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Modelling of Innovative SANEX Process Maloperations

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Abstract

The innovative (i-) SANEX process for the separation of minor actinides from PUREX highly active raffinate is expected to employ a solvent phase comprising 0.2 M TODGA with 5 v/v% 1-octanol in an inert diluent. An initial extract / scrub section would be used to extract trivalent actinides and lanthanides from the feed whilst leaving other fission products in the aqueous phase, before the loaded solvent is contacted with a low acidity aqueous phase containing a sulphonated bis-triazinyl pyridine ligand (BTP) to effect a selective strip of the actinides, so yielding separate actinide (An) and lanthanide (Ln) product streams. This process has been demonstrated in lab scale trials at Jülich (FZJ).

The SACSESS (Safety of ACtinide SEparation proceSSes) project is focused on the evaluation and improvement of the safety of such future systems. A key element of this is the development of an understanding of the response of a process to maloperations. It is only practical to study a small subset of possible maloperations experimentally and consideration of the majority of maloperations entails the use of a validated dynamic model of the process.

Distribution algorithms for HNO_3, Am , Cm and the lanthanides have been developed and incorporated into a dynamic flowsheet model that has, so far, been configured to correspond to the extract-scrub section of the i-SANEX flowsheet trial undertaken at FZJ in 2013[1]. Comparison is made between the steady state model results and experimental results. Results from modelling of low acidity and high temperature maloperations are presented.

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Keywords: TODGA; innovative SANEX; i-SANEX; process modelling; maloperation; minor actinide; lanthanide; americium; europium; solvent extraction

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1. Introduction

In order to assess the safety of proposed solvent extraction systems it is necessary to understand how they will respond to process upsets or 'maloperations'. Among the questions that need to be answered are:

- Will the maloperation give rise to hazardous concentrations of any species? The hazard in question may be nuclear (criticality) or chemical (e.g. third phase formation resulting in more general failure of solvent extraction equipment to perform as expected).
- Will the maloperation result in misrouting of one or more species? This may give rise to hazards in downstream plants (e.g. activity limits in effluent treatment plants could be exceeded).
- Will the maloperation result in alarms being triggered in a timely manner? There is a requirement to be able to detect maloperations and respond to them before a hazard is realised.
- Is the proposed remedial action timely and safe? It is necessary to be sure that any proposed actions taken to recover from a maloperation will achieve the desired outcome and will be safe. It should be noted that returning all feeds to flowsheet conditions is not necessarily safe when there is an abnormal distribution of material within a plant.

In principle it would be possible to study all such maloperations experimentally on suitable rigs, but in practice the very large number of possible variations on maloperations makes this approach prohibitive. The more practical approach is to develop a model of the process in question and restrict experimental maloperation trials to those required for model validation. The models developed for such work need to have a number of key characteristics:

- They must by dynamic. A limited amount can be learned from steady state sensitivity studies, but maloperations are inherently dynamic with transient conditions often being worse than the ultimate steady state.
- They must be able to cope with a wide range of conditions. By their nature maloperations are likely to take the plant outside of its normal operating envelope. The model needs to be able respond correctly to these conditions.

An understanding of the imitations of the model including the range of validity is required to inform interpretation of model results. For example it may be known that under certain conditions the distribution value of some species is large but unquantified. A model incorporating this limited understanding would be likely to predict correct routing of the majority of this species, but would be unable to give a reliable quantification of decontamination factors.

This paper describes the development of a dynamic model of the extract / scrub section of an i-SANEX flowsheet and illustrates the model capabilities with examples of two maloperations.

2. Model Development

Correlations to describe the equilibrium distribution of HNO_3, Am, Cm, Y, and lanthanides from La to Lu into mixtures of TODGA and 1-octanol in TPH have been developed based on results from batch distribution experiments. Extraction of acid was first modelled separately for TODGA and for 1-octanol and then the differences between the results from the superposition of the two models and experimental results for the distribution of acid into various TODGA / 1-octanol mixtures were used to determine stability constants for $nHNO_3$.TODGA.octanol complexes where $n = 0$ gives antagonism at low acidity and $n \geq 1$ gives synergistic extraction at higher acidities. Various models were developed for the extraction of the actinides and lanthanides, these in general allowing complexes of the form $M(NO_3)_3.nHNO_3.m$TODGA, $n = 0, 1$, $m = 1 – 4$. It was found that models allowing $m = 1 – 4$, offered very little improvement over models allowing only $m = 2, 3$. Models allowing both $m = 2$ and $m = 3$ were significantly better than models where m was allowed to be only either 2 or 3. For lighter lanthanides, models with $m = 3$ only were better than those with $m = 2$ only whilst for heavier lanthanides the converse was true. The data available for the construction of the models related almost entirely to the extraction of trace quantities of An/Ln. The limited data that are available for heavily loaded systems relates mainly to the lighter lanthanides and this indicates that extraction into TODGA is predominantly or entirely as tris- complexes[2]. In light