GENIORS

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Safety Review minutes, including recommendations for future R&D which could eliminate, reduce or mitigate hazards

Authors : Mr. David GRAHAM (NNL), Ross Harris (NNL), Jo Keane (NNL)

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Summary

This document details the recommendations from an internal NNL safety review on the Head End and Finishing sections of a Concept Euro-GANEX plant. It also summarises the outcomes from the consortium review held at the 2018 Winter meeting at Antwerp.

Approval

Date	By
2019-11-01 16:43:51	Mr. Chris RHODES (NNL)
2019-11-05 09:26:19	Mr. Stéphane BOURG (CEA)

GENIORS

GEN IV integrated oxide fuels recycling strategies

Safety Review of a concept Euro-GANEX Reprocessing Plant

Authors: Ross Harris (National Nuclear Laboratory)

Jo Keane (National Nuclear Laboratory)

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EXECUTIVE SUMMARY

This report summarises the latest findings with regard to the hazards and safety considerations involved with the implementation of a nuclear fuel reprocessing plant operating the Euro-GANEX process flowsheet. The report describes the outcomes of a Think Tank event aimed at hazard identification and prioritisation, and the output of an NNL safety review conducted on the head and finishing areas of a concept design of a Euro-GANEX based plant [1] (These form part 1 and 2 of this report respectively).

The Think Tank participants represented a cross-section of both industry and academia at all levels of experience. The exercise produced a list of credible hazardous scenarios, the likely consequences of the hazards and identified potential areas for future study to enable mitigation.

The NNL safety review considers the major foreseeable hazards and where appropriate, mitigations for the head end and finishing processes. These are presented in tabular form in section 3.2. The review has identified the following recommendations for consideration to progress the industrial readiness of the Euro-GANEX process:

1. Consider the benefits of removing curium prior to processing at an early stage in the process rather than incorporating it in the product.
2. Process to confirm that the fuel (including failed fuel) can be shown to be free from sodium prior to processing.
3. Further research/modelling into in-growth of pure metals is required to confirm the potential for associated hazards.
4. A review is needed to determine which fuels can successfully undergo voloxidation.
5. Further work is required to understand the gas generation rates at each stage of the Head End process, for normal operations and fault scenarios.
6. Consider the impact on chemical separation of Pu(VI) in the dissolved fuel feed.
7. Further work is required to understand the fault conditions under which actinide crystallisation could occur in the head end process, and what the impact of this would be on the chemical separation process.
8. Further work is required to investigate if dissolution can be performed within a single unit, minimising the generation and transport of Pu-rich solids.
9. Further work is required to understand how electrochemical dissolution performs under different acidic conditions, and at different currents.
10. Work is required to look into the use of ozonolysis as an alternative to Ag(II) assisted dissolution.
11. Further research is required into whether nano-particles/ colloids would provide a problem within the head end or chemical separation processes.
12. Further work is required to understand the potential for secondary solids to form within the head end process under maloperations.
13. Further research is required to understand where BTP and AHA would be routed to and how they may decompose within the Pu & MA finishing line and to what extent they produce a hazard.
14. Consider how Np and other actinides recycle within the flowsheet and whether there is a different oxidising agent other than hydrogen peroxide that would produce a more homogeneous MA product.
15. Further work is required to understand the gas generation rates at each stage of the Pu & MA finishing line, for normal operations and fault scenarios.
16. Further work is required to understand optimum temperatures for the finishing line processes and the associated safety margins.
17. Further work is required to determine the consequences of ligands from the chemical separation process degrading within the evaporator.

18. Consider the potential for red oil reactions to occur in the event of solvent carry over from the chemical separation process.
19. Consider the requirements associated with the Plutonium & Minor Actinide (PuMA) product and whether this needs to be a powder based product or whether a less mobile form could be generated (such as a gel based particle).
20. Further work is required to look at the heating and calcination of Pu/MA oxide solids considering the higher volatilities of compounds such as Am oxide.

GLOSSARY

AHA	Acetyl hydroxamic acid
Aq Raff	Aqueous Raffinate
BEIS	UK government Department for Business, Energy and Industrial Strategy
BTP	Bis tryazinyl pyridine
CFA	Conditions For Acceptance
CML	Concentrate Mother Liquor
DEHiBA	N,N-di-2-ethylhexyl-isobutyramide
DF	Decontamination Factor
DMDOHEMA	N,N'-dimethyl-N,N'-dioctylhexyloxyethyl malonamide
DOG	Dissolver Off Gas
FPs	Fission products
FR	Fast Reactor
GANEX	Grouped Actinide Extraction
GENIORS	GEN IV Integrated Oxide fuel Recycling Strategies
HAL	Highly Active Liquor
HAN	hydroxylamine nitrate
HLW	High Level Waste
HM	Heavy Metal
MA	Minor Actinide
MEO	Mediated Electrochemical Oxidation
MOX	Mixed Oxide Fuel
NNL	National Nuclear Laboratory
OML	Oxalate Mother Liquor
PuMA	Plutonium & Minor Actinide
PUREX	Plutonium Uranium Extraction
R&D	Research and Development
SACSESS	Safety of Actinide Separation Processes
SNF	Spent Nuclear Fuel
SO3-Ph-BTP	2,6 Bis(5,6- di(3-hydroxysulfonylphenyl)-1,2,4-Triazin-3-yl)Pyridine
TODGA	N,N,N',N' tetra octyl diglycolamide
TRU	Trans-Uranic Elements
VOG	Voloxidation Off Gas

CONTENTS

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1. INTRODUCTION

The European Horizon 2020 GEN IV Integrated Oxide fuel Recycling Strategies (GENIORS) programme combines the efforts of 24 academic and industrial European partners to improve current recycling of spent nuclear fuel, and develop future recycling strategies to be implemented in the 4th generation of nuclear reactors (expected to enter operation by 2030) [1].

Euro-GANEX (Grouped Actinide Extraction) is an advanced aqueous reprocessing flowsheet developed as part of the European Union funded Safety of Actinide Separation Processes (SACSESS) project [2]. Though it is broadly similar to the widely used Plutonium Uranium Extraction (PUREX) process, the GANEX process utilises different extraction chemicals to extract a transuranic actinide product rather than a pure plutonium product. The benefits of this type of extraction are two-fold: the absence of pure plutonium in the product increases its proliferation resistance, and the smaller quantities of actinides sent to high level waste (HLW) reduces the heat loading of waste packages. Full recycling of actinides can result in a reduction in the time required for HLW to reduce to reference levels from ~100,000 years to ~500 years [3]. This increases the quantity of waste that can be incorporated per HLW container, reducing overall size, and potentially cost, of storage facilities.

National Nuclear Laboratory (NNL), as part of the GENIORS programme, has produced a concept design of an advanced reprocessing plant operating a Euro-GANEX process flowsheet to reprocess spent Gen IV fast reactor Mixed Oxide (MOX) fuels [4]. Safety is of paramount importance at all stages of design. It is crucial to consider the potential hazards of a process and how to mitigate them as the design develops from an initial concept so potential risks are minimised. Safety considerations often have a large influence over the direction of a design, therefore inclusion from an early stage minimises the need for re-work. A safety review of the Euro-GANEX process and the concept design of a full scale Euro-GANEX plant must therefore be considered, this document summarises the latest safety review findings.

This document comprises of two parts:

- Part 1 is an extension of a safety review of the chemical separation flowsheet of the Euro-GANEX process performed through the SACSESS programme [5]. For this work, a consortium review was held at the GENIORS 18 month project meeting held in Antwerp, Belgium, October 2018. This study enhanced the safety evaluation of the whole chemical separation flowsheet, this review took recommendations produced from earlier work [5] and evaluated the hazards for a concept reprocessing plant operating a Euro-GANEX process.

- Part 2 presents a review of the concept Euro-GANEX reprocessing plant outlined by GENIORS report PD06 Deliverable 8.1 [4]. The concept design represents a first-attempt at representing the reprocessing plant in its entirety, presenting the challenges of advanced homogeneous reprocessing of fast reactor fuel on proposed Head-End and Finishing operations. This part of the review considers the Head-End and Finishing operations, to draw-out additional operational hazards previously not evaluated in Euro-GANEX safety reviews and provide a holistic perspective of the flowsheet.

This document should be read in conjunction with the SACSESS Euro-GANEX process description [2], SACSESS Euro-GANEX safety review [5] (included as Appendix 2), and the GENIORS concept design of a Euro-GANEX reprocessing plant [4].

2. PART 1 – GENIORS THINK TANK SAFETY REVIEW – HALF YEAR MEETING, 23-25TH OCTOBER 2018 ANTWERP, BELGIUM

2.1. THINK TANK SAFETY REVIEW METHODOLOGY

The consortium safety review of the Euro-GANEX process took the form of a Think-Tank style event chaired jointly by NNL and the University of Leeds. The review, which spanned two three-hour sessions (on consecutive days), was designed to engage members of the consortium from a variety of disciplines and experience levels to identify potential hazards, assign priorities and suggest mitigations. Where mitigations could not be identified immediately, ideas for potential Research and Development (R&D) were discussed and recorded.

The objectives of the event were two-fold: to engage the GENIORS community, obtaining input from a variety of experts from both industry and academia; and to disseminate and share knowledge between members and younger professionals.

The group-based safety review was based on two documents produced for the SACSESS programme (D31.1b SACSESS safety assessment methodology [6] and D31.3 full safety of a demonstration Euro-GANEX plant [5]). These set out a description of a reprocessing flowsheet based on the Euro-GANEX process and some of the potential hazard scenarios. To expand upon the work of the SACSESS programme, the GENIORS safety review focussed on addressing the recommendations and areas for further study identified through the SACSESS safety evaluation [5], these concerned only the 1st and 2nd separation stages (the Chemical Separation section of the reprocessing plant – see Figure 1).

2.2. KEYWORDS:

The Think Tank was not conducted in the same manner as other safety reviews which interrogate the plant in a systematic manner to identify hazards, causes, consequences and mitigations. Instead, the four groups, each of 8-10 researchers, were provided with keywords to guide conversation and debate. The output from the Think Tank was therefore designed not to consider every possible hazard arising from each part of the plant, but to compliment other reviews by identifying hazards which may have not previously been captured. The output from the initial safety review carried out under SACSESS (detailed in D31.3) [5] was used as a starting point. This report presented a number of recommendations that were converted into criteria used to guide the group's thinking process:

1.	Explosion/flammability of materials	(recommendation 1)
2.	Toxicity of materials	(recommendation 2)
3.	Effects of radiolysis	(recommendation 4)
4.	Effects of hydrolysis, degradation of other chemical reactions	(recommendation 4)
5.	Effects of contaminated solvents	(recommendation 5 & 6)
6.	Extent of NOx (and other hazardous gases) production	(recommendation 7)
7.	Effects of operating outside of the defined flowsheet envelope, e.g. temperature	(recommendation 8 & 10)

For each criterion, participants were asked to develop a list of hazards, safety issues and technical risks.

2.3. BATTERY LIMITS & FLOWSHEET:

The battery limits applied to this exercise closely mimic those of the SACSESS review (Appendix 2):

- Only the 1st and 2nd cycles of the Euro-GANEX Chemical Separation flowsheet (Figure 1) were considered. Exceptions to this were made when considering hazards which initiated in the chemical separation cycles but would not present a hazard until they reached known downstream processes (e.g. product finishing furnaces).
- The feed was assumed to be fast reactor oxide fuel dissolved in nitric acid and free of cladding.
- Centrifugal contactors are assumed to be the technology employed for all solvent extraction operations.
    - It has been noted that centrifugal contactors may not be appropriate for the flowrates expected in the first cycle.
- The final form of the product is unknown. As such, the products are assumed to be suitably purified streams of uranium, fission products, actinides and lanthanides, each dissolved in nitric acid and held in storage tanks.
    - As there are currently no Conditions For Acceptance (CFA) for the products, it is unknown what would constitute acceptable levels of impurities. Therefore, the products will be assumed to be as pure as possible and mal-operations will be defined as the point at which the products do not meet the CFA of subsequent plants.
- It is assumed that product from sections of plant will be buffer stored and sampled prior to passing to subsequent plant sections however, fault scenarios whereby out of specification liquors can pass from one section to the other were considered.
- It is assumed that any vessel in which it is expected that fissile material will be present will be designed to be criticality safe and the plant will be designed with sufficient radiological shielding to mitigate dose uptake (area specific shielding will be appropriate for the expected dose in that area).

For the purpose of the Think Tank, the following compounds were specifically considered, however miscellaneous process feeds or the products of degradation may have also been identified:

- DEHiBA - N,N-di-2-ethylhexyl-isobutyramide
- DMDOHEMA - N,N’-dimethyl-N,N’- dioctylhexylethoxymalonamide
- TODGA – N,N,N’,N’ tetra octyl diglycolamide
- Nitric acid
- Hydrazine
- Odourless Kerosene

Figure 1 Illustrates the chemical separation flowsheet presented at the Think Tank event.

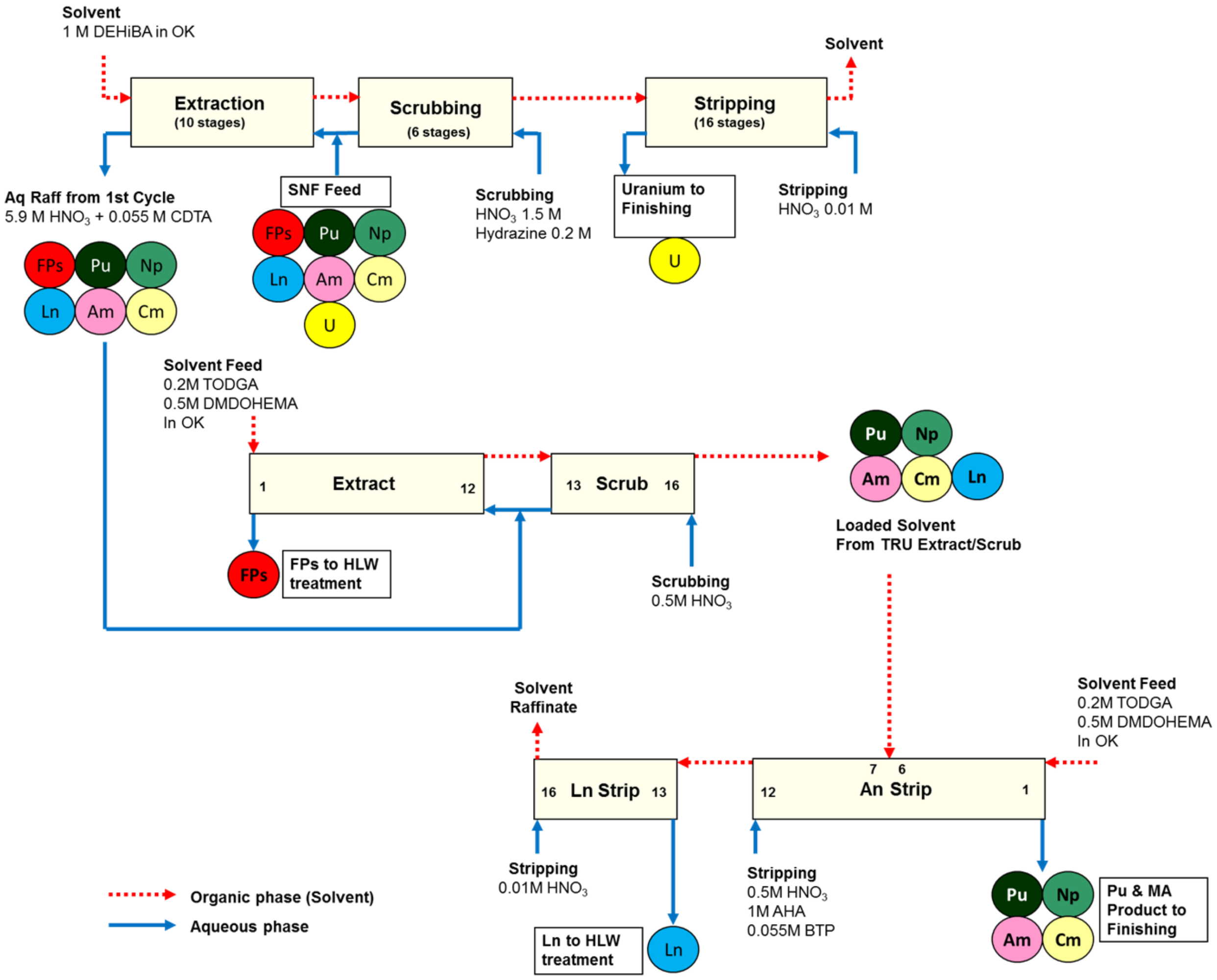

Figure 1 - Chemical Separation flowsheet of the Euro-GANEX process (1st and 2nd cycles combined)

2.4. THINK TANK AGENDA

Day 1:

- Introduction
    - Objectives and outputs of the exercise
    - Introduction to the process to be used
    - Assigning researchers to groups
- Information share on Euro-GANEX
    - Presentation of the hazard criteria (the output of the SACSESS work [7])
    - Technical criteria and their meaning
    - Technical information available to the groups (e.g. flowsheet information)
- Breakout Session (facilitated discussion)
    - Brainstorm hazards, issues, and their effects
    - Group and prioritise hazards
    - Provide feedback to the other groups
    - Collate common outputs and agree priorities
- End of day 1

Day 2:

- Introduction
    - Refresh on objectives and outputs
    - Refresh on common outputs of Day 1
- Breakout Session (facilitated discussion)
    - Brainstorm R&D to eliminate/reduce hazards, issues and their effects
    - Group, collate and prioritise ideas
    - Provide feedback to other groups
    - Collate common outputs and agree priorities
- Conclusions from Think Tank
- Feedback from participants
- End of day 2

2.5. THINK TANK SAFETY REVIEW OUTPUT – DAY 1 HAZARD IDENTIFICATION

Table 1 – Summary of Hazards Identified

ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
1	Flammability/Explosion Effects of Radiolysis	Hydrogen generation from the radiolysis of aqueous and organic phases.	Hydrogen has the potential to form an extremely explosive atmosphere. An explosion often inflicts greater damage and loss of life compared to fire alone. A sudden large scale escape of volatile liquids or gasses which could produce a cloud of flammable/explosive vapour is one of the greatest process plant hazards, especially if the cloud causes impacts beyond the site boundaries [7]. The presence of radioactive material introduces an additional hazard as an explosion would result in the release of this material into the environment. The effect of a hydrogen explosion would be amplified by the presence of low molecular weight organics.	Engineered solutions/mitigations exist to manage hydrogen as an explosive atmosphere. However, the most appropriate action would be to eliminate the risk of hydrogen production If possible.
2	Flammability/Explosion	Flammability of low molecular weight hydrocarbons e.g. Odourless Kerosene (OK). Formation of low molecular weight molecules could result from the damage of larger organic molecules from either radiolysis or degradation.	Consequences/likelihood are temperature dependent, ultimately resulting in explosion at higher temperatures. The misrouting of these low molecular weight hydrocarbons to the evaporators present in product finishing would result in ignition (see line number)	Organic compounds such as DEHiBA, DMDOHEMA and TODGA are expected to be of too high a molecular weight to pose a significant hazard (relative to OK). Accumulation of a significant amount of these hydrocarbons would most likely occur in storage tanks, especially if these

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ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
				are not agitated. Understanding expected doses and degradation products and managing solvent inventory accordingly (clean/bleed and replace).
3	Flammability/Explosion	The passing of flammable/organic material (DEHiBA/TODGA/DMDOHEMA) to the product finishing evaporator feeds.	The heating of organics in the presence of nitric acid could initiate a red oil excursion, a highly explosive event.	The finishing stream should have a steam strip column positioned before the evaporator to ensure no organics reach the evaporator. However, The Chemical Separation section of the plant should be designed to minimise and if possible eliminate the opportunity to entrain organics to the product finishing sections. A solvent float-off system on buffer storage tanks may be suited to this.
4	Flammability/Explosion	Electrical malfunction/electrical charge or another ignition source providing substantial energy into a system containing heated flammable and explosive substances.	Ignition of flammable liquids, mixtures or gasses within the process.	This will likely be mitigated through engineering design, ensuring all equipment is ATEX rated to prevent the generation of a spark. Inertion could prevent explosive atmospheres from forming.
5	Flammability/Explosion	The use of hydrazine within the flowsheet. Hydrazine has previously seen applications as rocket fuel/propellant. It is flammable at high temperatures, can decompose via radiolysis to form hydrogen, and can become hydrazoic acid if reduced by Tc, which	Fire, breach of primary containment, release of radioactive material.	Alternative reductants to hydrazine should be investigated.

ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
		itself is highly explosive.		
6	Flammability/Explosion	The formation, recycle and accumulation of self-heating solids/crud/precipitate within the system caused by maloperation.	Potential to increase the temperature of the system which may in turn cause the thermal degradation of organics to low molecular weight species which are more flammable.	This would be the result of a maloperation, causing solids to be present within the chemical separation section, or reactions forming precipitates.
7	Toxicity of materials	Unknown toxicity of new components or new compounds that are generated via radiolysis/degradation products and subsequent chain/side reactions.	Unknown effects on operators.	The toxicity of the components and the potential degradation products, and associated species was unknown at the time of recording. Therefore these need to be investigated prior to use.
8	Toxicity of materials	The use of concentrated nitric acid.	Potential injury to operators if not handled correctly, in the event of a maloperation involving a loss of containment.	The hazards of operating with nitric acid are well known and understood.
9	Toxicity of materials	Leakage from storage tanks and pipework.		These hazards are a common process plant hazard, with well-established mitigations.
10	Toxicity of materials	Acetyl hydroxamic acid (AHA) and hydrazine are known toxic chemicals.	Hazards to workforce managing chemicals from receipt to buffer storage of reagents.	Toxic chemical hazards are a common process plant hazard, with well-established mitigations.
11	Effects of Radiolysis	Degradation of ligands e.g. due to radiolysis and hydrolysis	This could alter the Pu and Np speciation and cause misrouting of material, resulting in a criticality (in the worst case), and/or effect product specification. Misrouting of radioactive material to areas of plant with inadequate radioactive shielding could occur.	An understanding of the dose rates, rates of degradation, effect of degradation product on the process is required.

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ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
			Low levels of misrouting could cause slow build-up of material/activity, above hazards apply. Organic degradation products could partition to the aqueous phase and cause issues as above.	
12	Effects of Radiolysis	Changes in the REDOX reactions due to degradation of reagents within the separation processes, affecting extraction chemistry.	• Misrouting of material • Formation of precipitates • Enhanced corrosion This could lead to a criticality, organic material misrouted to the finishing evaporators and vessel failure. The consequences are similar to ID 11.	Research is required to fully understand the effects of radiolysis on the REDOX reactions taking place. I.e. the degradation products formed, the rate of formation, the extent to which the solvents would be subject to radiation, and the effects of the degradation products on the extraction chemistry.
13	Effects of Radiolysis	Different contactor setups between the first and second cycles in the Euro-GANEX process means that the operating lifetimes of solvent will differ	Similar consequences to ID 11	
14	Effects of hydrolysis, degradation and other chemical reactions	Degradation products will affect the physical properties of the liquid phase e.g. viscosity, interfacial tension.	An understanding of the operational envelope and physical properties of a system is vital to normal operations of a plant. If the physical (hydrodynamic) properties change from what is expected the efficiency of unit operations could be affected, potentially leading to improper extraction and therefore misrouting of fissile material or solvent (see ID 11).	Research is needed to establish the variation in physical properties brought about by the presence of degradation product. Predictions can then be made regarding their impact on the performance of the system and what constitutes a normal operational envelope.
15	Effects of hydrolysis, degradation of other chemical reactions	Formation of degradation products which could result in precipitation of solids Accumulation of solids/ fissile material	Build-up of solids which could cause blockages in pipework and contactors. The accumulation of material within an area of plant not designed for solids in terms of shielding	Need to understand how to remove any solids/blockages. Need to understand the tolerance of the solvent extraction equipment with regard

ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
			and criticality geometry.	to solids. Understanding of what degradation products are and what the potentials to form solids are. Consider maloperation studies?
16	Effects of hydrolysis, degradation or other chemical reactions	Improper washing of solvent could accumulate radioactive material in areas of plant not adequately shielded. (Radiological protection)		See row 11
17	Effects of hydrolysis, degradation or other chemical reactions	Nitration of aromatic compounds already present or formed in the organic phase	Nitro-aromatics present an explosion risk (tri-nitro-toluene being the most well-known)	As above, an understanding of the nitration reactions required to form these compounds. A solvent specification with a knowledge of aromatic content and expected consequences required.
18	Effects of hydrolysis, degradation or other chemical reactions	Formation of sulphates from degradation of 2,6-Bis(5,6- di(3-hydroxysulfonylphenyl)-1,2,4-Triazin-3-yl)Pyridine (SO_3-Ph-BTP) in actinide strip could lead to metal sulphates	Metal sulphates could precipitate or undergo chemical reactions not envisaged. SO_3-Ph-BTP and the degradation products of it can exacerbate corrosion of the plant.	Understand the degradation chemistry of SO_3-Ph-BTP and expected effects in process. GENIORS is moving away from SO_3-Ph-BTP to CHON actinide strip reagents.
19	Effects of hydrolysis, degradation or other chemical reactions	Secondary waste generation from solvent treatment steps e.g. steam strip, solvent wash, etc.	Increased waste inventories requirement for waste treatment plants	Understand possible waste treatment scenarios and the wastes which these will generate. Understand all end-to-end wastes produced.

ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
20	Effects of operating outside of the defined flowsheet envelope /effects of contaminated solvents	The feeding of out-of-specification chemicals into the process, e.g. • Contaminated solvent from improper washing • Out of specification chemicals	• Improper routing of material • Precipitation of solids • Unanticipated chemical reactions /side reactions • Redox chemistry • Change in operating envelope	Plant operational controls can minimise the possibility of this type of maloperation. Work needs to be undertaken to fully understand the safe operating envelope in terms of the aforementioned modes of maloperation.
21	Effects of operating outside of the defined flowsheet envelope	Misrouting of fissile material due to maloperation e.g. of flows to an area which is not criticality-safe.	Criticality Event.	The most significant hazard discussed was that of a criticality. This would take the form of a misrouting of fissile material which can have several different fault-initiating events (or maloperations). E.g. loss of AHA feed could lead to a misrouting of Pu in the An/Ln strip sections.
22	Effects of operating outside of the defined flowsheet envelope	High concentration of acid within the stripping sections of the contactor banks.	Fissile material will make its way into the solvent recycle system resulting in a recycle of Pu (posing a criticality risk), and the recycle of lanthanides (which are heat-generating and could expose un-shielded areas to high doses of radiation). High acid concentrations could also enhance ligand degradation and corrosion of plant equipment.	Need to define operational envelope.
23	Effects of operating outside of the defined flowsheet envelope	Low concentration of acid in the scrubbing sections of the flowsheet.	This could cause the precipitation of Pu and/or the formation of a third phase. This poses a criticality risk.	Need to define operational envelope.
24	Effects of operating outside of the defined	Misrouting of chemicals through inefficient solvent extraction.	This could affect product specification through not removing impurities which effect fuel	

ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
	flowsheet envelope	This could be caused by using the incorrect rotor speed or poor mixing. Contamination of solvent could change the distribution ratios of material, resulting in misrouting of material.	performance. Misrouting of fissile species could cause a criticality incident. Misrouting of organic species could result in fire/explosion.	
25	Effects of operating outside of the defined flowsheet envelope	Temperature variations from the normal operational envelope.	This could, at extremes, cause organic species to reach flash point resulting in fire or explosion.	The flash points of the solvents used were not to hand at the time of the review. The effects of temperature variation on the behaviour of flows around the system are too complex to understand at this point.
			Distribution ratios, which describe the extent to which a species is dissolves in the organic and aqueous phases respectively, are extremely sensitive to temperature fluctuations (by as little as 10°C). Therefore variations in temperature could upset the solvent extraction processes and misroute material, potentially causing a criticality or explosive situation. The effects of lower than expected temperatures may affect the physical properties and rheology of the system, potentially leading to unpredictable flow conditions and inadequate extraction or the misrouting of material. Low temperature could result in precipitation and crystallisation of actinides.	The full effect of elevated temperature on degradation product is not, at present, fully understood. This should be considered when investigating the formation and effects of degradation products.
26	Effects of operating outside of the defined	Incorrect chemical feed from head end operations.	Broadly speaking, incorrect chemical feeds will affect the delicately balanced solvent extraction	This scenario covers a broad range of maloperations all resulting from an

ID:	Criteria	Credible Scenario	Consequences	Notes / Recommendations
	flowsheet envelope		system. Problems such as the misrouting of material and enhanced corrosion could result from this fault scenario. Hazards such as a criticality or a loss of containment could occur. If solids are present, the contactors could block causing similar problems.	incorrect feed material being passed to the chemical separation section of plant from the head end.
27	Effects of operating outside of the defined flowsheet envelope	An increase in pressure in the system above the normal operating envelope will result in a shift in the gas-liquid equilibrium whereby a greater proportion of volatile components of the gaseous phase will dissolve into the liquid phase.	This could result in the transfer of volatile components to areas of plants not designed to handle volatile and flammable materials. Solubility of gasses in liquid phases in highly sensitive to temperature and so gasses could come out of solution as the liquid is heated, potentially causing an accumulation and explosion. Variation in pressures could result in the disruption of flows, potentially causing back-flow.	Engineering design should consider passive pressure management systems. Define the pressures at which gas solubility becomes a problem.
28	Effects of operating outside of the defined flowsheet envelope	An accumulation of precipitated corrosion product from the system could block ports and pipework.	This would be a particular issue within the centrifugal contactors whereby a blockage of flow could misroute material and potentially lead to a recycle of fissile material and criticality hazard.	Understand the operating envelope with regard to solid content within the system.
29	Effects of operating outside of the defined flowsheet envelope	Changes in stream density, potentially the result of a higher heavy-metal loading.	Density differences which fall outside of the normal operating envelope may affect the separation of phases within the contactors, thus changing the efficiency of separation. The result of this will be the misrouting of solvent, fissile material, and highly active species which may travel to areas which do not meet minimum radiological shielding requirements.	See row 14.

2.6. THINK TANK SAFETY REVIEW OUTPUT – DAY 2 HAZARD PRIORITISATION & ACTIONS TO ADDRESS ISSUE

Table 2 presents the output from the second Think Tank session. The groups were asked to identify the highest priority hazards and what research efforts could contribute towards their mitigation.

Table 2 – Summary of Hazard prioritisation on a group basis

Group	Priority (highest to lowest)	Hazard	Comments	Actions to Address Issue
1	1	Flammability and explosion hazard presented by low molecular weight organics	Connected to the extent of radiolysis within the system.	Flowsheet trials and modelling of low molecular weight organic production process kinetics via radiolysis. Research into the generation of radiolysis products and their interactions.
	2	Flammability and explosion hazard presented by carrying of organics through to finishing evaporators	This includes red-oil excursions	Understand conditions under which organics can reach the evaporators. Research organic complexant behaviour in the product. Research organic destruction engineering options.
	3	Flammability and explosion hazard presented by hydrogen production from radiolysis	Most likely to be problematic in storage vessels Vessels are passively vented. Hydrogen assessments can be performed, including modelling. Other processes/reactions could produce hydrogen e.g. corrosion.	Flowsheet trials and modelling of hydrogen production process kinetics via radiolysis. Compatibility/corrosion studies to understand material interactions.

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Group	Priority (highest to lowest)	Hazard	Comments	Actions to Address Issue
	4	Flammability and explosion hazard presented by the use of hydrazine		Research is required to understand interactions with Tc forming hydrazoic acid. Alternatives to the use of hydrazine in the process should be investigated.
	5	Flammability and explosion hazard presented by the recycle of self-heating crud	Build-up of fission products in recycled liquors leading to a rise in temperature sufficient to create hot-spots. Management of this may be achievable through an online monitoring system.	Need to understand the heat generating capabilities of cruds. Research should be focussed on the conditions which cause recycles to occur and how to avoid them.
	6	Flammability and explosion hazard presented by electrical malfunction		This hazard can be managed through engineering design of the system and manufacturing standards.
2	1	Insufficient solvent extraction, potentially caused by corrosion products within the process liquors.		Corrosion trials are required to identify the corrosion products likely to form and how these impact upon solvent extraction operations. Modelling could then predict the likely outcomes from the presence of corrosion product in the process liquors.
	2	Effects of operating outside of the defined flowsheet envelope, high Pu concentrations, variations in feed from head end operations		Existing online monitoring techniques for fissile material should be incorporated into future designs. Where these techniques are not appropriate, the development of new techniques should be considered. The Pu loadings of the solvents to be used needs to be fully understood prior to scale up.

Group	**Priority (highest to lowest)**	**Hazard**	**Comments**	**Actions to Address Issue**
3	1	Degradation of solvents through radiolysis	The flowsheet currently operates using two solvent loops, is it possible to reduce this to one to reduce the effects of solvent degradation?	An understanding of the G values (a measure of the number of species decayed or formed per joule of energy absorbed) throughout the system is needed. Modelling and simulation techniques should be employed to gain an understanding of the effects of solvent loop configuration on the extent of radiolysis and degradation product generation.
	2	Flammability and explosion hazard presented by hydrogen (from radiolysis)		Engineering design should consider abatement
	3	Effects of contaminated solvent – solvent clean up and recycle	Solvent must be cleaned and recycled within the process to minimise wastes and costs.	An understanding of the extent to which degradation product will accumulate within the solvent is required.
	4	Effects of operating outside of the defined flowsheet envelope – understanding what the normal operating physical parameters are.		This requires extensive laboratory experiments to determine the operational envelope, with the chosen chemicals. Future design work should consider results from such experiments such that the system attempts to stay within these bounds.
4	1	Flammability and explosion hazards		See group 1 actions
	2	Secondary Processes		Secondary processes such as solvent washes, head end operations and finishing sections of the plant need to be better defined to enable a better understanding of the chemistry involved.

Group	Priority (highest to lowest)	Hazard	Comments	Actions to Address Issue
	3	Process Simplification		Efforts should be made throughout the design of the chemical flowsheets to simplify the system, whilst maintaining functionality, so that the opportunities for hazards to arise are minimised.
	4	Mechanistic understanding of the process prior to design and build phases	Unlike the PUREX process, the Euro-GANEX process will need to be fully understood at all levels prior to implementation – safety practices/studies will require this.	The plant safety systems must be considered and understood in some detail, these will be defined by the hazards.

3. PART 2 – HEAD END & SAFETY REVIEW

3.1. SAFETY REVIEW METHODOLOGY

The NNL safety review was conducted in line with the safety review methodology produced under SACSESS [6]. Table 3 details the list of questions which are applied to each process line in turn to systematically consider potential mal-operations.

The flowsheet which this safety review was based on is presented in Figure 2 in the Annexes to this report. The chemical separation section of the flowsheet has previously been subject of a safety review under SACSESS [5] and is further considered in Part 2 of this report therefore this internal safety review was focused on the head end and finishing processes.

The review covered the head end process and the Pu & minor actinide (MA) finishing line as these are the areas with the greatest hazards. The output of the review is captured in tabular format. The review focusses on issues relating to the chemical processes rather than design concerns. Where a question from Table 3 is not included in the safety review output, this is due to the review team concluding that there were no relevant hazards associated with that question for the select process under review. Where possible, potential mitigation is specified for the highlighted hazards, however in some instances there is insufficient design information to suggest mitigation. Where further work is required to understand the chemical process this is raised as a recommendation for further work.

Table 3 – Chemical Conditions and Specific Questions for Consideration as part of the SACSESS Safety Reviews

SACSESS Safety Review Methodology Questions	
Chemical Condition Under Consideration	**Specific Questions to be Presented to Safety Review Team**
A) Chemicals / nuclides relevant to flowsheet stage under normal operations	A1) feed chemicals / nuclides under normal operations?
	A2) product chemicals / nuclides under normal operations?
B) Loading / concentration	B1) loading / concentration range at which process is designed to work?
	B2) effects if higher loading / concentration?
	B3) effects if lower loading / concentration?
C) Required flowrate (or feed rate) conditions	C1) flowrate (or feed rate) range at which process is designed to work?
	C2) effects if flowrate (or feed rate) too high?
	C3) effects if flowrate (or feed rate) too low?
D) Required temperature conditions	D1) temperature range at which process is designed to work?
	D2) is the reaction exothermic or endothermic?
	D3) are any of the feeds / products self heating?
	D4) effects if temperature too high?
	D5) effects if temperature too low?
E) Degradation (e.g. due to hydrolysis, radiolysis, temperature)	E1) are there any credible causes of degradation?
	E2) products of degradation?
F) Flammability / explosion	F1) potential under normal operations?
	F2) flammable gas generation as a result of degradation?
	F3) potential under maloperations?
G) Solids presence	G1) could any solids be carried forwards from previous stages?

SACSESS Safety Review Methodology Questions	
Chemical Condition Under Consideration	**Specific Questions to be Presented to Safety Review Team**
	G2) insolubility of feed / product chemicals present under normal operations?
	G3) insolubility of degradation products?
	G4) insolubility of feed / product chemicals present under mal-operations?
	G5) mechanisms for crystallisation?
	G6) mechanisms for precipitation?
	G7) any other mechanisms for plating out / solids formation?
H) Likelihood of pressurisation	H1) is the reaction likely to generate significant quantities of gases (types, evolution rates)?
J) Expected process requirements for industrialisation	J1) batch process or continuous process?
	J2) what size / shape vessel does the process require?
	J3) are there any known technologies which would not be suitable?
K) Chemical compatibility (with other process chemicals and likely plant materials)	K1) feed and product materials compatible under normal operations?
	K2) products of degradation compatible?
	K3) materials compatible under mal-operations?
	K4) will any of the chemicals / nuclides present under abnormal conditions affect the operation of the flowsheet in any way which has not already been considered?

3.2. SAFETY REVIEW OUTPUT

3.2.1. HEAD END PROCESS

Table 4 – Safety Review of Head End Process

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
Shearing and Voloxidation	1.	A1 Feeds under normal conditions	Radiological and criticality hazards associated with the fuel feed.	The radiological/criticality hazards associated with spent fuel are well understood. Design will need to be shielded and designed to be criticality safe (engineering issues).	
	2.		Increased Cm content – higher neutron dose.	Needs to be taken into account in future plant design. Neutron shielding will be required.	Concern is for entire fast reactor reprocessing route throughout the whole plant. **Recommendation 1: Consider the benefits of removing curium at an early stage in the process rather than incorporating it in the product.**
	3.		Reprocessing with short cooling times gives rise to increased problems from short-lived radionuclides and resulting heat load and radiolytical products (hydrogen).	The process will need to be suitably shielded. Off-gas will need to consider abatement and accumulation of short lived volatiles.	Review what an appropriate cooling time for reprocessing this type of fuel is.
	4.	A2 Products under normal conditions	Voloxidation off gas, containing tritium, noble gases and semi-volatiles	Specific voloxidation (VOLOX) off-gas system (not in scope of review). Design will need to consider plating-out of volatiles/semi-volatiles.	To inform the off-gas design, the potential for plating out of volatiles & semi-volatiles needs to be quantified.

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	5.		Production of ruthenium tetraoxide - oxidation and explosion risk (when using strong oxidants e.g. ozone)	Conventional voloxidation does not run at a high enough oxidation potential to cause the production of a tetraoxide. This would only be an issue if a highly oxidising process was used or the temperature of voloxidation exceeded normal levels.	
	6.		Fuel is high burnup and will be generating a lot of heat. Fuel could react with air and generate NO_x	Design of the off gas system needs to be able to abate anticipated levels of NO_x.	To inform the off-gas design, the potential for NO_x generation needs to be quantified.
	7.	A1 Feeds under fault conditions	Oxidation of any remaining Na on the fuel leading to fire hazard in the voloxidation stage or in the shearing cave. A failed fuel pin could contain Na and then release sodium into the system.	Potential to inert shearing however cannot inert voloxidation Thorough clean up required prior to shearing	Na in the system would pose a significant hazard. **Recommendation 2: Process to confirm that the fuel (including failed fuel) can be shown to be free from Na prior to processing.**
	8.		Crimped fuel would not undergo voloxidation or be exposed to acid. Bulk fuel could end up being routed with ILW – criticality concern. This would result in the discharge of radionuclides to dissolver off-gas (DOG) intended for voloxidation off-gas (VOG), which may not result in abatement of these radionuclides	Design needs to ensure fuel does not crimp when sheared	
	9.	A2 Products under fault conditions	Recovery of spent fuel dust from the off gas system may become an issue. This would be technically difficult however electrostatic precipitation may be an option. If large Pu regions from MOX blended fuels (not fault fuels but the agglomeration of large particles) may not undergo voloxidation at all	The generation of dust in the head-end is part of the process. The engineering is designed to minimise the generation and to maximise transfer to the dissolver. Dusts that enter the DOG are further managed. Collection and then off-gas treatment system, i.e. scrubbers and High Efficiency Particulate (HEPA) filters. The two-stage dissolution process is	

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
				designed to dissolve high Pu content fuels and therefore the system should be able to cope with large Pu regions, even if Voloxidation does not occur for these regions.	
	10.	B2 Loading/ concentration - higher	Higher throughput of fuel pins: higher carry over of volatile fission products – not enough oxidation in VOLOX. Volatiles would be released in the dissolvers and would be released though the dissolver off-gas (DOG) system. Higher quantities of solids and fuel would go through the second dissolver route due to incomplete dissolution and would therefore increase throughput, saturating and heading towards ILW solids route. Potential criticality concerns.	Consider designing the Dissolver Off gas system (DOG) to similar standards as those of the Voloxidation Off Gas (VOG) system.	
	11.		Concentration of tritium dissolved into the nitric acid. This is recycled in the plant and concentration continuously increases, increasing the radiation dose of the streams. If the concentration of Kr was higher than expected in the dissolver, through failure or lack of Voloxidation, then the Kr would be released to the DOG system. This would be a problem if Kr abatement was located in the VOG system and not the DOG system.	The recycled acid will need to be cleaned.	The acid recycle will need to be cleaned periodically to prevent build-up of nuclides such as tritium and Kr in the process. Existing nitric acid recovery processes may need to be reviewed to ensure tritium is removed to prevent recycle and accumulation. A mechanistic understanding of the routing of tritium with differing process conditions within head end and the dissolver is required.
	12.	B2 Loading/ concentration -lower	No problem with lower fuel loading.		

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	13.		Lower air flow to VOLOX – as per higher fuel loading see rows 10.		Preferable to use air for the voloxidation. Using oxygen would introduce additional fault scenarios. O_2/Ar mixture or stronger oxidants e.g. NO_2/O_2 mixture will need to be used to achieve process aims.
	14.	C – Flow/feed rates			It was considered that the faults associated with flow/feed rates were suitably captured by B – loading/concentrations.
	15.	D – Temperature range at which process is meant to operate.	If temperature deviates from ideal temperature, less efficient oxidation will occur. This will have similar consequences to high fuel throughput (10).		
	16.		An exothermic runaway reaction could occur if fuel already pulverised when it reaches air.	This is a design/engineering issue. Counter current gas flow orientation and a zoned furnace could mitigate this hazard.	
	17.	E - Degradation	Radiolysis of the air by the fuel could result in the generation of NO_X.	The off gas system should be designed to cope with NO_x – including large, fault scenario volumes.	
	18.	F - Flammability/ explosion	Residual Na on fuel, covered by 7. Any in-growth of pure metal in the fuel could create flammability problems when sheared and exposed to the aqueous nitric acid in the dissolver.	See ID 7 mitigation.	Assumption that cladding is stainless steel (not zirconium or another metal with potential fire/explosion hazards). **Recommendation 3: Further research/modelling into in-growth of pure metals (ε-particles) is required to confirm the potential for associated hazards.**

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	19.	G1 - Solids present	Solids will be expected in the process and therefore the processes will be designed as such	VOG and DOG designed to cope with particulates	
	20.	G7 – Plating out	Potential problems with plating-out of volatiles in the off gas system.	Provision is needed to clean off gas system.	
	21.	H – Pressurisation	Thermal excursion would lead to increase in gas generation	Design to be able to withstand maximum credible gas generation. Vessels, Pipework and fittings will be designed to withstand maximum credible pressures.	
	22.	J2 - Size/shape of vessels	Potential for criticality in the process	Vessels will need to be designed in criticality safe geometries where possible. Any areas where dust could accumulate must be accessible to allow for clean-up to minimise build-up.	
	23.	J3 Known technologies not suitable	Voloxidation of higher Pu concentration fuels is known to have issues due to the lower density decrease when oxidising PuO_2 relative to the oxidation of UO_2. The Pu does not burst out of the cladding to the same degree resulting in fuel being left in the cladding. This may require the use of strong oxidants to achieve process aims and may limit the efficiency of the process. Such high burnup fuel and high Pu concentrations are not currently processed – greater shielding considerations etc.	Design should consider the benefits of voloxidation for the proposed feeds (see SACSESS recommendation Aq3 – [8]) Issues for design to consider.	**Recommendation 4: A review is needed to determine which fuels can successfully undergo voloxidation.**
Node 2 – Figure 2,	24.	A1 Feeds – fault scenario	Un-pulverised fuel leading to reduced dissolution (assuming dissolver designed for powder feed). Increased criticality risk through	Dissolver designed to be criticality safe geometry and fault tolerant. Dissolver is a rotary wheel where the basket size will be	Review the requirement for an NO_2 sparge. There may be a requirement to remove I which would also require

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
streams 5-14 and 17			carry over of fuel into ILW waste. Concerns were raised over the required size and number of continuous dissolver(s) for target throughput of 5 tHM/day 30 %Pu spent fuel.	determined from criticality constraints.	an air sparge (See 31).
	25.	B2 – higher concentration acid	Foaming acid dissolver – problems with carry-over of liquor/solids foam in to off gas system. Problems with carryover of product into different streams. Higher acidities can alter the dissolution of various metals. These can form tacky-solids and create criticality issues	The concentration of nitric acid will need to be closely controlled	Concentrations not currently known and need defining. Concentration will need to be monitored and controlled.
	26.	B3 - Low acid concentrations	Unexpected solids forming, reduced dissolution rates. Potential for hydrolysis – precipitation of the metals as hydroxides. Increased radiolytic H_2 into off gas stream. Excess solid to ILW as above.	The concentration of nitric acid will need to be closely controlled. Engineering could consider methods whereby it would be impossible to feed chemicals in the incorrect quantities, or at least provide sufficient buffer storage and sampling of feeds prior to use.	Issues with expected throughput of gases **Recommendation 5: Further work is required to understand the gas generation rates at each stage of the Head End process, for normal operations and fault scenarios.**
	27.	B2 - High NO_x concentration	NO_x is entrained in stream and can generate stable nitrous acid which can affect down-stream chemistry. NO_X can affect actinide oxidation state causing improper routing of material. Could further increase foaming – due to the presence of solids.	Holding tank with chemical/species monitoring is required prior to chemical separation	
	28.	B3 - Low NO_x concentration	Less Pu(VI) reduction, resulting in Pu(VI) feed to solvent extraction – this would affect the solvent extraction chemistry and potentially route Pu with U product		**Recommendation 6: Consider the impact on chemical separation of Pu(VI) in the dissolved fuel feed – expected recycle through plant.**
	29.	B2 - High fuel loading	Could result in the crystallisation of actinides and other solids – leading to criticality		**Recommendation 7: Further work is required to understand the fault**

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
			concerns.		**conditions under which actinide/solid crystallisation could occur in the head end process, and what the impact of this would be on the chemical separation process.**
	30.	B3 - Lower fuel loading	May cause problems if the lower loading carries into chemical separation. This would affect heavy metal (HM) solvent loading and fission product decontamination factors (DFs).	Buffer tank online monitoring prior to chemical separation.	Should not present a problem for this section of plant.
	31.	B3 - air sparge (for I removal) – too little air sparge	I carried forward: Discharge of I to off gas system and down-stream plants. I carried into chemical separation where it reacts with solvent. Likely to accumulate in solvent and cause a potential reactivity problem with degradation products.	Solvent wash process may need to be able to remove I /iodated degradation products. This may affect solvent purge rates.	
	32.	B2 – High solids loading in centrifuge	Blockage of centrifuge, potential criticality hazards.	Issue for engineering.	
	33.	B3 - Loss of feeds to centrifuge	Loss of either the dissolved fuel or wash to the centrifuge for an extended period of time will result in the heat-generating solids drying and caking onto the bowl. This can also result in a criticality hazard and/or excess NO_x/gas formation	Design to ensure a backup wash supply is available to the bowl. Centrifuge to be designed to criticality safe geometry.	
	34.	D4 – Dissolver temperature too high	Risk of an exothermic reaction, high temperature would increase reaction and lead to foaming Safety issues with the foam – dissolver product in the DOG which would be less shielded and lead to increased discharges and increase dose.	Design to ensure temperature is suitably controlled.	

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
			Could have back flow of foam into volox. Introduction of water into volox – reactivity of volox issues Foaming could also carry solids to DOG. Blockage problem with wet powders – which could amount to a criticality problem. Excessive vapour released into DOG.		
	35.	D4 - NO_x conditioning too hot	Less efficient Pu(VI) reduction		See Recommendation 6.
	36.	D5 – Dissolver temperature too low dissolver	Dissolution not complete, see 27 Potential crystallisation, see 30		
	37.	D5 - Temperature too low NO_x condition	Comparable to high temperature, see 35		
	38.	F2 – Flammable gas from degradation	Radiolysis – formation of hydrogen	hydrogen management philosophy is required for all vessels and tanks	See recommendation 5
	39.	F3 – Flammable gas from maloperation	If wash is water could have hydrolysis problems similar to that in dissolver.	H_2 management philosophy is required for all vessels and tanks	See recommendation 5
	40.	G5 - Solids present	Low temperature or high acid concentration could cause crystallisation, see 30.		
	41.	G7 - Plating out of solids	Off gas system, secondary solids e.g. zirconium molybdate, Ru/Rh/Cs/etc solids (VOG). Accumulation of Pu through incorporation into solids leading to increase in dose. Criticality hazard	Off gas system cleaning/inspection possibility Shielding on off-gas system designed with consideration of fission/activation product solids	

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	42.	H - Pressurisation	Blockages caused by solids and heat generating material		See recommendation 5.
	43.	K4 - Material compatibility	No foreseen problems	Will be an engineering materials consideration	
Silver dissolver through to aqueous mixer	44.	General	Major concern with regard to scale of fast reactor (FR) reprocessing – Pu-rich solids and residues are an issue and design should be focussed with eradicating their existence/accumulation in the plant. The presence and accumulation of undissolved Pu-rich oxide residues from the primary dissolver to the aqueous mixer is of major concern especially for carry through to chemical separations	Design considerations to look at technologies which minimise the transport of Pu-rich solids.	**Recommendation 8: Further work is required to investigate if dissolution can be performed within a single unit, minimising the generation and transport of Pu-rich solids.**
	45.	A1 – feeds under fault conditions	All high and low concentration of feeds has been covered previously. Less silver nitrate: less dissolution and therefore carry over of Pu solids into ILW – this would present a criticality risk Low or high acid concentrations in the anolyte: ineffective dissolution and potential for Pu crystallisation. High acid concentration in catolyte: no issues Low acid concentration in catolyte: may deplete nitric acid leading to hydrogen generation and precipitation of solids and electro-deposition onto cathode.	Monitoring the process (rather than basing it on a specified time interval) should identify this fault. See recommendation 5 & 9.	**Recommendation 9: Further work is required to understand how electrochemical dissolution performs under different acidic conditions, and at different currents.**

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	46.	B - concentrations	Iodine in the feed to the dissolver would form silver iodide which would deplete Ag ion concentration – as low Ag in 45 Low current – incomplete dissolutions. High current – likely to damage a component of the dissolution equipment. Cell (secondary dissolver) would heat up. More current than reactions require – oxygen production at anode. Cathode – depleted acid that could ultimately lead to hydrogen production.	See recommendation 8 Equipment would be protected via fuses	
	47.	D -Temperature	High temperature (e.g. from loss of cooling) – would result in ineffective dissolution, see Recommendation 8. Boiling of liquor leading to vapour in off-gas and/or foaming – see 34 Low temperature – could result in the crystallisation of Pu/U	See Recommendation 7	
	48.	E-Degradation			N/A
	49.	F - Flammability/ explosion	Failure of the membrane in the dissolver could cause mixing between oxygen and hydrogen forming an explosive mixture.	Argon blanket and purging	Eventual adoption of this technology is unlikely as ozonolysis is more likely to provide better control and easier management **Recommendation 10: Work is required to look into the use of ozonolysis as an alternative to Ag(II) assisted dissolution.**

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	50.	G - solids	Silver halides may precipitate and collect in the centrifuge. These would carry through to ILW. This could be an issue if i is present	Removal of iodine through air sparge	
	51.	H - pressurisation	Potential for pressurisation in the event of increased gas generations see recommendation 4.	Engineered safety systems e.g. pressure relief valves	
Aqueous Mixer	52.	General			Missing a conditioning acid feed and depleted U/ substitute metal feed. Aqueous mixing would be required in the buffer tank to keep it all moving and homogeneous
	53.	A1 – Feeds under normal conditions	Pu nano particles will accumulate as an interfacial crud which will effect centrifugal contactor performance in the chemical separation stage and present a criticality issue. These can also misroute, block contactors etc. These will carry through the entirety of chemical separation.	Research is being undertaken at NNL to find out how tolerant centrifugal contactors are to solids. Development of a suitable screening/clarification technology to remove these particles is currently ongoing.	**Recommendation 11: Further research is required into whether nano-particles/ colloids would provide a problem within the head end or chemical separation processes.** **Recommendation 12: Further work is required to understand the potential for secondary solids to form within the head end process during buffer storage or under maloperations.**
	54.	A1 – Feeds under faults conditions	Carry over of sodium and silver would not be an issue for the aqueous mixer.		

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
			Concentrate mother liquor (CML) from finishing process is recycled into the aqueous mixer. Therefore fault condition exists whereby oxalate could be added into this tank. This could affect solvent extraction processes.	Monitoring of the concentration of key chemical species within the aqueous mixer/buffer tanks is required prior to discharge of liquors to the chemical separation process Monitoring of the composition of the CML prior to its addition to the buffer tank is required, by monitoring the concentrations of key chemical species.	
	55.	A1 – Feeds under faults conditions	Solids present in the aqueous mixer could block the centrifugal contactors when fed to chemical separation stage (covered by SACSESS review).	Monitoring of the aqueous mixer.	Assume there is a gas purge through tank to remove trace hydrogen and NOx.
	56.	B – loading concentration	High or low concentration of acid – could allow formation of precipitates during storage. This would be a problem for chemical separation. High acid would result in more NO_X sent to off gas. Low acid – precipitation, solids, Pu, criticality, Increase hydrogen generation.	Monitoring of the aqueous mixer is required prior to use in the chemical separation process See Recommendation 5 See Recommendations 7 & 12. See Recommendation 5	Review the potential for secondary solids formation within the buffer tanks.
	57.	D – Temperature	High temperature – liquor would evaporate off and concentrate, increased gas generation, concentration effects Low temperature could result in precipitation and crystallisation of actinides.	Liquor would be similar to Highly Active Liquor (HAL) would require active cooling. Online monitoring will establish fault See Recommendation 7.	See Recommendation 5

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	58.	G – Solids	Could get settling out of any remaining solids leading to undesirable hot-spots and criticality concerns. Could also get foams	Method of agitation/suspension required – Engineering needs to be considered	

3.2.2. PU & MA FINISHING LINE

Table 5 – Safety Review of Pu & MA Finishing

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
Pu and MA Finishing – considered as a whole section	59.	A1 Feeds Faults	Lanthanide and fission product carry over from chemical separation area. This could increase the radiation dose in this area of plant above expected levels. Issues with the metal content in the evaporators being too high. The presence of organics in the evaporator is an explosion risk. The presence of Bis-tryazinyl-pyridine (BTP) and AHA in the feed could cause corrosion issues. AHA could undergo hydrolysis to hydroxylamine nitrate (HAN) and acetic acid which is associated with a runaway exothermic reaction.	Control of chemical separation to minimise potential carry over See Recommendation 13	**Recommendation 13: Further research is required to understand where BTP and AHA would be routed to and how they may decompose within the Pu & MA finishing line and to what extent they produce a hazard.** A ligand destruction/removal stage (steam strip or kerosene wash) prior to evaporation may be required. Work is ongoing to obtain whether these ligands would interfere with precipitation processes.

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	60.	B Loading / Concentration (Feeds In)	Higher Pu + MA concentration – caused by low organic flow in An strip. Could be accompanied by carry over of organic phase. (See 58). Higher concentration of hydrogen peroxide feed to valence conditioning could precipitate An as solids – heat generation and criticality concerns Low concentration of hydrogen peroxide feed to valence conditioning, in addition to low residence time in harp tanks could cause Pu(VI) to be present which will not precipitate. Accumulation and recycling through Oxalate Mother Liquor (OML) would occur – criticality risk	Suggestion that H_2O_2 should not be used if HARP buffer storage used.	**Recommendation 14: Consider how Np and other actinides recycle within the flowsheet and whether there is a different oxidising agent other than hydrogen peroxide that would produce a more homogeneous MA product.**
	61.		Insufficient quantity of oxalic acid for the quantity of metal fed would lead to a high concentration of product in the Oxalate Mother Liquor (OML) as precipitation would be incomplete. This would lead to product in the CML which is then recycled High concentration of OML to precipitation leads to incomplete destruction of oxalic acid which is then recycled via the Concentrated Mother Liquor (CML) into the aqueous mixer further affecting chemical separation	Monitoring of the OML/CML prior to recycle will be required.	
	62.		Low concentration oxygen feed to first calcination furnace – incomplete combustion resulting in carbon and carbon monoxide in MA product and carbon monoxide in the off gas, giving rise to explosion hazard.	Work needs to be undertaken to optimise the argon-oxygen mixture	**Recommendation 15: Further work is required to understand the gas generation rates at each stage of the Pu&MA finishing line, for**

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
			High concentration oxygen feed to first calcination furnace – very fast oxidation, and increased rate of gas generation.	See Recommendation 15	**normal operations and fault scenarios.**
	63.		Concentration of air (usually argon inerted) to the second calcination furnace –no major issues. Concentration of moisture in gas feed to second calcination furnace – could lead to moist product and therefore hydrogen generation in product cans during storage.	Dryer on the air feed lines. Monitoring of product specification and moisture content.	
	64.	C Flowrates	Higher flow of product into evaporation would result in a lower concentration of product – no new chemical hazards (dependent on control arrangements for evaporator). Low concentration of product in evaporator output would lead to a larger percentage of plutonium being recycled to the aqueous mixer. Similar effects to low concentration (see 60) Lower flow of product into the evaporator – no hazards identified, assuming evaporation continues to a specified concentration rather than time limited. If time limited then there could be an issue with over concentration and generation of solids.	Evaporation monitored via concentration rather than time based.	
	65.	D Temperature – MA evaporator	Higher temperature in the Pu & MA evaporator: over concentration, precipitates out solids that would settle in tanks; insufficient oxalic acid feed if followed through to precipitation; more product in the liquid phase than expected leading to recycling of product.	Online monitoring of evaporator to ensure correct concentration is achieved and guide amount of oxalate needed	

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
			Significantly higher temperatures could lead to flash boiling and liquor going to the off-gas Lower temperature in the Pu + MA evaporator – evaporate less feed, lower concentration. Will increase flow to the OML recycle system (depending on evaporator control arrangements). OML evaporator or harp tank may flood due to unexpected volume flows.		
	66.	D Temperature – Valency Conditioning	Higher temperature in the Valency Conditioning unit may decompose hydrogen peroxide which would generate oxygen and hydrogen. Could affect hydrogen management system safety case. Lower temperature than expected in the Valency Conditioning unit – insufficient valence conditioning leading to recycle of plutonium as Pu(VI) via the OML recycle.	See Recommendation 15	**Recommendation 16: Further work is required to understand optimum temperatures for the finishing line processes and the associated safety margins.**
	67.	D Temperature – Precipitation reactor	Higher than expected temperature in the precipitation reactor - increased solubility of the oxalate products, increase rate of precipitation, decrease efficiency of precipitation – recycle more products via OML and CML creating criticality concerns from the accumulation of material within the process. Lower than expected temperature in the precipitation reactor – kinetically not fast enough for chemical reactions, product quality and morphology affected, effecting product quality. This would imply more product left in aqueous and recycled via OML system with possibility of precipitation in the OML system. The precipitation of solids and an increase in	Monitoring the concentration of key chemical species within the recycle stream and within the buffer tanks prior to chemical separation can protect against criticality by limiting the feed into the process, preventing the net accumulation of fissile material within the system.	See Recommendation 16

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Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
			the concentration of Pu within the recycle presents a criticality risk.		
	68.	D Temperature – Filtration unit	No issues		
	69.	D Temperature – Calcination	Higher temperature than expected in the drying furnace – could sinter powder and trap carbon in product. Product quality issue. Lower temperature than expected in the drying furnace – more water and carbon in the product. Product quality and storage issues, potential for H_2 generation during storage which could present an explosion hazard. Two furnaces – drying furnace (air atmosphere) designed to decompose oxalate and get rid of majority of water, and the calcination furnace (argon atmosphere) designed to control surface area and eliminate residual water. High carbon results from incorrect operation of drying furnace (high or low temperature) whilst excess moisture requires too low temperatures in the calcination furnace	Engineering controls to closely control temperature	
	70.	E Degradation	Evaporation would degrade water-soluble extractants and complexants that make it out of chemical separation which could potentially result in explosion risks and the blockage of the evaporator with degradation products (which causes a pressurisation risk). Degradation product build up in filtration – could result in mechanical blockages, engineering issue.	Look into how to avoid the transfer of organics from chemical separation to evaporation and precipitation.	**Recommendation 17: Further work is required to determine the consequences of ligands from the chemical separation process degrading within the evaporator.**

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
	71.	F Flammability	Carbon monoxide from the calcination process could be explosive – See Recommendation 3 Potential for red oil explosion within the evaporator - See Recommendation 16	Purge / dilute flow rate.	**Recommendation 18: Consider the potential for red oil reactions to occur in the event of solvent carry over from the chemical separation process.**
	72.	H Pressurisation	A red oil excursion type reaction would present a pressurisation hazard – see 70 Hydrogen peroxide could react and degrade to water and oxygen The heating/decomposition of oxalate is gas-generating presenting a pressurisation hazard.	Off-gas systems should be sized to accept worst case gas generations.	See Recommendation 15.
	73.	G Solids present	Entrainment of dust in off gas towards powder product end – this would cause radiation dose and criticality concerns if accumulation occurs. This would also cause an enhanced aerial discharge problem if the off gas system was not designed to handle this entrainment. There is also the potential to block the off gas system.	Engineering issues Shielding around off gas	Potential for electrostatic precipitation technology to collect fine particles from the off gas but this itself could be associated with a criticality hazard.
	74.	J Expected process requirements for industrialisation	The suitability of the following technologies is under question and would ultimately require further work in each area to determine whether it is the most appropriate technology for this design: Mediated Electrochemical Oxidation (MEO) – difficult for use in a HA environment due to complex maintenance and batch-wise process.		
			Use of hydrogen peroxide as an oxidising agent- less hazardous alternatives exists.	See Recommendation 14	

Processes	ID:	Question	Concern	Potential Mitigation	Notes / Recommendations
			An oxalate based – powder producing finishing flowsheet for high Pu/MA will lead to high airborne concentrations due to the fine particles generated and high dose rate associated with Am.	See Recommendation 19	**Recommendation 19: Consider the requirements associated with the Plutonium & Minor Actinide (PuMA) product and whether this needs to be a powder based product or whether a less mobile form could be generated (such as a gel based particle).**
	75.	K Chemical compatibility	Sulphate degradation products from ligands at MA evaporator could lead to chemical compatibility issues (see 58)		
	76.	Other remarks	Am oxide has a higher volatility than Pu oxide. This could become a problem in the calcination furnace. This could potentially lead to a volatilised americium oxide which can be misrouted. This could cause the americium to plate out, potentially to an area with insufficient radiological shielding. This would also provide out of specification product due to incorrect Pu:Am ratios.		**Recommendation 20: Further work is required to look at the heating and calcination of Pu/MA oxide solids considering the higher volatilities of compounds such as Am oxide.**

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3.3. SUMMARY OF RECOMMENDATIONS FROM NNL SAFETY REVIEW

Table 6 - Summary of the recommendations made in the Safety Review

No.	Recommendation
1.	Consider the benefits of removing curium prior to processing at an early stage in the process rather than incorporating it in the product.
2.	Process to confirm that the fuel (including failed fuel) can be shown to be free from sodium prior to processing.
3.	Further research/modelling into in-growth of pure metals is required to confirm the potential for associated hazards.
4.	A review is needed to determine which fuels can successfully undergo voloxidation.
5.	Further work is required to understand the gas generation rates at each stage of the Head End process, for normal operations and fault scenarios.
6.	Consider the impact on chemical separation of Pu(VI) in the dissolved fuel feed.
7.	Further work is required to understand the fault conditions under which actinide crystallisation could occur in the head end process, and what the impact of this would be on the chemical separation process.
8.	Further work is required to investigate if dissolution can be performed within a single unit, minimising the generation and transport of Pu-rich solids.
9.	Further work is required to understand how electrochemical dissolution performs under different acidic conditions, and at different currents.
10.	Work is required to look into the use of ozonolysis as an alternative to Ag(II) assisted dissolution.
11.	Further research is required into whether nano-particles/ colloids would provide a problem within the head end or chemical separation processes.
12.	Further work is required to understand the potential for secondary solids to form within the head end process under maloperations.
13.	Further research is required to understand where BTP and AHA would be routed to and how they may decompose within the Pu & MA finishing line and to what extent they produce a hazard.
14.	Consider how Np and other actinides recycle within the flowsheet and whether there is a different oxidising agent other than hydrogen peroxide that would produce a more homogeneous MA product.
15.	Further work is required to understand the gas generation rates at each stage of the

No.	Recommendation
	Pu & MA finishing line, for normal operations and fault scenarios.
16.	Further work is required to understand optimum temperatures for the finishing line processes and the associated safety margins.
17.	Further work is required to determine the consequences of ligands from the chemical separation process degrading within the evaporator.
18.	Consider the potential for red oil reactions to occur in the event of solvent carry over from the chemical separation process.
19.	Consider the requirements associated with the Plutonium & Minor Actinide (PuMA) product and whether this needs to be a powder based product or whether a less mobile form could be generated (such as a gel based particle).
20.	Further work is required to look at the heating and calcination of Pu/MA oxide solids considering the higher volatilities of compounds such as Am oxide.

4. REFERENCES

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5. APPENDIX 1 - EURO-GANEX FLOWSHEET

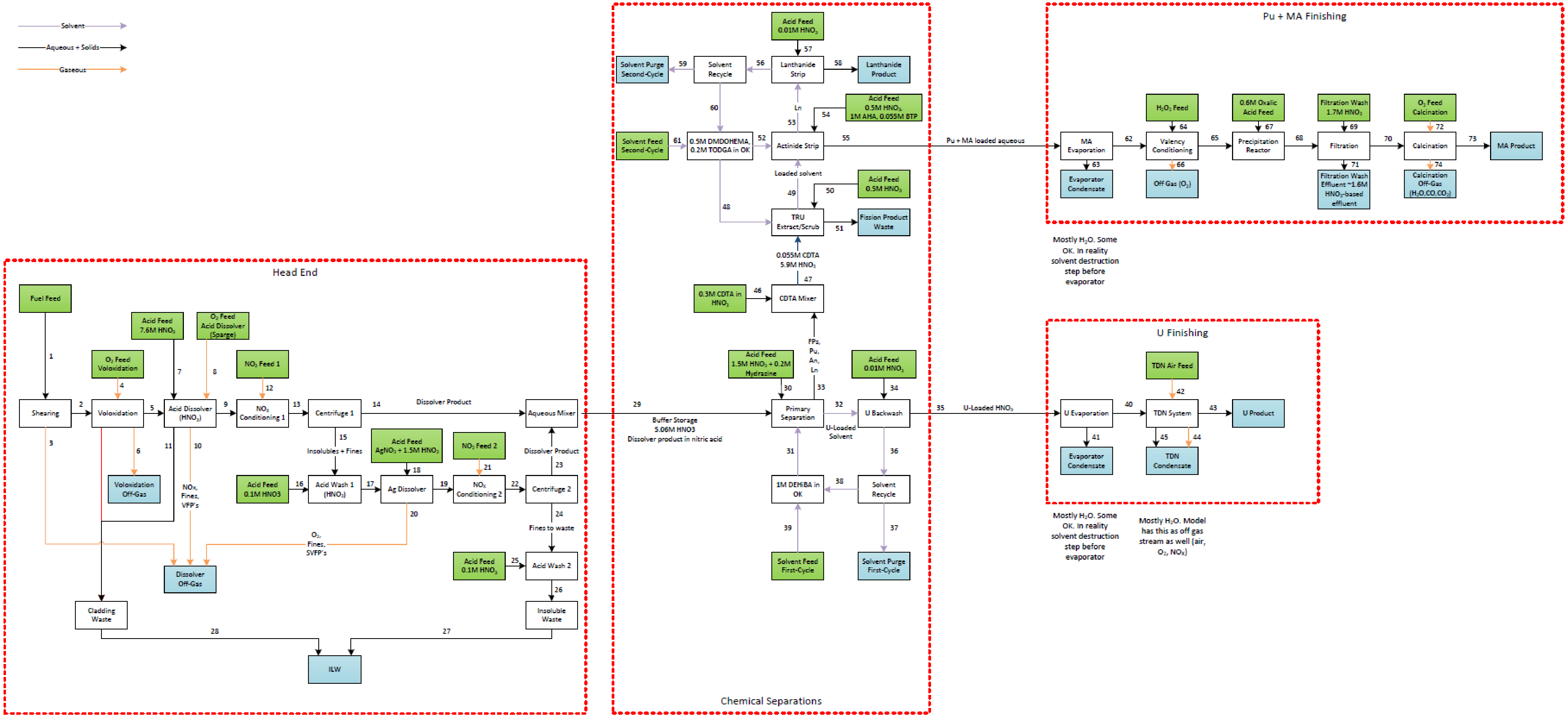

Figure 2 - Euro-GANEX Flowsheet including Head End and Finishing

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6. APPENDIX 2 – FULL SAFETY REVIEW OF A DEMONSTRATION EURO-GANEX CHEMICAL SEPARATION STAGE PLANT

For reference purposes, the safety review of the Euro-GANEX process undertaken as part of the SACSESS programme has been included, in its entirety, as an appendix. Some formatting may differ from the original however the content remains unchanged.

EUROPEAN COMMISSION
Community Research

SEVENTH FRAMEWORK PROGRAMME

SACSESS

Collaborative Project

Co-funded by the European Commission under the
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SACSESS
Safety of actinide separation processes

Full Safety Review of a Demonstration EURO-GANEX Chemical Separation Stage Plant

Authors: Jo Fagan, Dave Graham,
Chris Rhodes & Andrew Chadwick (NNL)

Keywords: SACSESS Combined Safety Assessment Methodology, Safety Review Methodology, SACSESS Flowsheets

SACSESS project – Contract Number: 323282
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Summary

A Safety Review was conducted on normal and mal-operations for a demo-scale EURO-GANEX process. This report details the findings of the Review and suggests research topics and possible hazard management strategies.

Approval

Rev.	Short description	First author	WP Leader	Coordinator
1	Initial issue	J Fagan and D Graham	C Rhodes	S. Bourg
2	Updated after SACSESS meeting	A Chadwick, J Fagan and D Graham	C Rhodes	S. Bourg
3	Updated after SACSESS community comments	A Chadwick, J Fagan and D Graham	C Rhodes	S. Bourg

Distribution list

Name	Organisation	Comments
R Garbil	EC DG RTD	
All technical participants	SACSESS	
Governing board members	SACSESS	

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Introduction

This document presents a Safety of ACtinide SEparation proceSSes (SACSESS) safety review of European Grouped Actinide Extraction (EURO-GANEX) Chemical Separations for normal and mal-operations based on the Combined Safety Assessment Methodology developed by NNL [1]. The information detailed in this report for normal operations is based on an initial review undertaken by NNL, which was then validated and enhanced at the SACSESS project meeting in Gothenburg, Sweden in 16-18 September 2014.

Mal-operations were assessed solely at the SACSESS project meeting with all of the SACSESS community having the opportunity to input to the review.

The review meeting followed the format discussed in Reference [1], based on the Process Description provided in Reference [2]. The flowsheet detailed in Reference [2] is repeated as Figure 1 below.

This report gives a summary of the findings of both reviews, gives recommendations for future research based on the findings and also details a high-level Hazard Management Strategy (HMS) for eliminating or mitigating the hazards raised.

Table 3 below shows the questions, against which the safety reviews were conducted.

The review was primarily conducted to inform the SACSESS scientific community of possible hazards of the process on an industrial scale. As such, while important engineering issues were raised, they were not discussed as it would not be the remit of the SACSESS community to resolve them.

Usually, issues and concerns highlighted by a Safety Review of a design are actioned against an individual to resolve as the design proceeds. Due to the low Technology Readiness Level (TRL) of this flowsheet and the collaborative nature of this project, this was not deemed to be an appropriate mechanism. Instead, these areas have been highlighted as recommendations for further research.

Table 1 – Chemical Conditions and Specific Questions for Consideration as part of the SACSESS Safety Reviews

SACSESS Safety Review Methodology Questions	
Chemical Condition Under Consideration	**Specific Questions to be Presented to Safety Review Team**
A) Chemicals / nuclides relevant to flowsheet stage under normal operations	A1) feed chemicals / nuclides under normal operations?
	A2) product chemicals / nuclides under normal operations?
B) Loading / concentration	B1) loading / concentration range at which process is designed to work?
	B2) effects if higher loading / concentration?
	B3) effects if lower loading / concentration?
C) Required flowrate (or feed rate) conditions	C1) flowrate (or feed rate) range at which process is designed to work?
	C2) effects if flowrate (or feed rate) too high?
	C3) effects if flowrate (or feed rate) too low?
D) Required temperature conditions	D1) temperature range at which process is designed to work?
	D2) is the reaction exothermic or endothermic?
	D3) are any of the feeds / products self heating?
	D4) effects if temperature too high?
	D5) effects if temperature too low?
E) Degradation (e.g. due to hydrolysis, radiolysis, temperature)	E1) are there any credible causes of degradation?
	E2) products of degradation?
F) Flammability / explosion	F1) potential under normal operations?
	F2) flammable gas generation as a result of degradation?
	F3) potential under maloperations?
G) Solids presence	G1) could any solids be carried forwards from previous stages?
	G2) insolubility of feed / product chemicals present under normal operations?
	G3) insolubility of degradation products?
	G4) insolubility of feed / product chemicals present under mal-operations?
	G5) mechanisms for crystallisation?
	G6) mechanisms for precipitation?
	G7) any other mechanisms for plating out / solids formation?
H) Likelihood of pressurisation	H1) is the reaction likely to generate significant quantities of gases (types, evolution rates)?
J) Expected process requirements for industrialisation	J1) batch process or continuous process?
	J2) what size / shape vessel does the process require?
	J3) are there any known technologies which would not be suitable?
K) Chemical compatibility (with other process chemicals and likely plant materials)	K1) feed and product materials compatible under normal operations?
	K2) products of degradation compatible?
	K3) materials compatible under mal-operations?
	K4) will any of the chemicals / nuclides present under abnormal conditions affect the operation of the flowsheet in any way which has not already been considered?

Flowsheeting

The EURO-GANEX process was modelled on g-Proms process modelling software.Figure 1 below give the details on flowrates and species throughout the process.

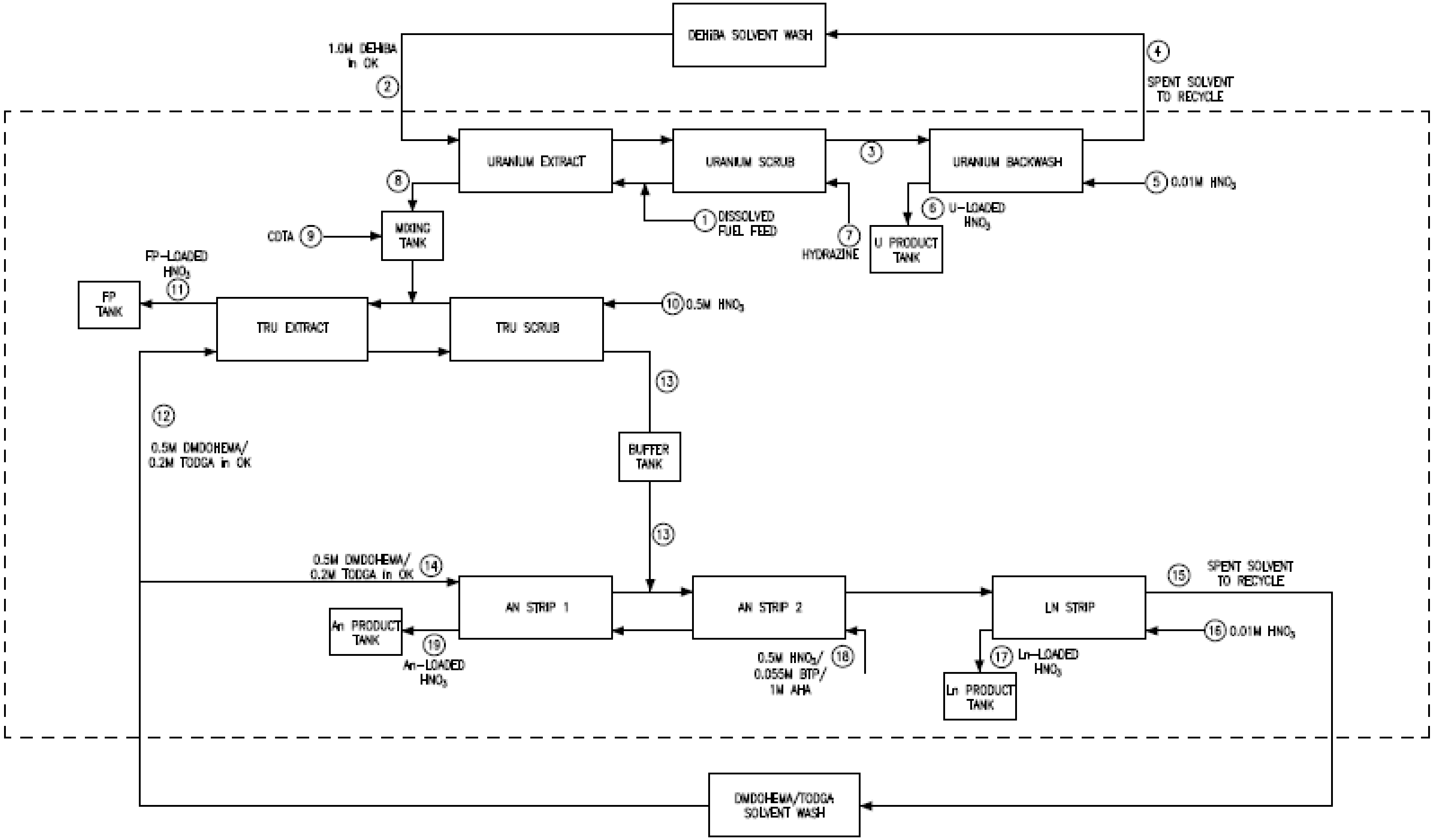

Figure 1 – EURO-GANEX Chemical Separation Flowsheet (dotted line indicates battery limits for review)

Process Overview:

- The battery limits (limits to where the design begins and ends) were set as the GANEX 1st Cycle (U GANEX) and the EURO-GANEX 2nd Cycle, as illustrated by the dotted line in Figure 1.The head-end processes are omitted as they were outside of the battery limits for the reviews, due to the unknown processes that would be utilised in the head-end.
- The fuel feed is assumed to be a fast reactor oxide which has been declad and dissolved in nitric acid and subsequently centrifuged to remove any particulates.
- Product Finishing is omitted as it was deemed to be outside the battery limits due to the final form of the products being unknown. As such, the products are assumed to be suitably purified streams of uranium, fission products, actinides and lanthanides, each dissolved in nitric acid and held in storage tanks.
    - As there are no current Conditions For Acceptance (CFA) for products, it is unknown what would constitute acceptable levels of impurities, therefore, the products will be assumed to be as pure as possible and mal-operations will be defined as the point at which the products do not meet the CFA of subsequent plants.
- Centrifugal contactors have been selected as the main technology for this design.
    - It was noted in the meeting that contactors may not be suitable for the GANEX 1st Cycle, however this was deemed to be an engineering issue and as such, was not discussed further.
- The buffer and mixing tanks in the process will be appropriately sampled to ensure the correct feed passes through to the next stage.
    - It is assumed that this fails in the mal-operations scenario to allow for unfiltered feed to pass through to subsequent stages.
- It is assumed that any vessel in which it is expected that fissile material will be present will be designed to be criticality safe and the plant will be designed with sufficient shielding to mitigate dose uptake.

Normal Operations

The normal operations safety review considered the questions from Table 3. Where a question is not noted below it was either considered to relate only to mal-operations or nothing notable was discussed.

The stream references are as detailed in Figure 1.

A1: Feed chemicals / nuclides under normal operations?

Each of the feeds was considered individually to identify any hazards or to highlight any areas where the hazards are currently unknown.

- Dissolved fuel feed – Stream 1
    - This stream has known chemotoxic/radiological/shielding/criticality hazards which are managed currently in the nuclear industry. Consideration will have to be given to the likely higher burn-up, high Pu concentration, variation of isotopic composition (particularly for U or Pu) or generally different fuel compositions that may form future fuels.
- N,N-di-(ethyl-2-hexyl)isobutyramide (DEHiBA) in Odourless Kerosene (OK) – Stream 2
    - A specialist synthesised chemical with unknown hazards. It was noted that the addition of DEHiBA to OK will result in the mixture having a higher flashpoint (~70°C for pure OK), providing confidence that the flowsheet would be operable in ambient conditions.
    - It is known that OK as a chemical can have different properties as a result of the nature of its manufacture, but it was assumed that for normal operations, the OK was within the Conditions For Acceptance (CFA) of the demonstration plant. While the composition and properties of odourless kerosene can be variable depending upon the source, the consistency of supply can be achieved by establishing a product specification with the supplier and ensuring that batches meet key process requirements (e.g. flash point, viscosity).

Recommendation 1: **In order to understand the implications of temperature fluctuations in the system it is necessary to know the explosive and flammable properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA. Therefore further work is required to determine the lower flammability limits of TODGA, DEHiBA, DMDOHEMA, BTP & AHA.**

Recommendation 2: **For industrialisation of this process it will be necessary to understand the toxic properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA so that the conventional and handling hazards can be suitably managed. Therefore further work is required to determine the toxic properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA so that they can be categorised in line with European Regulation No 1272/2008 on classification, labelling and packaging of substances and mixtures (Classification, Labelling and Packing [CLP] Regulations).**

- Nitric Acid (0.5M and 1.0M HNO_3) – Streams 1, 5, 10,16 and 18
    - Nitric acid will be used in the preparation of feeds for many stages in the process and will generally be supplied and used as a concentrated acid (>13M) stock. This is widely used within the nuclear industry and the hazards are well understood and managed.
- Hydrazine (0.2M in nitric Acid) – Stream 7
    - Hydrazine is flammable and toxic, however it is used in low concentration in solution rather than as a pure liquid (hydrazine monohydrate). There is extensive operational experience with the use of hydrazine in PUREX flowsheets. There is a potential issue with the use of hydrazine, as the reduction of technetium(VII) typically produces hydrazoic acid. The behaviour and routing of hydrazoic acid in the PUREX process is adequately understood and controlled. However, there is no information regarding the potential formation and routing of hydrazoic acid in the GANEX process.

Recommendation 3: The PUREX process has known issues associated with the production of hydrazoic acid, which is handled by Solvent Wash processes. Investigate whether similar issues are likely to be present within the EURO-GANEX system, and methods of treatment if they are.

- 1,2-Cyclohexanediaminetetraacetic acid (CDTA) – Stream 9
    - CDTA is not classed as a hazardous substance (based on information from the Material Safety Data Sheet [MSDS]), and has well defined and manageable hazards.
    - The full safety implications of CDTA interactions within the system – even in normal operations – are unknown.
        - It was noted that this is a more general comment that could apply to most of the chemicals in the system.

Recommendation 4: For each of the possible inventory permutations detailed in Table **and Table in Appendix 1 (normal operations and mal-operations), the behaviour in the process system, and in particular in storage tanks for a period of time, needs to be understood with relation to the following safety-critical aspects:**

		Species				
		Hydrazine/ Hydrazoic Acid	*CDTA*	*DMODOHEMA/ TODGA*	*DMODOHEMA/TODGA Degradation Products*	*HNO3/ AHA/BTP*
Tank	*U Product*	✗	✗	✗	✗	✗
	CDTA Mixing	✓	✓	✗	✗	✗
	FP	✓	✓	✗	✗	✗
	An/Ln Buffer	✗	✗	✓	✓	✗
	Ln Product	✗	✗	✗	✗	✗
	An Product	✗	✗	✗	✗	✓

- **Radiolysis**
- **Hydrolysis**
- **Degradation products**
- **Chemical reactions**
- **Chronic precipitation**
- **Corrosive properties**

- N,N'-dimethyl-N,N'-dioctyl -2-(2-hexyloxyethyl) malonamide (DMDOHEMA) & N,N,N',N'-tetra-n-octyl-diglycolamide (TODGA) in OK – Streams 12 and 14
    - These extractants will have a higher flashpoint than OK For the purpose of assessing the hazards due to flammability of the solvent it was considered that pure OK will provide a bounding case
- 2,6-Bis[5,6-di(hydroxysulphonylphenyl)-1,2,4-triazin-3-yl] pyridine (SO_3-Ph-BTP) – Stream 18
    - This is a specialist synthesis chemical with unknown hazards (see Recommendations 1 and 2).
- Acetohydroxamic acid (AHA) – Stream 18
    - The hazards are well understood, however it has not been widely deployed at a large scale in the nuclear industry. AHA is known to decompose in nitric acid solution to hydroxylamine and acetic acid. Further decomposition of hydroxylamine generates the gaseous products N_2O and N_2. In addition to this, hydroxylamine nitrate can be unstable under certain conditions and has been known to result in explosions in some US nuclear plants. The GANEX operating conditions are considered to be well away from conditions for this, however, this needs to be confirmed. See Recommendation 4 with regards to further work

that is needed to fully understand the degradation products and chemical reactions which can occur in the GANEX process.

A2: Products chemicals / nuclides under normal operations?

Each of the products was considered individually to identify any hazards or highlight any areas where the hazards are currently unknown.

- Spent solvent (DEHiBA) – Stream 4
  - As with the feed itself, as a specialised chemical, the hazards are not well understood. However, it was noted that at any scale-up level, a defined solvent wash process would be required.

Recommendation 5: **For the process to be economically viable on a production scale it is necessary to clean up and recycle the spent DEHiBA (Stream 4) for reuse (Stream 2). Further work is required to develop this solvent wash process. Once developed a further safety review of this process will also be required.**

Recommendation 6: **For the process to be economically viable on a production scale it is necessary to clean up and recycle the spent DMDOHEMA / TODGA solvents (Stream 15) for reuse (Stream 14). Further work is required to develop this solvent wash process. Once developed a further safety review of this process will also be required.**

- Aqueous uranium product – Stream 6
  - This has known hazards through extensive experience of use in the nuclear industry. However, consideration will have to be given to any variation in the isotopic composition (i.e. use of HEU) and the impact that this would have on the use of GANEX for other future fuel reprocessing flowsheets. Hot tests of the GANEX-1 flowsheet have shown a small proportion of technetium and neptunium associated with the uranium product and the effect of this would have to be considered, although it would likely be negligible.
- Aqueous raffinate containing Fission Products (FP) – Stream 11
  - There will be radiological and shielding issues, however these are well understood and managed in the current nuclear industry.
- Spent solvent (TODGA & DMDOHEMA) – Stream15
  - As with the feed itself, as a specialised chemical the hazards are not well understood (see Recommendations 1 and 2). Again, it was noted that at any scale-up level, a defined solvent wash process would be required (see Recommendation 6).
- Aqueous lanthanide (Ln) product – Stream 17
  - The hazards are well understood and managed in the nuclear industry.
- Plutonium and minor actinide product – Stream 19
  - This stream has radiological and criticality considerations associated with both the plutonium and minor actinides such as americium and curium, but these are well understood and managed in the nuclear industry. This product stream will also contain the stripping reagents AHA/SO_3-Ph-BTP. AHA will decompose in nitric acid solutions to yield acetic acid and hydroxylamine. Further decomposition of hydroxylamine in nitric acid (by reaction with HNO_2 or reduction of metal ions) results in the evolution of N_2O and N_2. The long term stability of SO_3-Ph-BTP in nitric acid solution is unknown. Therefore, storage of the plutonium and minor actinide product will need to consider release of gases from decomposition of stripping reagents. The degradation of complexants and the impact upon the long-term storage of the Pu and MA product will be considered by Recommendation 4.

Recommendation 7: **In order to understand the potential toxic and corrosive consequences associated with using nitric acid in conjunction with various other compounds it is necessary to quantitatively understand the potential for NO_x generation.**

Therefore further work is required to determine the location and worst-case rate of evolution of NO_x gases throughout the EURO-GANEX process.

B1: Loading / concentration range at which process is designed to work?

- It was noted that the operating envelopes in which the chemical processes produce the desired products are currently unknown. If high accuracies in concentrations and loadings are required this may be challenging on a production-scale plant.
- If the DEHiBA concentration in Stream 2 is reduced, the uranium may not be completely extracted, however the threshold at which this would occur is unknown

Recommendation 8: Determine the range of flowrates and concentration ratios at which the chemical processes will work efficiently to define the operating envelope.

- Hydrazine is utilised to ensure the minimisation of technetium and neptunium in the uranium product (Stream 6), and would also act as a scavenger for nitrous acid (formed from degradation of nitric acid). Fluctuation in the hydrazine concentration could lead to more carryover of neptunium and technetium to the uranium product (Stream 6); however it is noted that there would be trace contamination and therefore this was considered a quality issue rather than safety issue.
    - Subsequent plants to process the uranium product will have Conditions For Acceptance (CFA) on product quality/composition. This will define how tightly the process must be controlled to ensure that the CFA are met.
- If the CDTA (Stream 9) concentration was lower than expected, there would be more carryover of zirconium and palladium through to the actinide separation stages which would then affect the quality of the An and Ln products (Streams 17 and 19).
    - As above, the CFA will dictate the range for acceptable CDTA concentration that ensures product quality.
    - In addition, the nitric acid concentration of the CDTA stream may affect subsequent extractions. If it is too low then extraction of the Pu/MA may be affected, but too high a concentration could lead to third-phase formation. Nitric acid is a component of a number of streams and all could possibly affect operations.
        - For normal operations, it is assumed that the nitric acid concentrations fall within the operating envelope (see Recommendations **8** and 9).

Recommendation 9: Define suitable CFA for each product and waste from the EURO-GANEX process to allow for process parameters (e.g. concentrations and flowrates) to be defined.

- Incorrect concentrations of solvents in Stream 12, DMDOHEMA & TODGA in OK, could lead to third phase formation and is therefore a criticality hazard. The concentrations at which this happens needs to be well understood.
    - This would only present a problem in mal-operations as the normal operating envelope would be bounded to prevent criticality.
- All radioactive species-bearing streams (Stream 17) would not present a criticality hazard under normal operations, most notably the Pu/MA and Ln product streams (Streams 17 and 19).
- Increased and decreased levels of each component in the HNO_3/SO_3-Ph-BTP/AHA strip (Stream 18) may challenge the product quality of the Ln and An product streams (Streams 17 and 19 respectively) depending on the relative makeup of the stream. However, no safety consequences are expected from normal operations.

The consequences of mal-operations leading to out-of specification concentrations (i.e. those falling outside a defined normal operating window) being fed into each process step is considered in the mal-operations review.

C1: Flowrate (or feed rate) range at which the process is designed to work?

- It was agreed that the process effects of increased/decreased flowrates of streams within the process would have similar consequences to increased/decreased concentrations so the findings from B1 are also valid for C1 in a normal operating envelope.

D1: Temperature range at which the process is designed to work?

- The process has only been tested under ambient temperature (30°C), or near to this. It is known that temperature has an effect on the distribution ratios of species within the process, but further investigation is required to define the optimal operating temperature for the process (See Recommendation 10).
    - There are no safety-critical cliff-edges with regards to temperature near the ambient operating temperature envelope, e.g. ignition temperatures are at least double (See F1 for more detail).

D2: Is the reaction exothermic or endothermic?

- Whether the extraction reactions would be exothermic or endothermic was generally unknown, and it is not known whether the scale-up to industrialisation would require cooling or heating.
- Uranium extraction is exothermic, however it is considered, based on the knowledge of the PUREX process, that this heat generation would be negligible in comparison to the self-heating of the dissolved fuel feed.

Recommendation 10: Further experimental and thermodynamic modelling work should be conducted to define the operating temperature range at which the defined separation factors are valid for each stage of the process (during normal operating conditions and fault conditions), and for the process as a whole.

D3: Are any of the feeds / products self heating?

- Stream 1 – high burn-up fuel – will be warmer than ambient and Stream 2, DEHiBA in OK, will be cool however the thermodynamics of this system are not fully understood.
    - Stream 1 may need to be cooled depending on thermodynamic modelling (see recommendation 10).
- The FP-loaded acid (Stream 11) may be heat generating, as will the An product stream (Stream 19), however this will affect storage tanks and downstream plant rather than this chemical separation stage considered by the design.

Recommendation 11: Determine the heat generation of product streams to then determine the engineering requirements of storage tanks and subsequent process plant.

F1: Is flammability/explosion a potential hazard under normal operations?

- The process is at ambient temperature (20°C) and therefore well below the flashpoint of OK (70°C), which is understood to be the bounding chemical.
- Hydrogen will be generated due to alpha radiolysis in storage tanks.
    - This could be controlled by purging the process with an inert gas, e.g. argon or nitrogen, during operation.

Recommendation 12: Determine the location and worst-case rate of evolution of hydrogen from the EURO-GANEX process to allow process venting requirements to be defined to prevent a possible explosive atmosphere.

G1: Could any solids be carried forward from previous stages?

- It is assumed that there will be a centrifuge on the dissolved fuel feed to ensure no solids enter the chemical separation stage of the flowsheet.

G6: Mechanisms for precipitation?

- The use of buffer and storage tanks in the system, or if the system lay dormant for a time, e.g. during recovery operations, could lead to precipitation due to radiolysis, hydrolysis and other mechanisms, which could in turn lead to criticality issues, however this is not fully understood (See Recommendation 4).
    - The use of filters in the buffer and storage tanks was discussed but it was noted that filter blockage could possibly lead to criticality events if left uncontrolled.
- Secondary precipitation of particulates, degradation products etc., could occur if solutions are left for a period of time before being processed, therefore if there are buffer tanks then additional filters may be required to scrub the fluids before they are fed back into the process
    - It was noted that filters within the process could blind leading to blockage issues, which could in turn lead to criticality events if left uncontrolled.

H1: Is the reaction likely to generate significant quantities of gases (types, evolution rates)?

- Areas where hydrogen or nitrogen/nitrogen oxides could be formed may generate pressure in the tanks. Therefore the system should be open vented to prevent pressure build up.
    - H_2 control could be achieved by purging with inert gas, as described in F1.

J1: Batch process or continuous process?

- It is likely that the chemical separation flowsheet will be operated continuously, however this will be defined by the head-end and finishing requirements.

J2: What size/shape vessel does the process require?

- The process is assumed to be made up of 5cm centrifugal contactors in suitably sized banks.
    - A preliminary analysis from an NNL criticality safety specialist has indicated that the volume of material held by contactors at the assumed process concentrations would not be sufficient to cause a criticality event. However, this should not be taken as a definitive criticality safety opinion on any future designs and does not cover potential mal-op scenarios.
- Buffer tanks and storage tanks will be of a suitable volume and be designed to be criticality safe as appropriate.

J3: Are there any known technologies which would not be suitable?

- Centrifugal contactors are the designated technology for the design and are found to be suitable at this design stage.
    - However if it is found that contactors would not be suitable in a more detailed design for some reason, e.g. insufficient residency time, engineering issues, etc., then other technologies are available, i.e. pulsed columns and mixer-settlers.
    - It was noted that the contactors may not be suitable for 1st Cycle GANEX, however this was considered an engineering issue and not considered further.

K1: Are feed and product materials compatible with likely plant material under normal operations?

- 1st Cycle GANEX and 2nd Cycle EURO-GANEX has been proven on a laboratory scale which showed no issues with material compatibility.
    - The long term effects of some of the solvents and complexants, e.g. SO_3-Ph-BTP, CDTA, AHA, are unknown as these have not been used on large industrial scale previously. This

could lead to potential unknown corrosion mechanisms or other chemical/materials interactions that only manifest over a longer period of time than achieved in laboratory tests, i.e. years compared to the days that laboratory tests take (See Recommendation 4).

K2: Are products of degradation compatible with plant materials?

- The degradation products of the solvents are relatively unknown and therefore this cannot be confirmed currently (See Recommendation 4).

Mal-operations

It was agreed with the SACSESS community that the following chemical conditions: feed chemicals/nuclides under fault conditions, loading/concentration deviations and flowrate deviations have similar results from a chemistry perspective, and therefore were considered as one. Again, the streams were taken in turn to evaluate deviation consequences:

- Dissolved fuel feed – Stream 1
    - An increase in expected U concentration in the feed would lead to the misrouting of U into the Ln and/or An product stream (Stream 17 and/or 19) as the DEHiBA solvent could not fully extract the U at a higher concentration.
        - It is unlikely this would be a safety issue, but may mean the U and TRU products would not meet CFA (see Recommendation 9).
    - An increase in Pu concentration could lead to possible third-phase formation. This would pose a serious criticality risk if it were to occur.
    - An increase in the concentration of nitric acid in the feed could lead to hydrolysis of the DMDOHEMA/TODGA solvent in the 2nd Cycle. This would result in the formation of ammonium salts and carboxylic acids, which would in turn lead to the liberation of CO_2, the formation of potential explosive compounds and third-phase formation of the Pu.
        - Although the above problem was identified, it was assumed that an engineered accountancy solution would eliminate the possibility of it happening.
- DEHiBA in OK – Stream 2
    - An increase in DEHiBA concentration/flowrate would lead to increased concentrations/misrouting of Tc, Np and FPs and possibly Pu in the U product stream (Stream 6). This could lead to criticality issues if the subsequent plant was not designed for this possibility. It would also pose product quality issues. In addition, the viscosity and flow parameters of the solvent would be affected, which would have an unknown effect on contactor performance (see Recommendation 8).
    - A decrease in DEHiBA concentration/flowrate would result in the misrouting of U to the An product stream (Stream 19). A low flowrate of solvent may also lead to hydrodynamic problems with the contactors resulting in entrainment of aqueous or solvent in the product streams.
- There will be a degree of hydrolysis of DEHiBA during normal operations however increased concentrations could increase the rate of hydrolysis leading to the generation of glycolic acids and CO_2 which could cause pressurisation of the system (see Recommendation 4).
    - If the concentration/flowrate was higher than expected then U would misroute to the Solvent Wash system (as yet to be defined). This could result in possible U precipitation in the Solvent Wash, which could lead to criticality issues (although this is unlikely unless highly enriched U is being reprocessed).
    - If the concentration/flowrate was lower than expected then the DEHiBA solvent would carryover into the nitric aqueous phase, causing hydrodynamic problems within the contactors.
- Hydrazine – Stream 7
    - A higher hydrazine concentration/flowrate would lead to the increased formation of hydrazoic acid.
        - In the PUREX system, hydrazoic acid is extracted by TBP/OK and is then removed in the Solvent Wash system. However, the behaviour of hydrazoic acid in the EURO-GANEX system (and the as yet undefined Solvent Wash) is unknown (see Recommendations **5** and 6).
    - A lower hydrazine concentration/flowrate would lead to increased losses of Np and Tc to the U product stream (Stream 6), resulting in a detrimental effect on the U product (see Recommendation 9).

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- 0.01M nitric acid strip – Stream 5
    - Increased concentration/decreased flowrate would impair the backwashing of U, resulting in the loss of U to the solvent wash process.
    - Reduced concentration/increased flowrate would be unlikely to impair U backwashing, it may have a detrimental effect on the hydrodynamic performance of the contactors, resulting in poor phase separation (especially if only water is fed to the contactors).
- CDTA in nitric acid – Stream 9
    - Increased CTDA concentration/flowrate is not thought to pose an immediate safety risk.
    - Decreased CDTA concentration/flowrate would lead to increased FPs, particularly Zr and Pd, carrying through to the An and Ln strip stages.
        - This is not deemed to be a safety issue, but may mean the An and Ln product would not meet subsequent CFA (see Recommendation 9).
    - Increased acid concentration could lead to third-phase formation, presenting a criticality risk, and also increased extraction of Fe and Sr, leading to recycle and accumulation within the contactors.
- TRU Extract and Scrub nitric acid – Stream 10
    - Increased concentration/flowrate of nitric acid at this stage could result in the recycling of TRU in the bank of contactors, which would then result in criticality issues.
    - Decreased concentration/flowrate of nitric acid could result in a backwashing of Pu from the solvent stream, which could then recycle through the TRU Extract and Scrub banks, leading to criticality issues. In addition, very low acidity (near water concentrations) could lead to Pu colloid formation, which could lead to criticality issues when plating out.
- TRU Extract and Scrub solvent –Stream 12
    - Higher TODGA/DMDOHEMA concentrations/flowrates are not seen to have any chemical significance, however the resulting higher viscosity of the fluid caused by higher concentrations may result in unforeseen performance issues with the centrifugal contactors.
    - Lower DMDOHEMA concentrations may lead to precipitation of Pu within the system, resulting in a serious criticality risk.
    - Lower TODGA concentrations would result in poor extraction of trivalent species, e.g. Am^{3+}, Cm^{3+}, Eu^{3+}, etc., which would then misroute to the FP waste (Stream 11). In addition, the maximum Pu loading in the solvent would be decreased by lower TODGA concentrations, increasing the possibility of third-phase formation.
    - Increased acid concentration would increase the concentration of the Pu/TODGA complexes beyond the solubility limit of the solvent leading to third-phase formation.
    - In the TRU extract and scrub stage there is a range of mal-operations which could lead to the recirculation of Pu and therefore higher concentrations of Pu. If the vessels are being design to be criticality safe geometry then this would need to consider the worst case Pu concentration.
- An and Ln Strip solvent – Stream 14
    - Higher TODGA/DMDOHEMA concentrations/flowrates will cause more TRU to route to the Ln product stream (Stream 17), which could lead to possible dose/criticality issues if the equipment in downstream plant does not account for these hazards.
    - Low TODGA/DMDOHEMA concentrations/flowrates would lead to Ln misrouting to the An product (Stream 19).
        - There was also the possibility of Pu third-phase formation if there is low (near zero) DMDOHEMA concentration.
- Ln Strip nitric acid –Stream 16
    - Higher acid concentrations could lead to Ln being misrouted to the second Solvent Wash process (again, as yet undefined).
    - Lower acid concentrations are not seen as a major problem, but there may be operability issues due to the effect very low concentration (near or equal to zero) would have on the hydrodynamic behaviour in the contactors. In addition, very low concentration acid

  concentrations could adversely impact on interface properties, e.g. crud formation and/or poor separation.

- An Strip aqueous –Stream 18
  - High BTP concentrations will cause Ln to misroute to the An product (Stream 19).
  - Low BTP concentrations will lead to Am and Cm in the Ln product (Stream 17) which could lead to criticality issues in the Ln product.
  - High AHA concentrations are not seen as a problem.
  - Low AHA concentrations will lead to Pu and Np in the Ln product (Stream 17), which is a major criticality concern. Pu precipitation could also take place, depending on how low the AHA concentration became.
  - High nitric acid concentration will impair the efficient backwashing of Pu and MA, resulting in losses to the Ln product. This could also present a criticality issue in the Ln product.
  - Low nitric acid concentration will lead to the co-stripping of Ln into the actinide product, resulting in detrimental impact upon the product quality.

D4/5: Temperature Effects

- The temperature effects on the process are as yet unknown. It is expected that the temperature will affect parameters such as:
  - Solubility limits of the solvents, i.e. 3rd phase issues.
  - Solvent decomposition
  - Distribution ratios in the GANEX-1 and GANEX-2 extractions
  - Physical properties of the different chemicals, e.g. density, viscosity, volatilities, etc.
  - Hydrolysis and radiolysis effects in the system
- It was agreed that not enough was known in general about fault temperature effects on the system as a whole (See Recommendation 10).
- Increased temperature could increase the volatility of the organics (e.g. OK which is considered to be the most onerous organic in the system, but its use is understood in the PUREX system up to 50°C) which could lead to pressurisation if the system is not suitably vented.

E1/2: Degradation

- Degradation products of the solvents will be created during normal operations, as well as in fault scenarios.
- Recent research by the SACSESS community suggests that the degradation products of the solvents can extract the targeted species as well as the original solvent, however it was noted that they had not been proven in allowing the nitric acid to strip the extracted species in subsequent stages.

F & H: Gas Generation

Gas generation within the GANEX system was considered as a whole, encompassing flammability, explosion and pressurisation risks.

- Hydrogen will be generated through radiolysis of different system components. This is of greatest concern during static conditions (See Recommendation 12).
- Carbon dioxide will be generated throughout the system.
- Nitrous oxides and oxygen will also be generated.
  - The majority of the above would only become major problems within enclosed tanks, it is expected that venting arrangements and a subsequent off-gas system would support the actual plant.

G3: Insolubility of degradation products?

- The dissolved fuel feed (Stream 1) could contain fine Pu particulates and also possible Zr particulates, which could lead to criticality issues if the Pu particulates drop out of suspension.
    - In addition, there would also be mechanical damage of the contactors if particulates were in the feed.
    - It is assumed that the head-end processes and filters or centrifuges would remove the majority of the particulate material in the feed.
- In current PUREX plants, the formation of an interfacial crud between the phases in the solvent extraction occurs. It is unknown but likely that this crud formation would also occur in a GANEX system.
    - The crud would pose a particular problem for the operation of centrifugal contactors and may lead to blockages or misrouting of streams.
    - This could lead to localised Pu build up and therefore criticality issues.
    - In the PUREX system, plant shutdowns and washouts are employed to ensure that cruds do not accumulate to such a degree that they cause operational problems.

Recommendation 13: The formation of an interfacial crud through complex interactions in the PUREX system is known. Investigate the possibility of interfacial crud formation in a GANEX system, the conditions under which it could form and the resulting effects.

- Corrosion of piping would lead to iron, chromium and other stainless steel constituents accumulating within the system, resulting in unknown interaction effects with the GANEX system.

G4: Insolubility of feed / product chemicals present under mal-operations?

- Problems associated with insoluble fission products have occurred in the PUREX process, leading to deposition and it is conceivable that similar issues could be encountered in the GANEX process. This would mainly be of concern in the primary separation stage before the CDTA complex is added.
- In the second stage, TRU extract and scrub, the accumulation and deposition of Pu containing solids could potentially occur. This is well understood for Pu in the PUREX system, however it is less well understood for the EURO-GANEX system, particularly under mal-operation conditions.

Recommendation 14: Investigate the possibility of solids deposition due to insolubility in the EURO-GANEX process.

Recommendation 15: Determine the possibility of Pu deposition in mal-operations temperatures and concentrations in the TRU extract and scrub stages.

G5/6: Mechanisms for crystallisation/precipitation?

- Chronic corrosion could lead to build up of corrosion products (e.g. iron) which could interact with the system (see Recommendation 13).
- Sublimation / crystallisation could occur in the ventilation system leading to plating out of solids in the vent, leading to long-term degradation and corrosion, which could possibly lead to plant shutdown if allowed to develop.
- Iodine may not be completely removed during the process. There is operating experience of the PUREX process which shows iodine accumulating in the solvent recycle route and it is conceivable that similar build up may occur in the primary (DEHiBA) cycle of the GANEX process..

Summary of Recommendations

A summary of the recommendations made in the Safety Review are given below:

No.	Recommendation	Priority
1	In order to understand the implications of temperature fluctuations in the system it is necessary to know the explosive and flammable properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA. Therefore further work is required to determine the lower flammability limits of TODGA, DEHiBA, DMDOHEMA, BTP & AHA.	High
4	For each of the possible inventory permutations detailed in Table 2 and Table 3 in Appendix 1 (normal operations and mal-operations), the behaviour in the storage tanks needs to be understood with relation to the following safety-critical aspects: - Radiolysis - Hydrolysis - Degradation products - Chemical reactions - Chronic precipitation	High
5	For the process to be economically viable on a production scale it is necessary to clean up and recycle the spent DEHiBA (Stream 4) for reuse (stream 2). Further work is required to develop this solvent wash process. Once developed a further safety review of this process will also be required.	High
6	For the process to be economically viable on a production scale it is necessary to clean up and recycle the spent DMDOHEMA / TODGA solvents (Stream 15) for reuse (Stream 14). Further work is required to develop this solvent wash process. Once developed a further safety review of this process will also be required.	High
7	In order to understand the potential toxic and corrosive consequences associated with using nitric acid in conjunction with various other compounds it is necessary to quantitatively understand the potential for NO_x generation. Therefore further work is required to determine the location and worst-case rate of evolution of NO_x gases throughout the EURO-GANEX process.	High
8	Determine the range of concentration ratios at which the chemical processes will work efficiently to define the operating envelope.	High
10	Experimental and thermodynamic modelling work should be conducted to define the operating temperature range at which the defined separation factors are valid for each stage of the process (during normal operating conditions and fault conditions), and for the process as a whole.	High
12	Determine the location and worst-case rate of evolution of hydrogen from the EURO-GANEX process to allow process venting requirements to be defined to prevent a possible explosive atmosphere.	High
13	The formation of an interfacial crud through complex interactions in the PUREX system is known. Investigate the possibility of interfacial crud formation in a GANEX system, the conditions under which it could form and the resulting effects.	High
15	Investigate the possibility of Pu deposition in mal-operations temperature and concentrations in the TRU extract and scrub stages.	High
2	For industrialisation of this process it will be necessary to understand the toxic properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA so that the conventional and handling hazards can be suitably managed. Therefore further work is required to determine the toxic properties of TODGA, DEHiBA, DMDOHEMA, BTP & AHA so that they can be categorised in line with European Regulation No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regs).	Low
3	The PUREX process has known issues associated with the production of hydrazoic acid, which is handled by Solvent Wash processes. Investigate whether similar issues are likely to be present within the EURO-GANEX system, and methods of treatment if they are.	Low
9	Define suitable CFA for each product and waste from the EURO-GANEX process to allow for process parameters (e.g. concentrations and flowrates to be defined).	Low
11	Determine the heat generation of product streams to then determine the engineering requirements of storage tanks and subsequent process plant.	Low
14	Investigate the possibility of solids deposition due to insolubility in the EURO-GANEX process.	Low

Table 2 – Summary of recommendations from the safety review (sorted by priority)

Hazard Management Strategies

Hazard Management Strategies (HMS) are developed at an early stage in projects to help inform the design process throughout the plant concept and development of the detailed design. Once the main hazard types are identified a series of options are identified to aid in the elimination or management of each hazard type. The draft HMSs presented here are listed in accordance with the following hierarchy:

- Eliminate the hazard
- Reduce the potential for the hazard to occur
- Isolate the hazard
- Contain the hazard by mitigating it’s effects
- Personal Protective Equipment (PPE)
- Discipline (operational controls)

As the HMS for each hazard may vary in different parts of the plant or process, multiple strategies for control of a hazard could be adopted. Many of the initial HMS candidates will not be possible at all points throughout the plant or process, justification of not adopting the higher items on the hierarchy will inform the safety justification for the design.

From the mal-op discussions it is considered that the main hazards associated with the GANEX process can be summarised as follows:

- Explosion due to:
    - Exothermic reactions leading to temperatures above solvent flashpoint
    - Explosion due to hydrogen generation
- Criticality due to:
    - Mis-routing of feeds (e.g. criticality due to mis-routing of plutonium)
    - Precipitation
    - Third phase generation
    - Recycle and accumulation of Pu within the process
- Release of radioactive material due to over pressure (pressurisation from gas generation)

Each of these is considered in turn below in relation to the HMSs in hierarchical order. Although it is assumed that the plant will be designed to minimise normal operation direct dose to operator, the fault of higher direct dose is also considered below.

Explosion due to exothermic reactions leading to temperatures above solvent flashpoint

- Design the plant such that heat generation in the plant is less than the passive heat removal from the plant
- Control concentrations to reduce the heat generation rate of the reactions
- Provide robust containment that would not be weaken under the effects of a temperature excursion
- Cooling systems to provide heat removal capability in excess of the maximum predicted heat generation from reactions.
- Provision of emergency detection of high temperature
- Provision of alarms and emergency stop systems on detection of high temperature
- PPE
- Evacuation

Explosion due to hydrogen generation

- Design the plant such that hydrogen generation in the plant is negligible
- Control feed concentrations to reduce the hydrogen generation rate of the reactions
- Inertion of areas where hydrogen generation is an issue
- Provision of forced ventilation systems in areas where hydrogen may generate to dilute the concentrations
- Provide suitable engineered ventilation and relief systems to prevent possible hydrogen build-up under mal-operation conditions
- Provision of alarms and emergency stop systems on hydrogen detection
- Evacuation

Criticality due to mis-routing of feeds (e.g. criticality due to mis-routing of plutonium)

- Design the plant such that mis-routing is not credible
- Safe-by-shape geometry of the plant
- Control of feeds to ensure that the potential for mis-routing is minimised
- Provision of alarms, and associated trips where appropriate, on detection of misrouted species
- Poisons provided at strategic parts of the process
- Provision of neutron monitors for the detection of Pu accumulation
- Criticality alarm and evacuation

Criticality due to Precipitation

- Design the plant and process such that precipitation is not credible
- Safe-by-shape geometry of the plant where possible
- Control of feeds to ensure that the potential for precipitation is minimised
- Poisons provided at strategic parts of the process
- Maintenance strategies to closely control any potential build-up of material (note potential to significantly impact routine dose uptake – see direct dose uptake below)
- Criticality alarm and evacuation

Criticality due to 3rd phase generation

- Design the plant such that third phase is not credible
- Safe-by-shape geometry of the plant
- Control of feeds to ensure that the potential for third phase is minimised
- Design flowsheet to ensure that there is adequate safety margins before third phase formation would occur
- Poisons provided at strategic parts of the process
- CIDAS alarm and evacuation

Release of radioactive material due to over pressure (pressurisation from gas generation)

- Design the plant such that pressurisation from gas generation is negligible
- Passive ventilation of plant such that pressurisation could not occur
- Pressure relief on areas where pressurisation is a potential hazard
- Provision of alarms and emergency stop systems on detection
- Evacuation

Direct Dose Uptake

- Minimise inventory in facility
- Provision of shielding at appropriate locations
- Maximise distance of material from operators & public
- Minimise requirement for operator physical intervention in plant
- Minimise maintenance requirements for plant
- Provision of gamma and proximity interlocks on any shielding penetration access routes
- Area gamma monitoring and alarms with associated evacuation
- Health Physics Monitoring and dose uptake management

Conclusions

The safety review of the EURO-GANEX chemical separations process, looking at both normal and fault operations, was successfully undertaken as detailed above. The main safety hazards that have been identified can be categorised as follows:

- Explosion due to:
  - Exothermic reactions leading to temperatures above solvent flashpoint
  - Explosion due to hydrogen generation
- Criticality due to:
  - Mis-routing of feeds (e.g. criticality due to mis-routing of plutonium)
  - Precipitation
  - 3rd phase generation
- Release of radioactive material due to over pressure (pressurisation from gas generation)

In some cases there is insufficient information to determine whether these hazards will be an issue within the GANEX process. Therefore a number of recommendations have been raised. These are detailed in section 4 below and have been categorised as either low or high priority.

In addition to the specific recommendations made below, some more generic safety issues were raised.
It was agreed that a safe-by-shape criticality philosophy should be employed. This would be incorporated into the design and layout of key equipment items – centrifugal contactors and storage tanks. In addition, the use of centrifugal contactors in the GANEX 1st Cycle – the U Extract, U Scrub and U Backwash sections – was questioned as there will likely be a carryover of fines or precipitates which could affect processing.

References

[1] Flint, L., SACSESS Deliverable D31.1a “Production of SACSESS Combined Safety Assessment Methodology: Summary of NNL Activity Against Task 3.1.1”, Rev. A, August 2014.

[2] Graham, D., NNL 13172 “Process Description of the EURO-GANEX Process”, Rev. A, August 2014.

Appendix 1 – Species Combination Tables

		Species						
		U	FP	An	Ln	DEHiBA	DEHiBA Degradation Products	HNO_3
Tank	U Product	✓	✗	✗	✗	✗	✗	✓
	CDTA Mixing	✗	✓	✓	✓	✗	✗	✓
	FP	✗	✓	✗	✗	✗	✗	✓
	An/Ln Buffer	✗	✗	✓	✓	✗	✗	✗
	Ln Product	✗	✗	✗	✓	✗	✗	✓
	An Product	✗	✗	✓	✗	✗	✗	✗

		Species				
		Hydrazine/ Hydrazoic Acid	CDTA	DMODOHEMA/ TODGA	DMODOHEMA/TODGA Degradation Products	HNO_3/ AHA/BTP
Tank	U Product	✗	✗	✗	✗	✗
	CDTA Mixing	✓	✓	✗	✗	✗
	FP	✓	✓	✗	✗	✗
	An/Ln Buffer	✗	✗	✓	✓	✗
	Ln Product	✗	✗	✗	✗	✗
	An Product	✗	✗	✗	✗	✓

Table 3 - Possible species combinations in the EURO-GANEX process tanks during normal operations (ticks indicate the possible presence of the chemical)

		Species						
		U	FP	An	Ln	DEHiBA	DEHiBA Degradation Products	HNO_3
Tank	U Product	✓	✓	✓	✓	✓	✓	✓
	CDTA Mixing	✓	✓	✓	✓	✓	✓	✓
	FP	✓	✓	✓	✓	✓	✓	✓
	An/Ln Buffer	✓	✓	✓	✓	✓	✓	✓
	Ln Product	✓	✓	✓	✓	✓	✓	✓
	An Product	✓	✓	✓	✓	✓	✓	✓

		Species				
		Hydrazine/ Hydrazoic Acid	CDTA	DMODOHEMA/ TODGA	DMODOHEMA/TODGA Degradation Products	HNO_3/ AHA/BTP
Tank	U Product	✓	✗	✗	✗	✗
	CDTA Mixing[1]	✓	✓	✓	✓	✗
	FP	✓	✓	✓	✓	✗
	An/Ln Buffer[1]	✓	✓	✓	✓	✓
	Ln Product	✓	✓	✓	✓	✓
	An Product	✓	✓	✓	✓	✓

Table 4 – Possible species combinations in the EURO-GANEX process tanks during

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[1] It is assumed that the chemicals from the subsequent stage may be present in the buffer/mixing tank, however it is not carried to the previous stage, e.g. DMODOHEMA/TODGA may be present in the CDTA mixing tank, but will not carry through to the GANEX 1st Cycle.

mal-operations (ticks indicate the possible presence of the chemical)