settler volumes were 10 ml]. Validation of the rig model revealed that in order to mimic rig behaviour it was necessary to assume a much lower stage efficiency for the rig mixer-settlers than was the case for the plant. This result was to be expected given the differences in decontamination factors observed between the rig and the plant, whilst running under broadly similar conditions (see Table 1 below). This is probably an artefact of the experimental rig and attributed to the miniature nature of the mixing and settling compartments and the very high Solvent:Aqueous (S:A) ratio (~9:1) used in the Pu backwash stages (1 – 10). Significant superstoichiometric ferrous consumption was observed in the trial which was successfully modelled. This demonstrates that the rig is reproducing a key aspect of the flowsheet i.e. the 'box effect'.

Table I. Decontamination Factors Obtained on Plant and in Rig Trials

	Magnox FLOWSHEET			Lab Trial 1		
	U Stream	Pu Stream		U Stream	Pu Stream	
Pu	1.30E+05	1		70	1	
U	1	4.30E6		1	2.9E4	

TECHNICAL FEASIBILITY OF A FERROUS SULPHAMATE/HYDROXYLAMINE FLOWSHEET

Previous work on the reduction of iron consumption in the U/Pu split box has concentrated on manipulating the acidity in order to affect the reactions implicated in the box effect. This approach has the advantage of not requiring any new reagents to be introduced to the plant but is ultimately limited in the extent to which it can be used to reduce ferrous consumption. A more radical approach to reducing ferrous consumption on the Magnox Reprocessing plant is the partial replacement of ferrous with hydroxylamine nitrate (HAN).[2] Hydroxylamine reduces Pu(IV) to Pu(III) according to the following equation, the kinetics of which have been determined by Barney.[3]

$$2\ Pu^{4+}\ +\ 2\ NH_3OH^+\ \longrightarrow\ 2\ Pu^{3+}\ +\ N_2\ +\ 2\ H_2O\ +\ 4H^+ \qquad \text{(Eq. 5)}$$
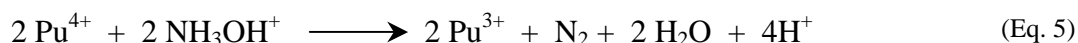
The reduction of Pu(IV) by Fe(II) under process conditions ([Pu] ~ 1 g/l, 0.5 - 2 M HNO_3) is very rapid. The reduction of Pu(IV) by HAN is slower and strongly inhibited by acidity, being inversely proportional to the fourth power i.e. $[H]^{-4}$. Generally HAN is considered effective at Pu back-washing under conditions of low acidity and therefore to achieve efficient U/Pu separations based on HAN requires flowsheet acidities usually below 1M HNO_3.

The relatively high acidity of the Magnox U/Pu split contactor (a consequence of a requirement to maintain a high U DF on the Pu product) means the use of HAN as the sole reductant is not appropriate. [The use of HAN for the separation of Pu from U was considered during Thorp development and pilot plant trials were undertaken, but eventually a salt-free flowsheet based on U(IV)/hydrazine was adopted.] Fortunately however, HAN also reduces Fe(III) thereby regenerating the 'fast' reducing Fe(II). In effect, Fe(III) catalyses the reduction of Pu(IV) by HAN, a reaction which has been studied by Barney in some detail and for a range of conditions.[4]

In order to design U/Pu split flowsheets using a mixed ferrous sulphamate/hydroxylamine feed, the process model was modified to include appropriate chemical data for reactions of hydroxylamine nitrate. Particular attention was paid to the following reactions:

- Pu(IV) reduction by HAN (aq)
- Fe(III) reduction by HAN (aq)
- HNO_2 scavenging by HAN (aq)

The new model was used to design a series of flowsheets to test the technical feasibility of an Fe/HAN flowsheet. A base case flowsheet was proposed, shown in Figure 6, which from modelling results gave excellent DFs for both Pu and U products. A series of model runs against the base case flowsheet were undertaken to ascertain the sensitivity of the flowsheet – primarily in terms of DFs, Fe and HAN consumption, and Pu recycle - to a number of process parameters. The process parameters considered included sensitive to:

- Temperature
- Ferrous Sulphamate feed
- HAN concentration

- Stage Efficiency
- Acidity (stage 1 feed)
- Stage 11 split acid flow (if any)
- Kinetics of Fe(III)/HAN reaction

In terms of flowsheet design, a number of these parameters were identified as key in the design of the flowsheet. For example, the net consumption of ferrous in the process model is very sensitive to the kinetics of the Fe(III)/HAN reaction. Unfortunately, these are not known with certainty for the process conditions and there are differing and incomplete rate equations in the open literature.[2,5,6] A study of the reduction of Fe(III) by HAN under process conditions and as a function of the process variables is currently underway and when results are available an updated kinetic expression will be incorporated in the models.

A series of flowsheet trials have now been performed including a basecase flowsheet and a very low Fe flowsheet, see Figure 4. Decontamination Factors (DFs) for two trials are given in Table 2. In both trials DFs for U product were better than those achieved with a FeSM only system demonstrating that mixed Fe/HAN systems are just as effective.
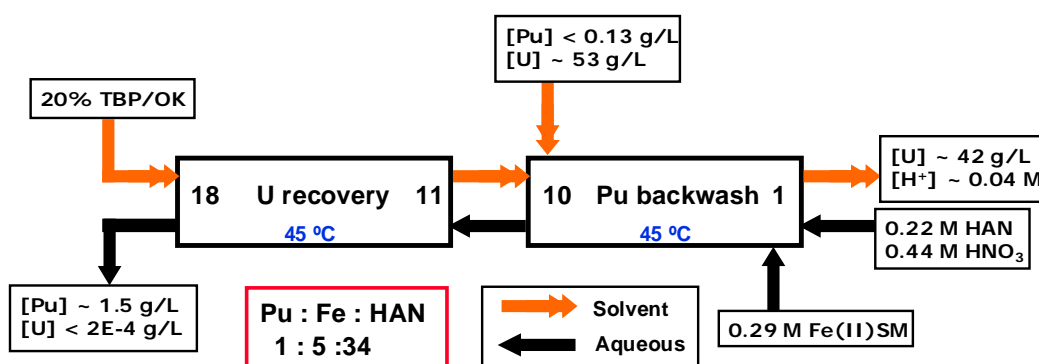

Fig. 4. Example of a 'basecase' Fe/HAN flowsheet (Trial 2) tested at lab-scale

Table II. Decontamination Factors Obtained on Plant and in Rig Trials

	Trial 2, Base case Fe/HAN			Trial 3, Very low Fe/HAN		
	U Stream	Pu Stream		U Stream	Pu Stream	
Pu	81	0.91		95	1.08	
U	1.02	1.85E5		0.98	8.95E3	

Interestingly, the third trial was performed to represent a flowsheet operating on the margins of what was believed likely to produce a working flowsheet and determine the tolerance of the flowsheet to very low ferrous concentration. The ferrous sulphamate concentration was reduced to such a level that the flowsheet is dependent on the reducing capacity of the HAN, operating either directly on the Pu(IV) or indirectly on the Fe(III). This is in contrast to the basecase flowsheet where there is probably sufficient ferrous to achieve operation without the HAN. The

Pu:Fe ratio of this flowsheet was about 1:1.5 and represents about 5% of the ferrous fed to the base case flowsheet.

CONCLUSIONS

A chemical model to describe the superstoichiometric ferrous consumption ('box effect') in a counter-current solvent process has been developed and incorporated within powerful solvent extraction process models. The chemical and process model has been validated against lab-scale experimental and plant operational data.

A programme of work to *partially* replace the FeSM feed with hydroxylamine (HAN) and thereby reduce waste arisings is well advanced. The process model has been developed to allow modelling of flowsheets operating under Fe/HAN conditions. Flowsheet trials on a miniature mixer-settler rig have shown that mixed-Fe/HAN flowsheets are as effective as Fe-only flowsheets for the separation of Pu from U.

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