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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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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 ≥ 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 $M(NO_3)_3.nHNO_3.mTODGA$, 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

of the fact that maloperations will typically result in high saturation situations, it was decided to use the models restricted to m = 3 for this work. Temperature dependent data allowed fitting of ΔG which was found to be -20.7 kJ/mol for acid, applied across all complexes, and in the range -79 to -96 kJ/mol for the metals.

Mass transfer modelling was based on a two film model with hydrodynamics originally developed for a mixer settler model, the droplet size being adjusted to give a stage efficiency similar to that observed in the i-SANEX trial undertaken at FZJ [1,3]. This fitting process compensates for uncertainty with regard to the mass transfer coefficient calculated within the model, whilst maintaining the ability of the model to predict the response to changing flows. Dynamic mass balances were modelled in the mixing and settling regions of each stage and a dynamic enthalpy balance was added to allow modelling of temperature transients.

The flowsheet utilised in the i-SANEX trial was scaled up to represent a 5 te/d plant (see Figure 1 below). It was assumed that the mass transfer performance of the full scale plant would be similar to that observed in the trial. It is not known whether this would in fact be the case and scaling effects remain a topic for further research. The composition of the active feed was based on the primary cycle raffinate that would be obtained from a PUREX plant reprocessing 40 GWd/te light water reactor fuel, it being assumed that 1 te of fuel gives rise to 5 m^3 of highly active raffinate. This gives an extractable metal loading in the feed totalling 0.0184 M compared to 0.0143 M used in the trial. Mixers were assumed to have a volume of 0.125 m^3 and settlers were assumed to have a volume of 0.25m^3 giving a residence time per stage of 5 – 10 minutes.

The model was implemented using the gPROMS process modelling package (version 3.7.1).
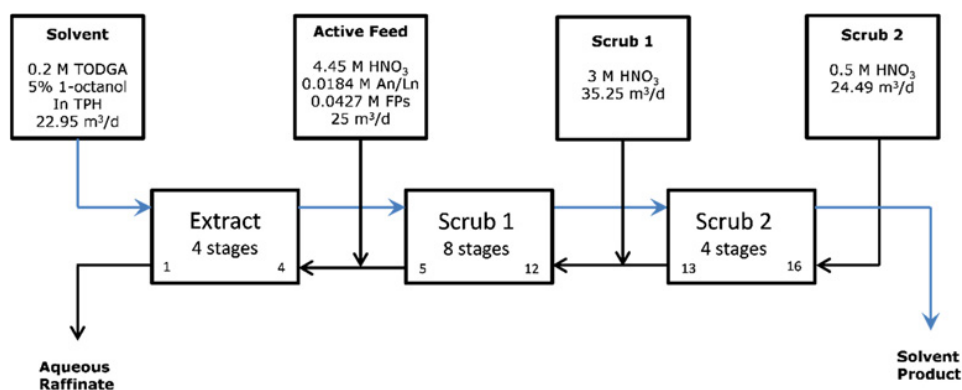

Fig. 1: i-SANEX flowsheet scaled to 5 te/d throughput.

3. Steady State Results

The model was run to steady state using the flowsheet and feed described above. Results are summarised in Figures 2 and 3 below. A number of points are apparent from these figures:
- In the extract section the reduction in concentration per stage is almost the same (factor of ~22) for each of the species considered. This is because, with the exception of the least extractable species in stages close to the feed stage, the mass transfer is limited by diffusivity rather than the distribution values.
- For most metal species the organic phase concentration is essentially constant through the two scrub sections. Total metal loading amounts to around 0.02 M in Scrub 1 rising to around 0.022 M in Scrub 2 where limited recycle of La and Ce is observed. These figures correspond to 30 – 33% of maximum theoretical loading. Aqueous phase concentrations reflect attainment of near equilibrium with the solvent.
- Distribution values predicted by the model for the scrub sections are generally somewhat higher than those observed in the trials[1,3]. For americium the trial indicated apparent distribution values in the range 600 to 1500

in Scrub 1 and ~30 in Scrub 2 as compared to model predictions of around 3000 in Scrub 1 and 40 in Scrub 2. Corresponding figures for europium are around 800 to 2000 in Scrub 1 and 200 in Scrub 2 from the trial as compared to 60000 in Scrub 1 and 230 in Scrub 2 from the model. Possible causes of the discrepancies include differences between model temperature (20 °C) and that in the trial (not stated in publications[1,3]) or the action of CDTA and oxalic acid complexants present in the trial but not the model.

- All metal species show an aqueous concentration peak at the feed stage. This effect is commonly seen in solvent extraction systems, sometimes accompanied by a corresponding concentration peak in the solvent, although this is not observed here. The predicted behaviour around the feed stage is in good agreement with that observed in the experimental trials.
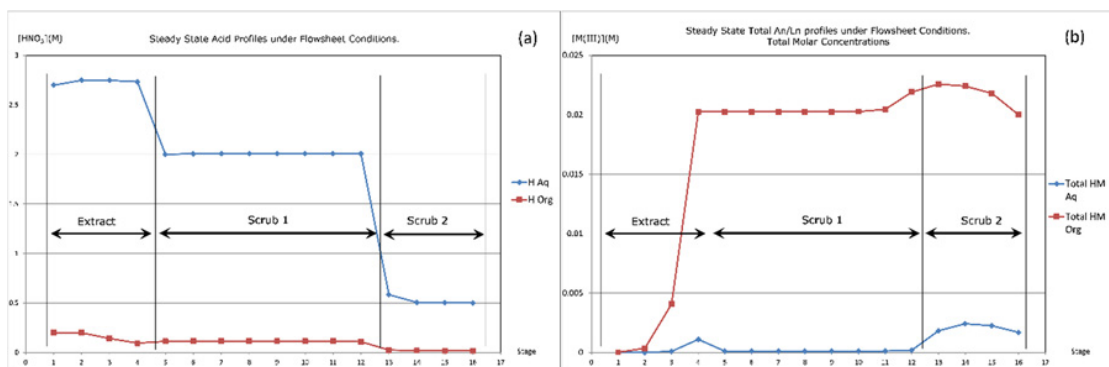

Fig. 2: Model Predictions of (a) Steady State Acid and (b) Total Heavy Metal profiles in the Contactor
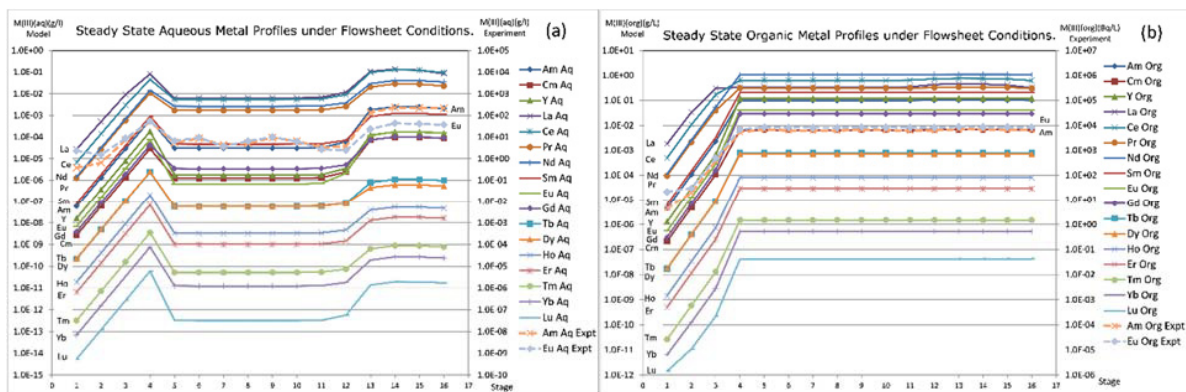

Fig. 3: Model Predictions and Experimental Results for Individual An and Ln Species in (a) Aqueous and (b) Organic Phases

4. Water Feed to Scrub 1 Maloperation

There are a great many possible maloperations to which a plant may in principle be subjected. One class of maloperation of particular concern is the reduction in, or complete loss of, acidity in one of the acid feeds. The particular case of reduction of the scrub 1 acid feed to near zero concentration has been modelled and is considered below. This maloperation has the effect of reducing the acidity in the scrub 1 section of the contactor to around 0.2 M from 2.0 M, whilst leaving the acidity of the scrub 2 largely unchanged at 0.5 M. The extract section acidity is also reduced from approximately 2.75 M to around 1.47 M. The reduction in acidity in the first scrub is such that solvent in equilibrium with the aqueous is no longer capable of carrying all the actinides and lanthanides being fed to the contactor. The less extractable species then get backwashed into the aqueous and carried back towards the extract section where the acidity is still adequate to re-extract the extractable metals. The resultant recycle builds

until such time as the solvent becomes saturated, at which point there is a significant breakthrough of lanthanides to the aqueous raffinate. This process is illustrated in Figure 4 below with the less abundant species omitted. These are all highly extractable species and their profiles do not change greatly in the course of this maloperation.

It will be seen that in the course of this maloperation, there are three possible ways in which a species may be impacted:

- More extractable species (Am, Y, Sm, Eu, Gd) are not greatly affected by this maloperation. They continue to be routed almost entirely to the solvent; although, as is discussed below for the specific case of americium, there is a significant loss of decontamination factor which varies between species.
- Lanthanum, the least extractable species, is almost entirely re-routed to the aqueous raffinate as a result of this maloperation. A transient recycle builds high local concentrations of La in the extract section, but as the maloperation progresses this collapses routing La to the raffinate.
- Other species with intermediate extractabilities (Ce, Pr, Nd) form significant recycles which persist until the steady state condition is achieved. These recycles will bleed materials out through both the raffinate and product streams.

5. High Temperature Maloperation

The steady state flowsheet has been run at 20 °C. As the extractability of all the actinides and lanthanides in TODGA based systems decreases sharply with increasing temperature (ΔG = - 79 to - 96 kJ/mol) it is to be expected that high temperatures could have an adverse effect on the operation of the contactor. To investigate these consequences, a maloperation model was run in which the temperature of all the feeds was increased to 60 °C. In order to ease numerical issues with the model, the increase was implemented as a sigmoid with most of the increase in the temperature of the feeds occurring between 0.5 and 1.5 hours. The model maintains an enthalpy balance, so it takes some time for the temperature through the contactor to rise to its final level, taking around 4 hours for the whole contactor to attain temperatures in excess of 59.5 °C. For the case run heat losses to the external environment were small so that the temperature of the contactor becomes very close to that of the feeds. The progress of the maloperation is shown in Figure 5 below with time 0 profiles omitted as these are the same as in Figure 4.

The general progress of the maloperation is similar to that of the low acid maloperation discussed above, with less extractable lanthanides recycling and ultimately breaking through to the aqueous raffinate. There are, however, some differences. Most notably, the recycle in the high temperature maloperation affects almost the whole contactor whereas in the water feed to Scrub 1 maloperation the recycle was mainly around the feed stage. The greater total accumulation of material in the recycle has the effect of making it slower to reach the ultimate steady state. In the case of the high temperature maloperation it is also seen that the recycle becomes dominated by a single species, Nd, in a way not seen for the other maloperation. Y, Am, Cm and lanthanides heavier than Nd continue to be routed predominantly with the solvent, whilst lighter lanthanides are routed almost entirely to the aqueous.

6. Discussion and Conclusions

The two maloperations described in this paper are representative of a much wider class of maloperation in which the maloperation results in a change of conditions such that solvent in equilibrium with the aqueous at some point in the contactor can no longer carry all the extractable metals being fed to the contactor. In general, this will cause the less extractable species to be backwashed and, provided that conditions remain more favourable for extraction, at some point closer to the solvent feed a recycle will start to develop. The presence of the recycle will impact on the distribution values of other species and may result in recycling or re-routing of species that would not do so in the absence of less extractable species. Even when the bulk routing of a species is not changed, many maloperations will lead to a reduction in decontamination factors which may be of concern, particularly when the actinides are impacted. Figure 6 below shows the impact of the two maloperations on americium profiles, and it will be seen that both maloperations lead to a significant increase in losses to the aqueous raffinate. These increase by around 2 orders of magnitude in the case of the water scrub maloperation and more than 3 orders of magnitude in the high temperature case. Model results can also be used to assess the likelihood of other hazards arising. For example solvent loading conditions could be compared against those that would give rise to third phase formation (once these have been fully characterised) to determine whether third phase is a credible hazard.
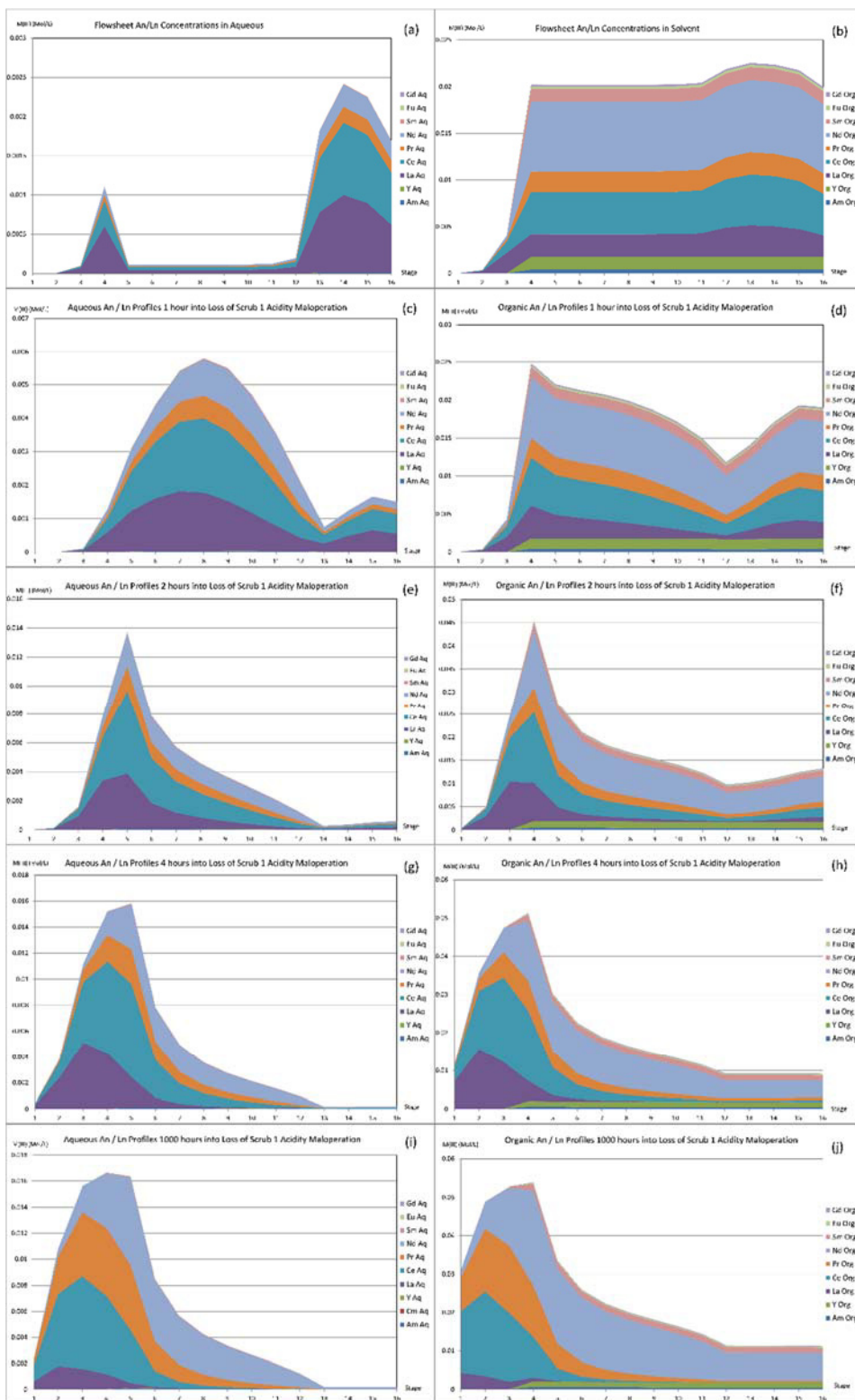
Fig. 4: Actinide and Lanthanide Profiles through the course of the water feed to Scrub 2 Maloperation
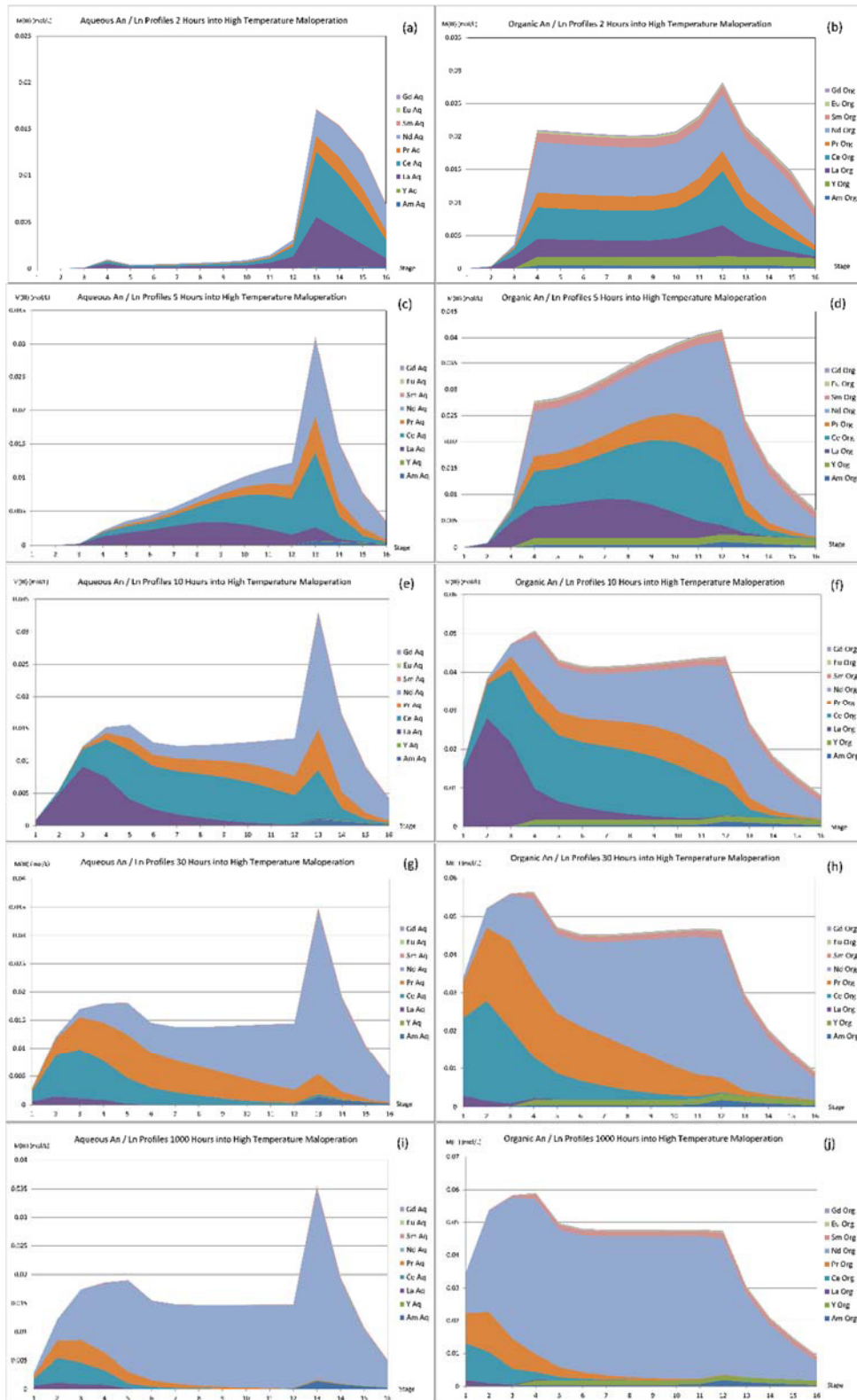
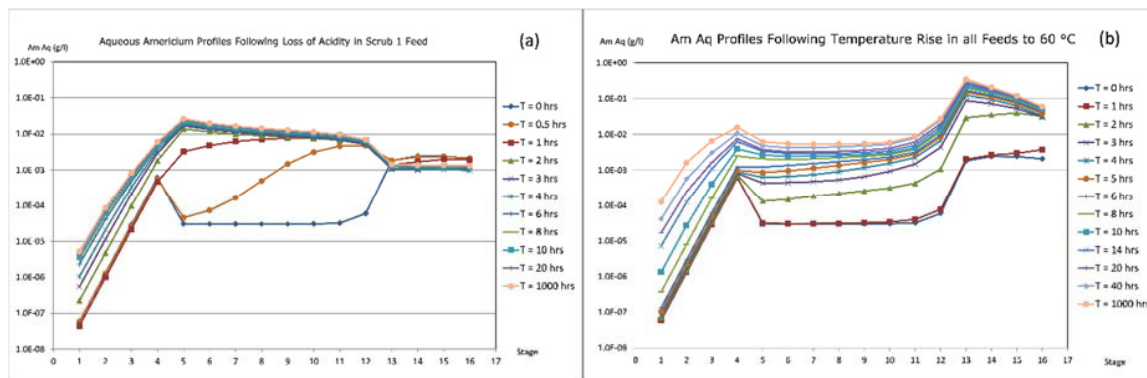Fig. 5: Actinide and Lanthanide Profiles through the Course of the High Temperature Maloperation.

Fig. 6: Variation of Aqueous Americium Profiles with Time in (a) Low scrub acidity maloperation and (b) High Temperature Maloperation.

Acknowledgements

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