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Status on solvent clean- up & recycling

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Summary

This report describes the progress made under the GENIORS project in the topic of solvent clean up and recycling for the GENIORS reference processes (i-SANEX, EXAM and GANEX). The recycle of organic solvents is a crucial yet often neglected component of the overall separation processes. As the technical maturity of the reference separation processes increase it is becoming increasingly important to develop the solvent clean up. A detailed literature review has been conducted to understand the state of the art and this work also builds on substantial studies of the radiolytic and hydrolytic driven solvent degradation processes and identification of solvent degradation products. This report focuses on some key aspects of this challenge: ? Degradation products and strategies for washing TODGA based solvents ? Fission product retention in solvents ? Development of a dose model to assess the impacts of radiation on solvents Based on the findings reported here it is concluded that future efforts need to focus on: 1. Further development of the solvent dose model is required to provide a flexible model that can be adapted to other flowsheets and allows changes to the process parameters / feeds to assess the impact upon solvent degradation in the process. This would allow assessment of the solvent dose in the i-SANEX process for example. 2. Further research, development and testing are required to assess options for the removal of degradation products from TODGA (or other diglycolamide) based solvents. This may include: ? Systematic evaluation of reagents for removal of the individual degradation products to assess whether there is a suitable combination of reagents to remove TODGA degradation products. This should also include testing of salt free reagents (such as tetramethyl ammonium hydroxide) to consider options for reducing volumes of waste streams. ? Evaluate solid sorbents for removal of species that are not readily removed by aqueous wash regimes ? Carry out testing using levels of degradation products that would be representative of process conditions (i.e. removal of degradation product after each cycle through the process) 3. Directions in solvent washing should focus on salt free reagents and process development that reduces the size of the solvent wash cycle plant footprint, i.e. reducing wastes generated, simplifying the process and ensuring process safety whilst meeting solvent quality requirements (these also need to be better defined)....

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EXEC SUMMARY

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- Degradation products and strategies for washing TODGA based solvents
- Fission product retention in solvents
- Development of a dose model to assess the impacts of radiation on solvents

Based on the findings reported here it is concluded that future efforts need to focus on:

1. Further development of the solvent dose model is required to provide a flexible model that can be adapted to other flowsheets and allows changes to the process parameters / feeds to assess the impact upon solvent degradation in the process. This would allow assessment of the solvent dose in the i-SANEX process for example.
2. Further research, development and testing are required to assess options for the removal of degradation products from TODGA (or other diglycolamide) based solvents. This may include:
    - Systematic evaluation of reagents for removal of the individual degradation products to assess whether there is a suitable combination of reagents to remove TODGA degradation products. This should also include testing of salt free reagents (such as tetramethyl ammonium hydroxide) to consider options for reducing volumes of waste streams.
    - Evaluate solid sorbents for removal of species that are not readily removed by aqueous wash regimes
    - Carry out testing using levels of degradation products that would be representative of process conditions (i. e. removal of degradation product after each cycle through the process)
3. Directions in solvent washing should focus on salt free reagents and process development that reduces the size of the solvent wash cycle plant footprint, i. e. reducing wastes generated, simplifying the process and ensuring process safety whilst meeting solvent quality requirements (these also need to be better defined).
4. Further tests can be undertaken to assess whether there is a concentration of degradation product that can be tolerated within the process. This would allow further assessment whether the impact of species that are difficult to remove can be mitigated using a low volume solvent purge.

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INTRODUCTION

Advanced solvent extraction flowsheets have been developed under the European Union framework programmes for the homogeneous and heterogeneous recycling of minor actinides in future fuel cycles. This includes the "EURO-GANEX" (EUROpean Grouped ActiNide EXtraction) flowsheet and i-SANEX (innovative Selective ActiNide Extraction) that were developed under past EU Framework Programme projects. The EURO-GANEX process provides homogeneous recycling of the minor actinides with the plutonium product, while the i-SANEX flowsheet was developed for the heterogeneous recycling of minor actinides. Design and optimisation of these flowsheets was primarily focussed upon achieving the desired performance, with high recovery of the minor actinides and minimised losses to waste streams as well as obtaining good fission product decontamination factors. However, safety and operability of the process are also important considerations in the development of actinide separation flowsheets. Subsequent assessment of the process safety under the SACSESS project identified key areas for further investigation to underpin the development of an industrial process. One of the areas highlighted by this review was the degradation of the solvent due to radiolysis and hydrolysis in the process.

There are two key issues associated with radiolysis and hydrolysis of the solvent. Firstly, the generation and accumulation of hydrogen from irradiation of the solvent presents a key safety consideration for the development and design of a process. Secondly, degradation of the solvent can have a detrimental impact upon the process performance. Solvent degradation may have a number of effects upon process performance, such as:

- Reduction of the complexant concentration impairs the extraction of key species (i.e. lower distribution coefficients). This may lead to increasing losses in the aqueous raffinate.
- Degradation products may form stronger complexes with the extracted species and inhibit stripping, thus increasing losses to the solvent raffinate.
- Degradation products may also complex and enhance the extraction of fission product species. This can have a detrimental effect upon the process performance due to the reduced DFs for fission products or retention in the solvent.
- Degradation products are also implicated in the formation of precipitates and cruds in the process which may interfere with the hydrodynamic performance.

For a process operating at te/d scale it is essential to minimise the waste arisings as it is impractical and costly, as well as environmentally unacceptable, to consider using the solvent on the basis of just a single pass through the process. Therefore, management of solvent inventory is a key aspect of the reprocessing flowsheet to maintain process performance while avoiding unnecessary losses / addition of fresh solvent and minimising waste arisings. Consequently, it is essential to understand the rate and extent of degradation within the process and develop solvent management strategies to maintain the solvent quality and process performance.

In actinide separation processes the solvent quality in a process is typically maintained by:

- Solvent washing – used to remove degradation products and residual activity from the solvent. In the PUREX process this is typically an aqueous wash process, employing caustic and carbonate solutions, to remove the acidic degradation products of TBP.
- Solvent purge – a low volume solvent purge involves a daily removal of a small quantity of the solvent and replacing with an equal volume of clean, unused solvent. This is typically employed to minimise the

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accumulation of degradation products not removed by a solvent wash process, such that that this low volume bleed maintains them at an acceptably low steady state concentration.

Therefore, in order to develop appropriate solvent management strategies, it is necessary to understand the degree of solvent degradation in the process:

- What is the radiation dose to the solvent in the process?
- What impact does the radiation dose have upon the degradation of the extractant and how often do additions need to be made to maintain the solvent composition?
- What degradation products are present?
- How quickly do the degradation products accumulate and what impact do they have?
- What level of degradation products need to be removed from the solvent?
- How frequently does the solvent inventory need to be changed?
- Can degraded solvent be managed by a low volume solvent purge or is a clean up cycle necessary?

This report provides a summary of the initial studies in GENIORS that have been undertaken to address these issues and assess the requirements for the clean-up and recycle of solvent.

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REVIEW OF SOLVENT WASH OPTIONS

PUREX

The PUREX process is the most widely employed industrial scale process for recycling spent nuclear fuel. This involves dissolving spent fuel in nitric acid (HNO_3) which is then filtered to remove insoluble particles and solids. The aqueous solution is then contacted with a solvent consisting of 20 to 30% v/v tributyl phosphate (TBP) in a hydrocarbon diluent, such as odourless kerosene (OK). Uranium and plutonium are complexed by TBP and partitioned into the organic phase. Separation of uranium and plutonium is achieved by the reductive backwashing of plutonium from the solvent using reagents such as U(IV) and hydrazine or ferrous sulphamate. Uranium is then stripped from the organic phase with a low concentration nitric acid solution. The solvent is then recycled to the start of the process. Throughout this extraction and backwash process the solvent has undergone degradation due to α/γ radiolysis and acidic hydrolysis, resulting in the formation of degradation products that can have a detrimental impact upon the process by extracting and retaining (additional) species, forming cruds or solids or otherwise affecting the separation process. To provide the context for later discussion of solvent degradation and clean up in the processes developed under GENIORS, it is necessary first to consider the PUREX system which is well studied and has industrially proven solvent clean up technologies.

DEGRADATION PRODUCTS

Radiolysis and hydrolysis of TBP and the hydrocarbon diluent results in the formation of a range of degradation products. The primary degradation products of TBP are, dibutyl phosphate (HDBP) and monobutyl phosphate (H_2MBP) and ultimately phosphate. These are formed through the sequential removal of the butyl chains form the TBP. These degradation products are readily abated in the PUREX process through solvent clean-up/regeneration methods. However, there are other degradation products that result from reorganisation of the butyl ligands and reaction with the kerosene diluent; both the major long chain hydrocarbon component and the minor aromatic/cyclic components. These products are not readily removed by the PUREX solvent regeneration process. These longer-term products, so-called as they accumulate much more slowly than the HDBP and H_2MBP components, that are abated, then build up over time and affect process performance through: increased retention of impurities such as Zr and Ru increased loss of products to the aqueous phase and poor phase disengagement. The degradation products arising from radiolysis of the diluent also include carboxylic acids, nitro and nitrate compounds, ketones and alcohols.

A number of methods have been evaluated for the clean-up and recycle of the solvent in the PUREX process. The most commonly used method involves washing the solvent with aqueous reagents to remove the acidic degradation products. These aqueous wash processes can be split into two broad categories: salt based and salt free. The salt based aqueous wash reagents produce a salt bearing (typically sodium containing) waste stream that requires further treatment and encapsulation, which contributes to the total volumes of waste generated from the process. Whereas the salt free reagents can be readily decomposed and ultimately, do not contribute to the final volume of wastes requiring treatment and storage.

WASH TECHNIQUES

SALT-BASED PROCESSES

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The most widely employed method of solvent regeneration in the PUREX process utilises an aqueous alkaline wash with sodium carbonate (Na_2CO_3) or sodium hydroxide (NaOH) [1] [2]. The NaOH/ Na_2CO_3 removes the low molecular weight acidic degradation products such as HDBP and H_2MBP, phosphoric acid and carboxylic acids arising from degradation of the diluent, as well as any U and Pu retained in the organic phase [3]. This has been adopted in plants such as Windscale in the UK and Savannah River in the US [4]. A typical solvent wash scheme in a PUREX flowsheet involves a series of washes, for example:

1. An initial wash with dilute nitric acid (0.1M HNO_3) may be performed to reduce the residual acid content of the solvent. This prevents carryover of excess acid and neutralisation of the reagents used in the subsequent alkaline washes.
2. Sodium carbonate wash. This is typically employed prior to a sodium hydroxide wash as the formation of carbonate complexes with residual U /Pu stripped from the solvent avoids the risk of precipitation. This ensures that U and Pu do not enter the sodium hydroxide wash where they would be expected to precipitate.
3. Sodium hydroxide wash.
4. A final dilute nitric acid wash is often used to re-acidify the solvent to minimise the risk of carbonate / hydroxide being carried over into the separation process [5].

This is just a general outline for a wash process and the exact conditions vary depending upon the flowsheet requirements. Secondary clean-up methods such as use of evaporation can allow removal of the heavier degradation products [6]. Whilst, alkaline washes using Na_2CO_3 / NaOH have become the standard method for the clean-up and recycle of the PUREX solvent, a range of alternative reagents have been investigated. There are a number of reasons for pursuing alternative clean-up methods, including a desire to reduce waste volumes by using reagents that do not generate salt bearing waste streams, improve the efficiency of the wash process to remove degradation products and enhanced stripping of activity or fission products from the used solvent.

An improvement on the Na_2CO_3 wash is the inclusion of potassium permanganate ($KMnO_4$) in the basic wash as employed by Hanford in the US [1]. The permanganate was helpful as it coprecipitates manganese dioxide in the solvent phase and subsequently absorbs the fission product complexing agent. One set of conditions tested were 0.01M $KMNO_4$ in 3 wt.% Na_2CO_3 at 50 ^{O}C. This showed an improvement of the DF of Zr-Nb and Ru by factors of 5 and 2 respectively. Further experiments with heavily degraded solvent (60wh/l) showed that 0.23M $KMnO_4$ in 0.25M Na_2CO_3 resulted in a DF of over 100 for Zr and a DF of 15 for the corresponding Zr ligand [7]. However, the problems with this formulation are that frequent ‘change out’ of wash solution is required and solid MnO_2 must be handled. MnO_2 collected at the interface but could be readily dissolved along with unreacted $KMnO_4$ in the organic phase with dilute nitric acid. The effectiveness of $KMnO_4$ compared to a normal carbonate wash was rapidly reduced after 3 contacts with solvent [8].

Calcium hydroxide (CaOH) has been tested as an alternative to Na_2CO_3 and NaOH and shown to be detrimental to the solvent quality as it was shown to accumulate in the organic phase, even leading to the formation of solids. [8, 9].

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Sodium sulphate (Na_2SO_4) at a concentration of 10% v/v was evaluated for the removal of HDBP and uranium from the spent solvent, however it was found to be less effective than Na_2CO_3. In addition, the authors stated that a gel was formed that required a HNO_3 wash to disperse[1] [9].

Sulphuric acid (H_2SO_4) has been used to remove residual radioactivity from TBP/OK organics at 10 M and 5 N it quantitatively removed residual uranium without affecting the settling time [9] [10]. It was found that the 5N H_2SO_4 gave a U DF of 85 but had next to no effect on the DBP concentration within the solvent giving a DBP DF of 1.2.

Room temperature Ionic liquids (RTIL) have been evaluated and shown to be provide limited removal of degradation products. An example of this is 1-alkyl-3-methyl-imidazolium chloride where alkyl = butyl, hexyl and octyl. These RTILS have been used to remove HDBP from used TBP-nDD. Butyl and hexyl were found to remove HDBP from used solvent without affecting the concentration of TBP giving HDBP DFs of 1.2 and 1.15. Pre-treating the solvent with water improved the HDBP DFs to 3 and 2.6 respectively [11].

SALT-FREE TECHNIQUES

When vitrifying the waste streams from the PUREX process one of the issues that poses limits on product loading is the amount of sodium that can be present. Therefore, alternative processes have been developed that avoid the use of reagents which add additional salts (sodium) to the process streams.

Alternative wash reagents based upon hydrazine have been investigated. These include hydrazine carbonate [12] and hydrazine oxalate [12, 13]. Hydrazine oxalate and carbonate have been shown to remove Pu, U and Zr from DBP and MBP containing solvents with between 94-99% removal. These showed promise for replacing Na_2CO_3 as a solvent wash method and have been tested in the CORAL facility in INDIA as a solvent regeneration technique when preceded by an oxalate wash [14]. However, there are concerns for the potential to produce hydrazoic acid in the process which can present an explosion hazard. The preparation and storage of hydrazine is also difficult due to its instability at room temperature. Hydrazine hydrate has also been found to be effective at removing HDBP and fission products such as Zr and Ru. The optimal concentration for the solvent wash process was reported to be between 0.2 and 0.5 M. This work demonstrated that that the decontamination factor obtained for DBP and fission products was comparable to Na_2CO_3. In a solvent contaminated with 270 mg/l DBP hydrazine hydrate was able to decontaminate the solvent to below 10 mg/l. After a total of three washes hydrazine hydrate achieved a DF of 15 for solvent contaminated with Ru, Rh, Zr and Nb whereas Na_2CO_3 obtained a DF of 14 [15].

Neat alkanolamines have also been investigated as a wash reagent where the diluent in the process contains nitroparrafins formed by the degradation of the diluent. Alkanolamines have been shown to be effective at the removal of nitroparaffins due to their preferential extraction of nitro compounds by salt formation. Alkanolamines were also reported to be very effective in removing ruthenium from the solvent. However, there are several issues with its use, including; cost, solubility of ligand (TBP) in the reagent, formation of stable emulsions can occur and it is less effective when diluted or when alkanolamine solutions are recycled [1, 8].

[1] This 'gel' may have been a very slow settling mixture, as can be observed with Na_2CO_3 with very degraded solvent.

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Hydroxylamine, in an alkaline solution, was shown to have promise in bench scale tests where it demonstrates comparable DFs to a potassium permanganate/sodium carbonate wash [12]. Hydroxylamine gives a solvent DF comparable to Na_2CO_3 in an experiment where a simulated contaminated solvent containing 0.1mM Zr, 0.2 mM U and 0.4mM DBP was washed with hydroxylamine in tartaric acid. It was shown that after 3 washes, up to 96.8% of U, 92.7% of Zr and 94.5% of DBP was removed from the solvent [6].

0.25 M Butylamine oxalate has been shown to be effective at removing acidic degradation products such as HDBP at pH 2. It has also been shown to be effective at removing 95 % of the Zr remaining in the solvent after the PUREX process at, a slightly higher pH of 4 [16]. However, these relatively stringent controls on pH for efficacy make process implementation a challenge due to acid carrier over.

Tetramethyl ammonium (Me_4N^+) has been shown to be as effective as Na_2CO_3 at removing HDBP and Zr impurities from spent TBP-containing solvents. Three different compounds of tetramethyl ammonium have been demonstrated with success: hydroxide, oxalate and carbonate. The solutions were mixed at 1:1 (O/A) ratio in concentrations ranging from 0.01-1 M [17]. This work also demonstrated that the tetramethylammonium reagents could be completely decomposed at temperatures above 150°C without producing any solid residue. Therefore, this offers the potential for a reduction in the process waste volumes without the issues relating to the stability and storage of hydrazine or hydroxylamine reagents.

Ammonium carbonate at a concentration of 10% v/v has been demonstrated to produce results almost identical to Na_2CO_3, albeit with the evolution of large volumes of gas. It was shown to have a slightly longer coalescence time for separation of the aqueous and organic phases than washes using Na_2CO_3 [9]. Further work has found that the optimal concentration for its use is between 5 and 10% v/v. Under these conditions it was found to remove Pu and U from the spent solvent to <5 mg/L (ppm) and for HDBP to <10 ppm [18].

SOLID SORBENTS

A range of solid sorbents have been tested for their ability to remove fission products that are not readily stripped from the solvent (such as $Ru^{103, 106}$, Zr^{95}, Nb^{95}) and the degradation products that retain these elements [1]. The different types of solid sorbents that have been used include macroreticular resins, hydrous titanium oxide, lead dioxide, alumina and silica gel [6]. Solid sorbents must have specific criteria to be suitable for use in a solvent clean-up process, including:

- Robust to withstand transfer operations without generating significant amounts of dust,
- Compatibility with process reagents
- Do not form hazardous materials or physically degrade,

All solid sorbents act in a similar manner to the basic washes and typically remove the acidic degradation products.

The use of activated alumina has been explored extensively with a range of different results reported. work has shown that around 70 % of the degradation products butanol, dodecanol, dodecanone and nitro compounds are removed. Pre-treating the alumina with base was also found to increase the effectiveness of alumina in removing degradation products as this makes the surface alkaline so the acidic degradation products are more effectively abated [19, 20, 21]. Activated alumina has also been used to treat TBP dissolved in nitro paraffins where it was found to significantly improve recycled solvent performance due to the removal of binding ligands [22].

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ORNL have developed a silica gel pre-treated LiOH for solvent treatment. The pre-treatment creates an aqueous alkaline layer adsorbed on the surface of the silica gel [6], that was found to be more effective for abating longer chain organic acids like butylarylphosphoric acid than the conventional solvent wash process.

ORNL have also evaluated many base treated exchange resins such as Dowex 50W-X4 and Zr loaded molecular sieves. In all cases it was found that it was easy to preferentially remove uranium from solvents containing DBP but much more difficult to selectively remove DBP [23]. For these reasons these solid sorbents have not been discussed in any greater detail.

Macroreticular resins such as amberlyst A-26 have been shown to have potential for the clean-up of degraded solvent [24]. In batch tests the resin was found to remove Ru, Zr, Mo and HDBP with distribution ratios above 500 for all species. High capacity of A-26 resin for sorbing extractant impurities was indicated in very preliminary column runs. The physical and chemical properties of the solvent product obtained from these tests was found to be equal to or superior to those of Hanford PUREX Plant carbonate washed material. However, they faced process issues such as the resin becoming crumbly and friable upon contact with acid. Consequently, it was proposed that the resin should only be used following an alkali wash of the solvent, a so-called secondary solvent clean-up process.

SUMMARY

Although conventional process flowsheets typically employ an alkaline wash, using Na_2CO_3/NaOH, for removing degradation products prior to recycling the solvent, a range of alternative options have been investigated and developed. One of the main disadvantages of these alkaline reagents is the contribution of additional salts in the waste streams that require further treatment and encapsulation. Consequently, a range of salt free reagents have also been investigated and shown to be as effective for removing degradation products arising from radiolysis and hydrolysis of the solvent. The salt free reagents that have been demonstrated to provide effective clean-up of the solvent include hydrazine oxalate, hydrazine carbonate, ammonium carbonate and tetramethylammonium compounds (hydroxide, carbonate and oxalate).

A range of solid sorbents have also been demonstrated to provide effective removal of degradation products from the solvent. In particular, they have been shown to be particularly useful in the removal of retained fission products that have proved difficult to backwash with conventional aqueous reagents. The most promising solid sorbents tested to date include activated alumina and macroreticular resins such as Amberlyst A26. However, they will present additional challenges with handling and disposal of the spent material.

TRUEX

The Transuranic extraction (TRUEX) process was developed from the PUREX process and aims to extract all of the transuranic elements (including the minor actinides instead of just U and Pu) and the lanthanides, to achieve separation from the fission products. The solvent system used in the TRUEX flowsheet is a combination of TBP and CMPO (Figure 1) diluted in a hydrocarbon diluent such as n-dodecane [25].

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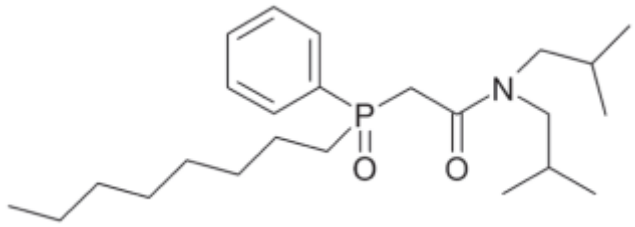


Figure 1 CMPO

DEGRADATION PRODUCTS

Many of the degradation products that occur in the solvent are similar to those found in PUREX as TBP is used in both processes. Consequently, the solvent will contain the TBP degradation products HDBP and H_2MBP. As discussed above for the PUREX process, these low molecular weight acidic products are cleaned by washing the solvent with Na_2CO_3 or NaOH. The addition of CMPO brings with it new degradation products such as: methyl octylphenyl phosphine oxide, octyl(phenyl)-N-monoisobutyl carbamoyl methyl phosphine oxide, dibutyl phosphoric acid, octyl(phenyl) phosphinic acid, octyl(phenyl) phosphinyl acetic acid [26], methyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphinic acid and phenyl(diisobutyl) carbamoyl nitromethyl phosphine oxide [27]. Fortunately, the Na_2CO_3 or NaOH wash also removes the majority of these phosphonic and phosphinic acids from CMPO degradation [28]. An additional issue that has been observed with the use of CMPO is with the impurities found in 'as bought' CMPO that result from the manufacturing process. Most of these impurities can be removed with a sodium carbonate wash. However, one of these impurities is not removed by this wash, octylphenylphosphinic acid (POPPA). POPPA is present at levels of <3% in manufactured CMPO so it contributes little to the degradation products [29].

WASH TECHNIQUES

SALT-BASED

Lab scale tests showed that an extraction solvent composed of 0.5 M or 0.75 M CMPO and 1.0 M TBP in Isopar-L can be effectively washed in Na_2CO_3 followed by an 2.0 M HNO_3 rinse at an O/A ratio of 3:1 [30]. In the US, TRUEX-style flowsheets have been operated with solvent wash techniques operating successfully, these include the Rocky Flats plant, where a 3 stage solvent wash followed by an acid rinse has been employed. Stage 1 was a 0.5 M K_2CO_3 followed by 2 stages of 0.25 M Na_2CO_3 with a final rinse of 0.1 M HNO_3 [31].

Another variation of the TRUEX process involves the use of the extractant dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) or CMP-TRUEX. In this process washing with 0.35-1.0 M Na_2CO_3 or NaOH solutions removes a large proportion of the low molecular weight degradation products [32]. However, this does not remove the high molecular weight acidic degradation products; it was therefore necessary to use a macroporous anion exchange resin.

A Na_2CO_3 wash followed by an acid wash has been shown to be effective in the removal of retained fission products from a TRUEX solvent that has been used to clean simulated tank waste. The 0.25 M carbonate wash (O/A ratio of 5) followed by a 0.1 M HNO_3 rinse effectively removed Hg, Cl, Re (Tc surrogate), Eu and Ru from the matrix. The subsequent acid wash, whilst used to re-acidify the solvent also effectively removed more Fe, Hg and

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Re. The solvent was recycled 17 times with no detectable change in solvent performance and only minor issues of HgO precipitation [33].

SALT-FREE

A salt free attempt at the Truex process, using 0.2M CMPO and 0.1M TBP in n-dodecane, using a two-step solvent clean-up method has been examined in Japan. The first step is a 0.2 M hydrazine oxalate wash that removes Pu, Zr and Mo. The second clean up step uses 0.2 M hydrazine carbonate which removes Ru, Pu and U (if any remains). This solvent can then be neutralised using a dilute acid wash and recycled back into the process [34].

In Japan, a flow sheet was developed for use on spent fuel from an FBR without adjusting acidity. The process used 0.2M CMPO and 1.2M TBP and the solvent wash step used a salt free set up. This involved hydrazine carbonate and hydrazine oxalate and tetramethyl ammonium hydroxide [34].

SOLID SORBENTS

TRUEX-NPH uses 0.2 M CMPO and 1.4 M TBP in an NPH diluent. The clean-up of this solvent system was evaluated by comparing the impact of using a carbonate wash and solid sorbents upon parameters such as phase separation time and Am distribution values [35]. It was found that the alumina and Amberlyst A-26 were similar in performance and they were both more effective than sodium silica gel as all phosphinic acids are removed by macro porous strong base anion exchange resins like Amberlyst A-26 or alumina. It was therefore decided that alumina was preferential as it is an inorganic sorbent so more resistant to degradation and radiolysis. The phosphate degradation products from TBP have a D_{Am} 1000 times greater than the corresponding phosphinic acids, so the degradation products of TBP are of much more concern for the process performance than those arising from degradation of CMPO.

Other studies have also shown that CMPO degradation products, such as phosphonic and phosphinic acids, can be removed by macroreticular anion exchange resins followed by a wash with a dilute sodium carbonate wash. [36] [37]

Other studies have also evaluated the use of a range of solid sorbents as the primary and secondary methods of clean up of degradation products present in the TRUEX solvent. The use of acid washed alumina, neutral alumina and Amberlyst A-26 were tested and activated neutral alumina showed the best outcome [38].

Further work looked into the use of goethite, alumina and activated charcoal as secondary TRUEX solvent cleanup techniques. Again, it was found that alumina (in this instance, acid washed) was particularly successful. In addition, activated charcoal was found to demonstrate some promise but goethite was ineffective. [26].

SUMMARY

CMPO is much less susceptible to radiolytic degradation than TBP due to the presence of the aromatic ring within the structure. Furthermore, the degradation products from CMPO exhibit D_{Am} <1000 smaller than those for TBP. Consequently, the degradation products from TBP present the more significant challenge to maintaining the performance of the flowsheet. In general, the clean-up and recycle of solvent in the TRUEX based solvents had been based upon the conventional alkaline washes with NaOH/ Na_2CO_3 previously employed in the PUREX process. Salt free reagents have also been evaluated for the washing and clean-up of TRUEX solvent. Hydrazine oxalate, hydrazine carbonate and tetramethylammonium hydroxide have been demonstrated to provide a viable

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alternative to the conventional alkaline solvent wash regime. Limited testing of solid sorbents has also demonstrated that alumina and macroreticular resins (Amberlyst A26) may provide an alternative option for clean-up of the TRUEX solvent.

TALSPEAK

The TALSPEAK (Trivalent Actinide Lanthanide Separations using Phosphorus Extractants and Aqueous Komplexes) process generally follows the UREX or TRUEX process and involves two extraction steps and one stripping step. The process utilises di-2-ethylhexyl-phosphoric acid (HDEHP or DEHPA) and diethylenetriamine-penta-acetic acid (DTPA) [25]. An improvement on this process is the advanced TALSPEAK which involves the use of 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) in place of HDEHP. This improved extractant has half the number of ether linkages which are the most susceptible to radiolytic rupture (either directly or diluent mediated). The TALSPEAK solvent is comprised of 0.3 - 0.5 M HDEHP in dodecane and an aqueous phase of 0.05 – 0.1 M DTPA in 1.5 M lactic acid (depending on which extraction or stripping step is being described). The advanced TALSPEAK process uses that same aqueous phase and the solvent phase consists of 1.0 M HEH[EHP] in nDD.

Another form of TALSPEAK is the Mixed Monofunctional Extractants (TALSPEAK-MME) process which utilises Cyanex-923 (a phosphine-oxide based extractant) in addition to HEH[EHP] [39].

DEGRADATION PRODUCTS

Irradiation studies have shown that up to a total absorbed γ dose of 200 kGy the concentration of HEH[EHP] and HDEHP remained relatively unchanged. Only very small amounts of H_2MEHP were observed in both TALSPEAK and less so in advanced TALSPEAK. Advanced TALSPEAK had a second degradation product which has not been definitively identified but is theorised to be monoethylhexylphosphonic acid. Although the concentration for HEH[EHP] remained relatively constant it was found that D_{Am} increased as the dose increased, presumably as a result of the small amounts of degradation product having a large effect on the extraction properties of the solvent. This could be attributed to the production of H_2MEHP or the proposed phosphonic acid [40]. Likewise in the original TALSPEAK process it has been observed that there is an initial increase in D_{Am} resulting from HDEHP radiolysis with a maximum D_{Am} presenting at a molar ratio of 2:1 HDEHP to H_2MEHP [41]. One of the major radiolytic degradation products of HDEHP is the diacid mono-substituted 2-ethylhexyl-phosphoric acid (MEHPA). The 2-ethylhexyl-phosphate ion is very basic and so this has a large effect on extraction as this species is a very strong complexant for metals.

WASH TECHNIQUES

Tests have shown that sodium carbonate washing of HDEHP containing solvents produced a very difficult to handle gel and contact with a loaded solvent results in complete gelation. The use of ammonium carbonate however proved effective and did not lead to the formation of any precipitates. A single step wash using 0.5 M ammonium carbonate at an S/A of 1:1 was shown to reduce the concentration of the degradation product MEHPA in the TALSPEAK solvent from 5% (w/v) to less than 0.3% (w/v) . [42] It has also been shown that concentrations of ammonium carbonate as high as 1 M can be used to remove impurities from the TALSPEAK solvent [43].

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An effective wash technique for Cyanex-923-containing solvents has been the use of 1 M NaOH followed by a 3 M HCl wash to remove unidentified acidic impurities present from the supplier. The removal of degradation products and contaminants after washing the solvent was confirmed by ^{31}P NMR [39].

SOLID SORBENTS

As with other P-containing solvents it has been shown that TALSPEAK solvents containing HEH[EHP] can be cleaned using a base treated alumina column. Further it was also shown that this column can also be regenerated by washing in methanol and UHQ water [44].

TRPO

The TRPO process involves the use of trialkyl phosphine oxides to co-extract An(III) and Ln(III) from a PUREX raffinate. One such solvent contains 30% Cyanex-923 dissolved in OK [25].

WASH TECHNIQUES

As Cyanex-923 is used in this process it means that the same wash technique used in the TALSPEAK MME process can be used, 1M NaOH followed by a 3M HCl wash. The removal of the degradation products from the solvent was confirmed by ^{31}P NMR [39]. It has also been shown that a simple wash of 5 % Na_2CO_3 followed by 1M HNO_3 is an effective wash technique for removing the radiolysis products from TRPO solvent [45].

SETFICS

The SETFICS process could be considered a modified TRUEX process as it relies on a similar CMPO based solvent system and aims to recover An and Ln from a PUREX raffinate. [25].

WASH TECHNIQUES

The SETFICS solvent was found to be effectively washed by 1 M NaOH. 98 % of the organic entrained uranium and plutonium was effectively removed from the spent solvent [46]. The authors also state that some precipitation was observed and assign it as being $Na_2U_2O_7$ and $Pu(OH)_4$ which was isolated by filtration

CHON BASED EXTRACTANTS

The next sections discuss the CHON based solvent extraction processes developed for minor actinide separation processes and which form the basis of reference processes in the scope of the GENIORS project.

DIAMEX FLOWSHEETS

The Diamide Extraction (DIAMEX) process was developed to coextract trivalent actinides and lanthanides from a PUREX raffinate. [25] The solvent was originally based upon the use of dimethyldibutyl-tetradecyl malonamide (DMDBTDMA) in a hydrocarbon diluent but this was subsequently replaced with N,N'-DiMethyl-N,N'-DiOctyl-HexylEthoxy-MalonAmide (DMDOHEMA). The DIAMEX flowsheet also uses small aqueous soluble organic ligands

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to prevent/suppress the extraction of unwanted fission products (Mo, Zr and Pd) that can accumulate in the solvent phase and affect product quality. [47]

DEGRADATION PRODUCTS

A comprehensive study of the degradation of DMDOHEMA has been undertaken and a number of degradation products have been identified, including [48]:

- Carboxylic acids
- Light amides
- Methyl octyl amine (MOA)
- Monoamide: N-methyl N-octyl hexyl oxybutanamide (MOHOBA)
- Acid amide: 2-(methyl(octyl)carbamoyl) 4-hexyl oxy butanoic acid (MOCHOBA)
- Secondary diamides (resulting from the loss of methyl or octyl chain on the nitrogen of one amide function). Dimethyl octyl-2-hexyloxyethyl malonamide (DMOHEMA), methyl diotyl-2-hexyloxyethyl malonamide (MDOHEMA)

Radiolysis and hydrolysis lead to the production of the acid amide, or the secondary diamides. For secondary diamides it was found that if the alkyl group on the amine was short enough (e.g. butyl as formed from DMDBHEMA) it would partition to the aqueous phase [49], thus reducing the concentration in the organic phase and potentially affecting the distribution values where the diamide played an active part in metal coordination. However, if the R group is long enough (e.g. octyl as formed from DMDOHEMA) then it could remain in the organic acting as a degradation product and having the opposite effect to those that partition to the aqueous phase. Acidic and basic solvent washes have shown promise for removal of these degradation products.

It is perhaps simpler to consider a degradation scheme due to radiolysis and hydrolysis of the diamide, as described by Camès et al (Figure 2). In this scheme the main products are identified and/or the general likeness of their functional groups (as is the case with C_3-C_6 carboxylic acids). [50]

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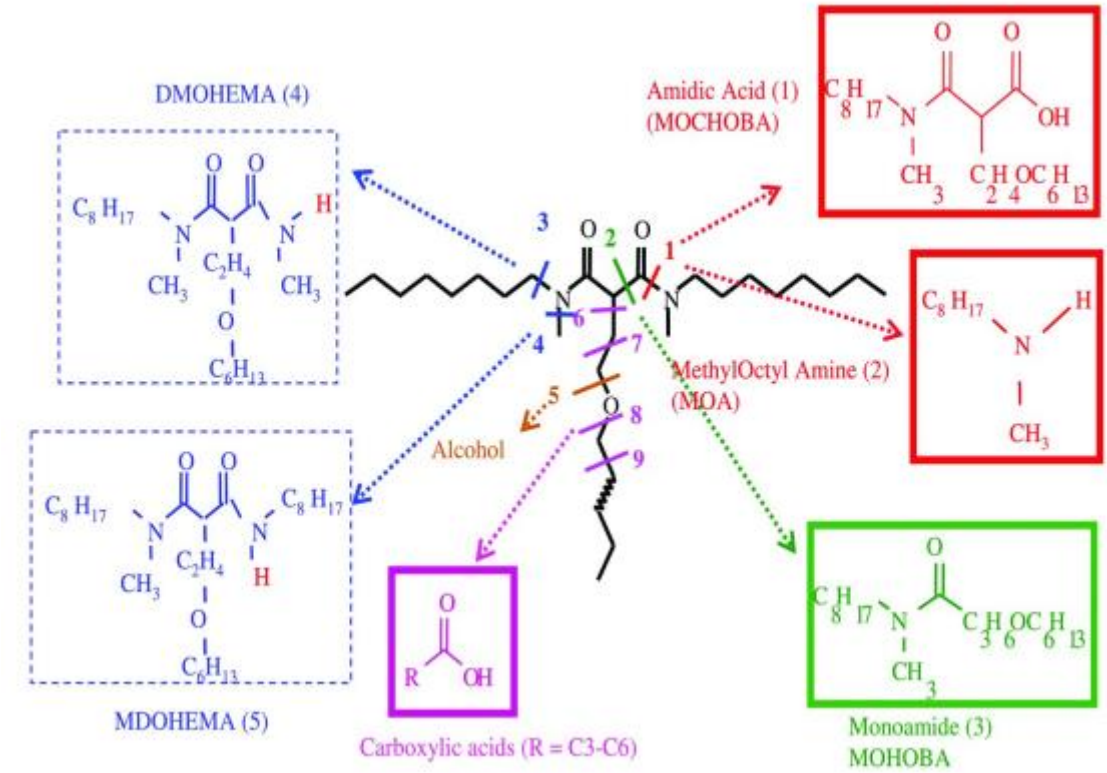


Figure 2: Simplified degradation scheme for DMDOHEMA as described by Camès et al. [50]

WASH TECHNIQUES

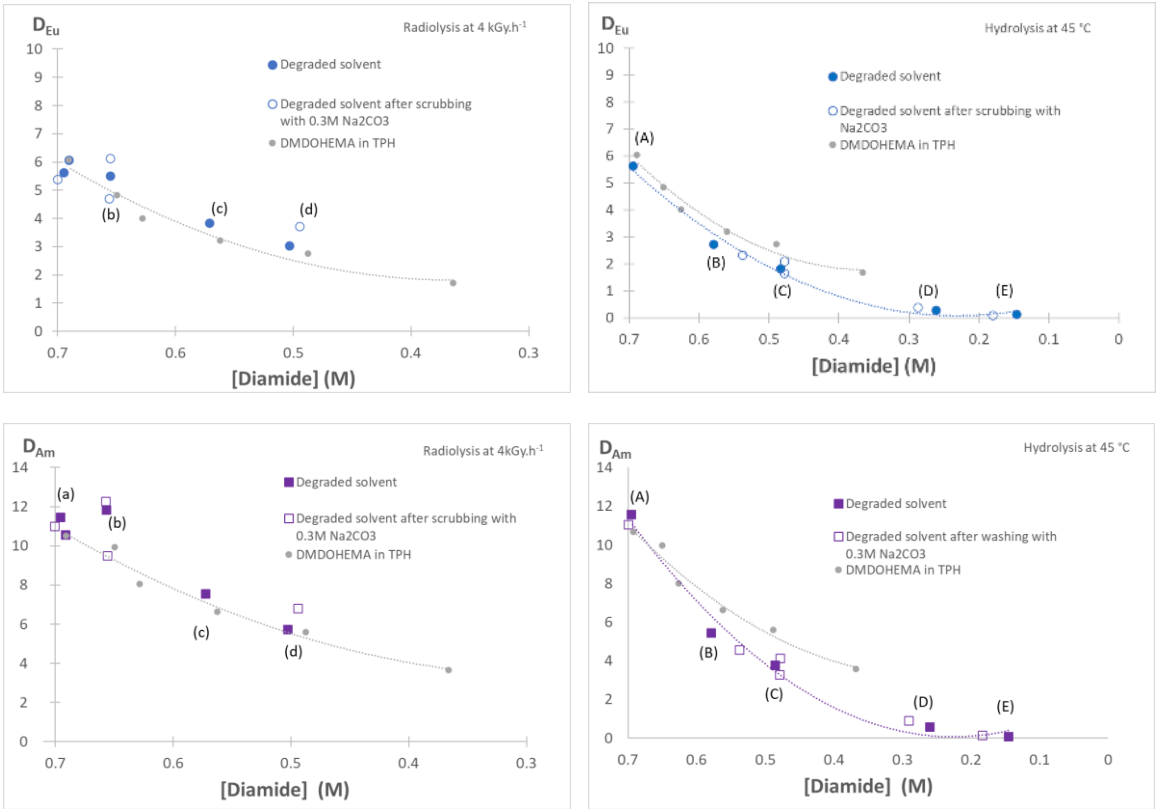
Initial solvent clean-up studies for the DIAMEX process assessed the effectiveness of acidic and basic washes to remove degradation products and the retained fission products from the solvent. This work demonstrated that an acidic scrub of 0.1 M HNO_3 (which simulates the scrubbing step in the DIAMEX process) was capable of quantitatively removing methyl octyl amide (MOA) from the solvent (in this instance this had been added rather than produced radiolytically). [48] In addition, with solvent that had been subjected to radiolytic degradation it was reported that between 60-100% of the basic degradation products were removed by a low acid scrub and all carboxylic acids with <6 carbon atoms [50]. This range of results was attributed to the possible presence of other unidentified basic degradation products that were not so readily removed from the solvent by a simple acid wash. It was concluded that the low acid scrub in the flowsheet would prevent the accumulation of MOA during operation of the flowsheet with a continuous solvent recycle. Different basic reagents have also been evaluated for their ability to remove the acidic degradation products, including the carboxylic acids and acidic amides. [48] The compounds studied were NaOH, Na_2CO_3, Me_4NOH and ammonium carbonate at a concentration between 0.1 M and 1 M. This work concluded that the type of base or concentration had little effect upon the scrubbing efficiency. It was found that the first base wash was ~80 % effective while a second base wash was found to be much less efficient, only removing ~20 % of the remaining acidic degradation products (following the first wash). In addition, it was necessary to centrifuge the samples to obtain good phase separation with the basic washes. The authors hypothesise that this was due to the difficulty in removing small amounts of carboxylic acids with a very basic scrub, so a small fraction remains in the solvent. It was also observed that the hydrodynamics were partially restored and settling time was decreased but not restored to the values for pristine

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solvent. Following two sequential Na_2CO_3 washes the extraction properties are improved compared to the unwashed solvent and align with those for a pristine solvent with similar (decreased) extractant concentration. It was also discovered that for hydrolysed samples the decrease in distribution ratios is not directly a result of the decreased extractant concentration. It is theorised that this is because of the increase in monoamide concentration which is not removed by acidic or basic washes. However, the authors note that this issue can be mitigated by constant removal of the acidic amide degradation products that leads to the formation of the monoamides.[48] Pd is best removed by ammonium carbonate (at ~70 % efficiency) compared to NaOH, Na_2CO_3 and TMAOH (30 % efficiency) but this is reversed in the case of Ru where ammonium carbonate is the least efficient (25 %) and the others are comparatively good (70 %). Therefore, to successfully abate both Pd and Ru it would be necessary to undertake both an ammonium carbonate wash and another alkali (sodium hydroxide or carbonate). [48] The authors also note that removing the Ru and Pd that remains is not as simple as undertaking another wash as the efficiency decreases each time; they postulate that this may be due to different speciation.

The DIAMEX process flowsheet was tested by CEA in Marcoule in 2005 with 0.65 M DMDOHEMA in TPH diluent [51]. This test included a 0.3 M NaOH wash with HEDTA (concentration not defined) wash section for the spent solvent using four centrifugal contactors with no issues reported [47] [52].

A second test was conducted on the solvent degraded by radiolysis and hydrolysis separately. The solvent was then washed with Na_2CO_3 and the distribution of Am and Eu was measured. It was found that solvent distribution ratios of Eu and Am returned to near pre-degraded levels after washing with 0.3 M Na_2CO_3 [53] (Figure 3).



Radiolysis (a): 0 MGy, (b):0.1 MGy, (c): 0.4 MGy, (d): 0.7 MGy or hydrolysis: (A) 0 week, (B): 1 week, (C): 2 weeks, (D): 4 weeks, (E) 8 weeks. Value obtained at 25 C with trace level concentration of metal in 3M nitric acid.

Figure 3: Distribution ratios of Eu and Am as a function of DMDOHEMA concentration in degraded organic phases, with and without washing. [53]

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Further studies have used a γ irradiation test loop to simulate ~1 year of plant operations for a DIAMEX-SANEX solvent of 0.5 M DMDOHEMA and 0.3 M HDEHP. At a total solvent dose of ~800 kGy and hydrolysis time of ~80 hours, this showed that following basic washes using sodium hydroxide (concentration not provided) the solvent behaved similar to the previous batch tests; the acidic degradation products (accounting for ~89 mol.% of the lost extractant) were eliminated by the caustic wash and only the diamide degradation products (~10 mol.%) remained in the solvent (Note: the extractant concentration was maintained during the test so these numbers are relative to the amount lost). In the case of this being MDOHEMA this is not an issue as it has very similar extraction properties to the parent DMDOHEMA. Further, no effect was observed on the distribution ratios of Mo, Zr, Fe, Pd and Nd or the settling times [54].

The CEA in France has used the MARCEL flow loop to induce radiolysis and hydrolysis of the solvent (DMDOHEMA in TPH; hydrogenated tetrapropylene) under continuous operations to examine the effect on the extraction and hydrodynamic properties of the solvent [50]. Coupling the continuous test to batch tests showed that the monoamide is a secondary degradation product formed from the degradation of amidic acid so when this is removed by continuous alkaline treatment the only degradation products left was MDOHEMA (see Figure 2). Through the batch tests they have also shown that the 0.1 M HNO_3 wash (removes MOA and light acids), a 0.3 M NaOH wash (removed amidic acids and more light acids). Through the continuous testing they showed that the distribution coefficients of Zr, Pd, Fe and Nd, surface tension, refraction index, settling time, viscosity, and density were all essentially unaffected during the tests. The only issue observed was an accumulation of Mo in the solvent and this is ascribed to the build-up of MDOHEMA and this further resulted in an increase in density and viscosity [50]. It is also worth noting that the authors mention heating the alkaline washing stages of the setup but provide no further detail of the temperature or reasoning for this.

SUMMARY

Testing of the DIAMEX flowsheet has demonstrated that the degradation products arising from hydrolysis and radiolysis of DMDOHEMA can be effectively managed with a combination of low acid and alkaline washes. These tests also demonstrated the use of salt free reagents, ammonium carbonate and ammonium hydroxide, for removing degradation products from the solvent.

Although the solvent wash was effective at maintaining the flowsheet performance it was not possible to remove some degradation products, particularly the monoamide and the diamides (DMOHEMA and MDOHEMA). Despite the difficulty removing these species it was found that their accumulation could either be mitigated or that they did not have a significant impact upon flowsheet performance. In the case of the monoamide, the accumulation of this species in the solvent was mitigated by the continuous removal of the acid amide, which acts as the precursor for formation of the monoamide. The diamide, MDOHEMA, has similar extraction properties to the parent DMDOHEMA and was not considered to have a significant impact upon the flowsheet, although it was implicated in the retention of Mo.

I-SANEX

The innovative SANEX (i-SANEX) process has been developed under European framework programmes to achieve the separation of minor actinides from fission products and lanthanides in a PUREX raffinate using a single solvent extraction cycle. This flowsheet is based upon a solvent composition of 0.2M TODGA + 5% octanol (v/v) in a hydrocarbon diluent (such as TPH). [25].

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DEGRADATION PRODUCTS

Radiolytic degradation studies of TODGA-based systems have produced very different results with the relative tolerance of the system to radiolysis and the effect of nitric acid. However, most studies have concluded that the major degradation products are those observed in Figure 4. [55] Other interesting facets of the radiolytic degradation have been the increase in extent of radiolysis which results from lower initial concentration of TODGA indicating that the degradation process is mediated by the diluent radical cation. [56] Further, it has been observed that the use of benzene as a diluent leads to much less radiolysis than n-dodecane and that the addition of the amide DHOA also supressed the degradation of TODGA. [57] [58]

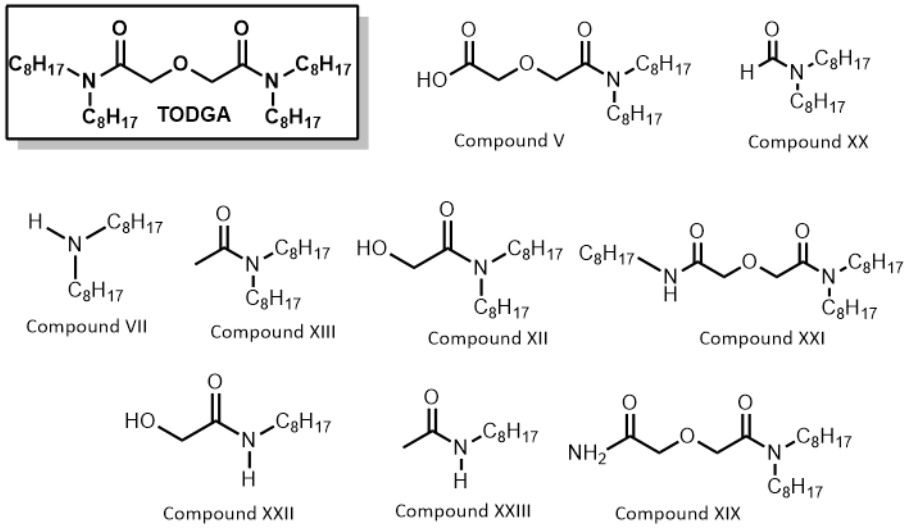


Figure 4: TODGA and selected degradation products resulting from radiolytic irradiation of *n*-dodecane solutions. Also provided below the images are the distribution values for those active in extractions.

SOLVENT WASH OPTIONS

Currently, there is no available information in the literature regarding the development of methods for the washing of TODGA based solvents for the removal of degradation products.

ALSEP

The Actinide Lanthanide Separation (ALSEP) process is being developed in the USA for the recovery of minor actinides from dissolved spent nuclear fuel following the removal of U, Pu and Np. The solvent in this flowsheet uses two extractants, a diglycolamide, N,N,N',N'-tetra(2-ethylhexyldiglycolamide (T2EHDGA), and a phosphinic acid based extractant, 2-ethylhexylphosphinic acid mono-2-ethylhexyl ester (HEH[EHP]), dissolved in dodecane.

DEGRADATION PRODUCTS

The degradation of both extractants has been studied previously. For HEH[EHP] the main product of radiolytic degradation is 2-ethylhexyl phosphonic acid (HEHP) which results from the cleavage of the C-O bond of the ester functional group in the parent molecule. Gamma radiolysis studies of T2EHDGA have identified a number of degradation products due to the cleavage of bonds at different points in the structure. The main radiolytic

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degradation products arise from cleavage of the ether linkage or the C-N bond. Rupture of the ether linkage leads to the formation of acetamide and glycolamides, while the rupture of the C-N bond produces trialkydiglycolamides or dialkylamidocarboxylic acids.

Tests with irradiated solvent confirmed the effect of the impact of solvent degradation upon process performance [59]. The increase in concentration of HEHP due to radiolysis of the solvent resulted in an increase in the Am D value during stripping, which led to a corresponding decrease in the separation factor for europium and americium. In addition, it was found that decreasing T2EHDGA concentration with increasing dose led to a reduction in the distribution values obtained for americium, europium and cerium in the extract section of the flowsheet.

SOLVENT WASH

Since the primary degradation products were found to be acidic compounds, such as HEHP and dialkyamidocarboxylic acids, an alkaline wash scheme was considered to be the most suitable candidate for development of a solvent clean-up process. The effectiveness of three alkaline reagents were assessed; 0.25 Na_2CO_3, 0.25M NH_4CO_3 and 0.25M NaOH [59].

Initially, the wash procedure was tested using an ALSEP solvent that had been doped with 0.015M octylphosphoric acid (to simulate HEHP) and an ALSEP solvent that had been irradiated to obtain a total absorbed dose of 780 kGy. A series of batch tests were performed to determine the impact of the degraded solvent upon distribution values for Am/Eu and Ce under the extract, scrub and strip conditions of the flowsheet. After performing the alkaline wash of the solvent these batch tests were repeated to evaluate the effectiveness of each of the reagents. The tests showed that washing with Na_2CO_3 and NH_4CO_3 were both capable of removing acidic degradation products to levels that restored the D_{Am} to the value observed with clean ALSEP solvent.

CONCLUSIONS

The clean-up and recycle of solvents has been considered for a variety of flowsheets developed for the reprocessing of spent nuclear fuel. Typically, washing with aqueous reagents is employed to remove degradation products and retained metals (fission products) from the solvent in order to permit the recycle of the solvent without it having a detrimental impact upon process performance. A wide range of reagents have been tested and the most widely used solvent wash process is typically based upon the use of alkaline reagents, Na_2CO_3 and NaOH, to remove acidic degradation products from the solvent. This is particularly suited to the organophosphorus extractants (e. g. TBP and CMPO) where the majority of the degradation products that arise due to radiolysis and hydrolysis of the solvent are acidic in nature.

Other reagents have also been shown to be as effective as the conventional alkaline reagents for the removal of degradation products. In particular, the use of salt free reagents such as ammonium carbonate, hydrazine carbonate, hydrazine oxalate, hydroxylamine (in basic solution) and tetramethyl ammonium hydroxide, offer the potential advantage of reducing the waste volumes generated in the process. However, there are some drawbacks to the use of the hydrazine reagents due to their stability and the potential formation and management of hydrazoic acid in the process.

A range of solid sorbents have also been evaluated for the clean-up and recycle of solvent in reprocessing flowsheets, both in terms of removing degradation products and also stripping retained fission products from the solvent. In particular, activated alumina and macroreticular resins (Amberlyst-26) have been shown to be

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effective for removal of retained fission products, such as Zr, Ru and Mo, as well as the acidic degradation products from the solvent.

While the development of solvent wash processes is relatively well defined for the organophosphorus reagents it is less mature for the new CHON based reagents, such as DMDHOEMA and TODGA, that are used in the EURO-GANEX and i-SANEX process flowsheets. Some studies have been carried out to develop a solvent wash procedure for the DIAMEX process to manage the degradation products arising from the radiolysis and hydrolysis of DMDOHEMA. This work has demonstrated that a combination of acid and alkaline washes can be used to remove the major degradation products from the solvent. In this case the low acid scrub in the flowsheet was shown to quantitatively remove mono-octylamine and carboxylic acids ($<C_6$). Washing with alkaline reagents removed the acidic amides and carboxylic acids. The continuous removal of the acidic amide wash shown to be effective at mitigating the accumulation of the monoamide degradation product, which arises from the degradation of the acid amide. Consequently, the only species not removed by acidic or alkaline washes was MDOHEMA and this was not considered to have a detrimental impact upon the DIAMEX process due to the similar extraction properties to the parent DMDOHEMA.

The solvent washing and removal of degradation products from TODGA based solvents is less well developed. Although a solvent wash test for the ALSEP process demonstrated that an alkaline wash was effective at restoring the performance of a solvent irradiated to 780 kGy, the primary degradation products in the process are likely to arise from the phosphorus based extractant HEH[EHP]. Therefore, further work is required to evaluate whether the conventional alkaline reagents are suitable for clean-up of TODGA based solvents.

Although, alkaline reagents are the most widely employed method for the clean-up of phosphorus based solvent systems and have been shown to be effective for malonamide (DMDOHEMA) solvents, further work should also consider the potential advantages offered by the salt free reagents.

In addition, the use of solid phase sorbents has been investigated and shown to provide an alternative option to aqueous reagents. In particular, solid sorbents, such as activated alumina and macroreticular resins, have proved effective at removing retained fission products that were difficult to remove with conventional aqueous washes.

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INFLUENCE OF THE MAIN TODGA DEGRADATION PRODUCTS AND STRATEGIES OF WASHING

CIEMAT: H. Galán, A. Núñez, I. Sánchez, L. Serrano, J. Cobos.

TWENTE: W. Verboom, R.J.M Egberink

From the point of view of security, one of the constraining points for the development of extraction processes is their resistance to the highly radioactive field and acid concentration where they must be used. Because of these conditions, the ligands employed suffer hydrolytic and radiolytic degradations that can lead to changes in the composition of the extraction system producing degradation compounds (DCs), changes in the physicochemical and chemical properties and therefore secondary waste increase, being all of them operational issues to be considered.

N,*N*,*N'*,*N'*-tetraoctyldiglycolamide (TODGA) is one of the best known and widely studied diglycolamides for the new actinide separation processes. It is well known that TODGA is resistant enough until moderate-high absorbed doses, although many studies identified the presence of at least 9 DCs [1-7]. Moreover, the proportion of these DCs depends on the experimental conditions applied during the studies. The structures of TODGA and its degradation compounds are shown in Figure 5. Some of these DCs have extracting properties that differ from those of the original performance of the system, which could give rise to substantial loss of efficiency of the process and technical problems. For that reason, the individual properties of these DCs have also been widely studied [6, 7]. Therefore, as TODGA based solvent will be recycled, it is very important to have in mind which of them will reduce the efficiency of the process, which could cause accumulation problems in the long term and which could be removed.

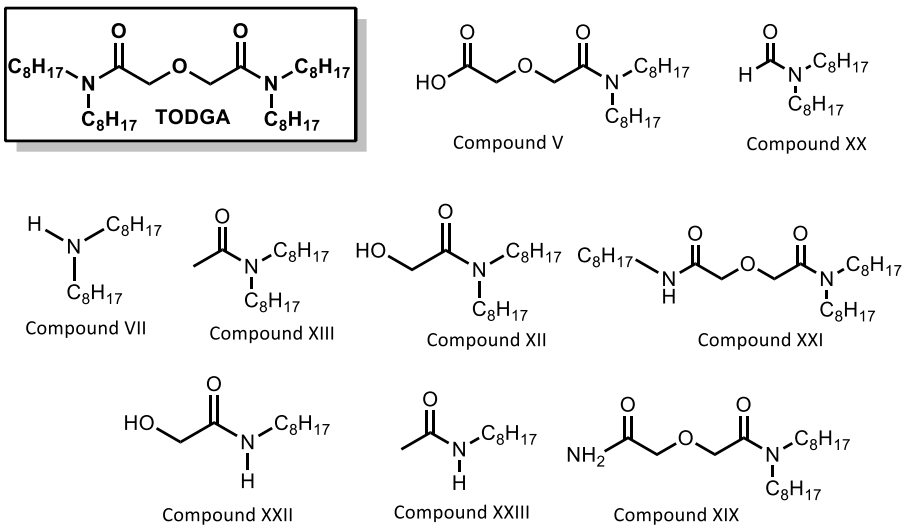


Figure 5 Structures of TODGA degradation compounds

DCs 2-hydroxyl-N,N-dioctylacetamide (DOHyA) (XII in Figure 5) and N,N-dioctylacetamide (DOAA) (XIII in Figure 5) are typically the most abundant DCs formed due to radiation and prone to accumulations because of their lipophobicity, it means, they will not be easily removed. When they were studied individually, DC XIII did not show remarkable extraction properties [7]. However, DC XII extracts efficiently FPs (Zr and Mo), and although it

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is weak extractant of Ln at high nitric acid concentration, its back-extraction takes place at a higher nitric acid concentration than TODGA does [7].

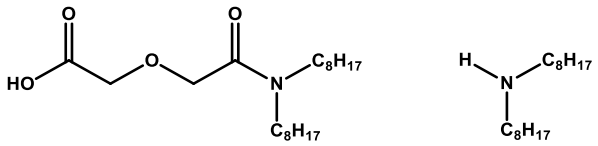
Moreover, two other abundant DCs due to TODGA degradation are N,N-dioctylamine (DOA -compound VII in Figure 5) and N,N-dioctyldiglycolamic acid (DODGAA: compound V in Figure 5), which have been found as partially responsible for insolubilities after irradiation of EURO-GANEX samples [8]. DODGAA does not extract too much Ln, but extracts moderately some FPs, and gives problems for the quantitative stripping of Ln due to metal coordination in the carboxylate group. This last behaviour has also been described by other authors [9]. And DC DOA gave rise to third phase formation when it was tested individually [7].

Based on all mentioned studies, a deeper study of the long-term behaviour of TODGA based solvents have been carried out to clarify the effects of these four DCs, their possible accumulations and the viability of common washing strategies to remove them. All DCs employed in this study were synthesized and supplied by W. Verboom group (TWENTE).

EFECTS OF MAIN DEGRADATION COMPOUNDS ON TODGA BASED SOLVENTS

INFLUENCE OF DODGAA AND DOA ON THE EXTRACTION OF LN/FP – SOLUBILITY PROBLEMS

DODGAA (compound V in Figure 6) and DOA (compound VII in Figure 6) have been found as partially responsible for some precipitation observed when EURO-GANEX irradiated samples were stored for a time [10]. Besides, DOA had shown third phase formation and solubility problems when it was tested individually at low concentrations (0.05 mol/L) by using OK + 5% octanol and OK as diluents [11]. For those reasons, both of them are considered as two of the most detrimental TODGA DCs. As the organic phases containing TODGA will be recycled and combined with fresh TODGA solvent, the possible problems due to their accumulation have been checked.



***N*,*N*-dioctyldiglycolamic acid**
DC V

***N*,*N*-Dioctylamine**
DC VII

Figure 6. Structure of diglycolamic acid (DODGAA = V) and *N*,*N*-dioctylamine (DOA = VII).

Particularly, the solubility problems and the limit of operability of TODGA solvents (0.2 mol/L TODGA+ 5% octanol in OK) containing increasing concentration of DODGAA and DOA (0.1, 0.2 and 0.4 mol/L each) has been tested for the extraction and the back-extraction of Lns and FPs from a simulated High Active Raffinate (HAR) solution[2], according to the schematic flow-sheet of the *i*-SANEX process (Figure 7, [12]). For that purpose, the different samples were contacted with 4 mol/L HNO_3 + 10% simulated HAR solution, followed by two scrubbing steps (3 mol/L HNO_3) and one stripping step (0.5 mol/L HNO_3). Neither masking agent had been used to study the real

[2] The synthetic HAR solution used corresponds to a PUREX raffinate with a volume of 5000L/t UOX fuel with an initial ^{235}U enrichment of 3.5%, thermal burn-up of 40 GWd/tHM and 3 years cooling [2].

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contribution of each DCs. TODGA has also been tested individually under the same experimental conditions to have a better comparison.

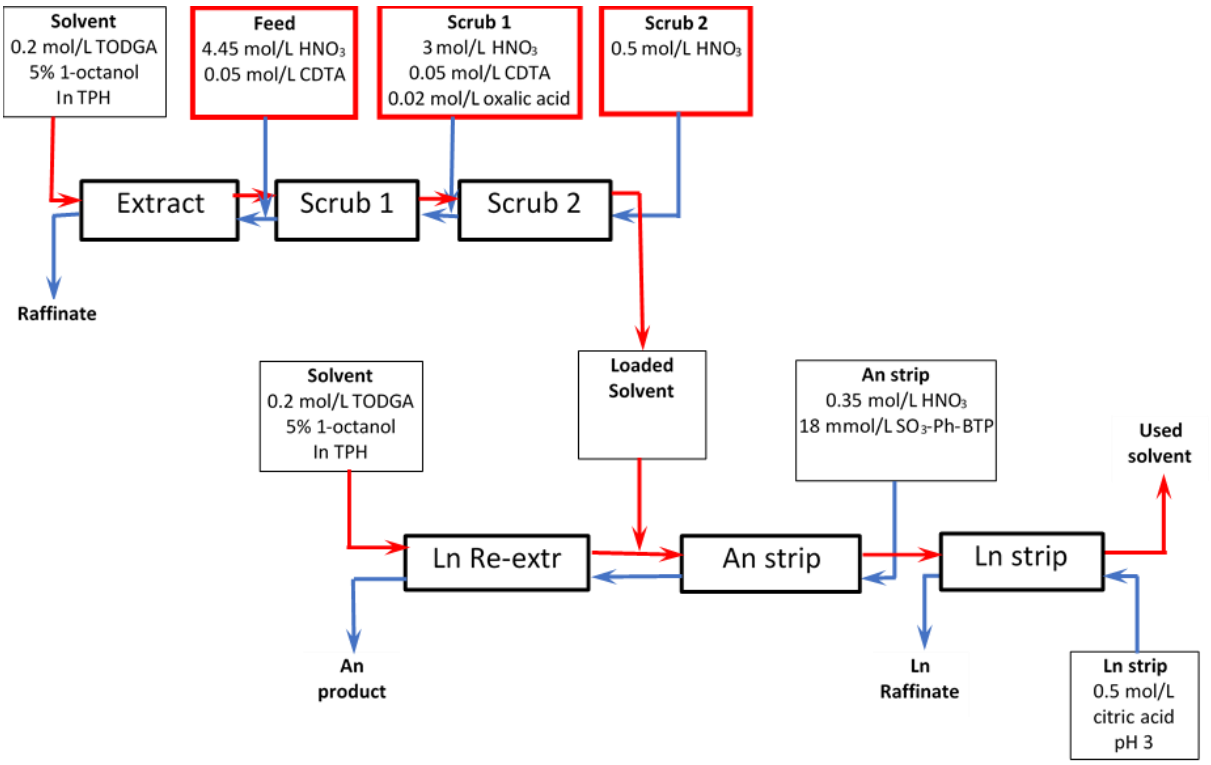


Figure 7. Flow sheet of the innovative SANEX demonstration process [12].

Table 1 shows the composition of samples tested and the behaviour observed after contacting with the corresponding aqueous phase. As expected, increasing concentration of the amine (DOA) and the acid (DODGAA), increased the probability of third phase formation. Crystals, gel or third phase formation were observed for all samples where the amine and/or acid concentration was 0.4 mol/L. Therefore, D values obtained at those concentrations of DOA and DODGAA have been rejected for the extraction results analysis.

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Table 1. Samples compositions and their behaviour during each step (ESS) of experiments carried out with TODGA and TODGA/DOA/DODGAA mixtures at 4 mol/L HNO_3 (Amine = DOA and Acid DODGAA).

0.2M TODGA +		0M Amine	0.1M Amine	0.2M Amine	0.4M Amine
0M Acid	Solubility / pre-equilibration	(N)			
	Extraction	(N, dark precipitate)			
	Scrubbing 1	(C)			
	Scrubbing 2	(C,TP)			
	Stripping	(N)			
0.1M Acid	Solubility /pre-equil.		(N)	(N)	(TP)
	Extraction		(N)	(N)	(C,TP)
	Scrubbing 1		(C)	(C)	(G)
	Scrubbing 2		(C,TP)	(C,TP)	(G)
	Stripping		(N)	(G,TP)	(G)
0.2M Acid	Solubility /pre-equil.		(N)	(N)	(N)
	Extraction		(N)	(N)	(N)
	Scrubbing 1		(N)	(N)	(G)
	Scrubbing 2		(N)	(N)	(G)
	Stripping		(N)	(G,TP)	(G)
0.4M Acid	Solubility /pre-equil.		(N)	(N)	(N)
	Extraction		(G)	(N)	(G)
	Scrubbing 1		(G)	(G)	(G)
	Scrubbing 2		(C,TP)	(TP)	(G)
	Stripping		(TP)	(G)	(G)

(N) Normal, (TP) third phase, (C) crystals, (G) gelled

Extraction (4 mol/L HNO_3) **Scrubbing 1**(3 mol/L HNO_3) **Scrubbing 2** (3 mol/L HNO_3) **Strip.** (0.5 mol/L HNO_3)

Figure 8 shows the distribution ratios of Ln and FP from a HAR solution at 4 mol/L by TODGA and TODGA/DOA/DODGAA mixtures. It is well known that TODGA, in absence of masking agents, is an efficient extractant of Zr, Mo and Pd [2]. Zr and Pd extraction seems to be the most affected by the presence of DODGAA and or DOA (blue, green or red lines in Figure 8, depending on the concentrations). It is appreciated a decrease in Zr extraction, meanwhile Pd extraction shows an important increase with all mixtures tested, and particularly for samples containing mainly DOA. On the other hand, Ln are slightly less extracted in presence of DCs, but their extraction is still high enough.

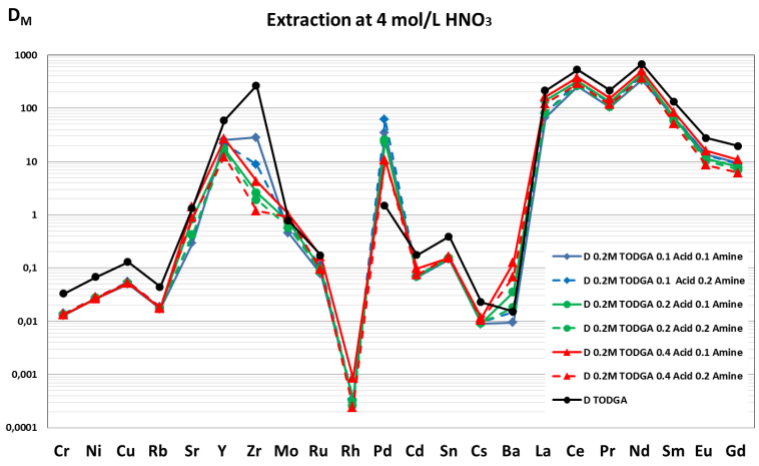
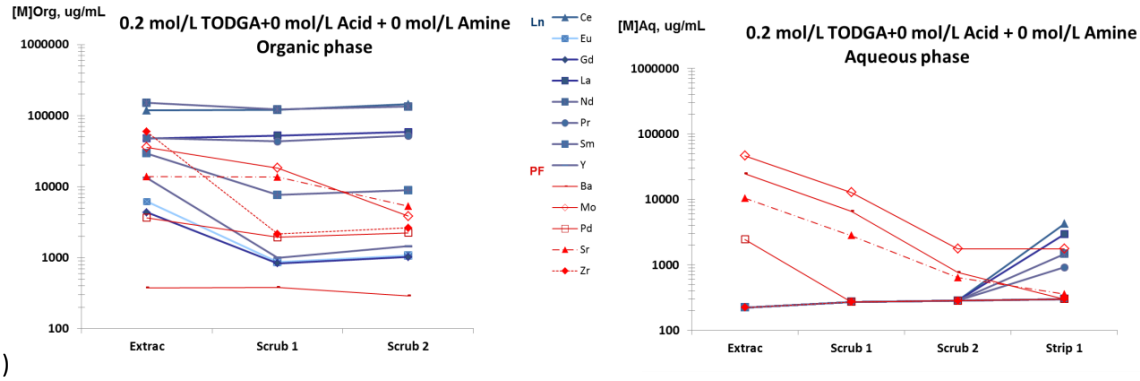


Figure 8 Ln and FP distribution ratios obtained with TODGA and TODGA+Amine+Acid at 4 mol/L HNO_3.

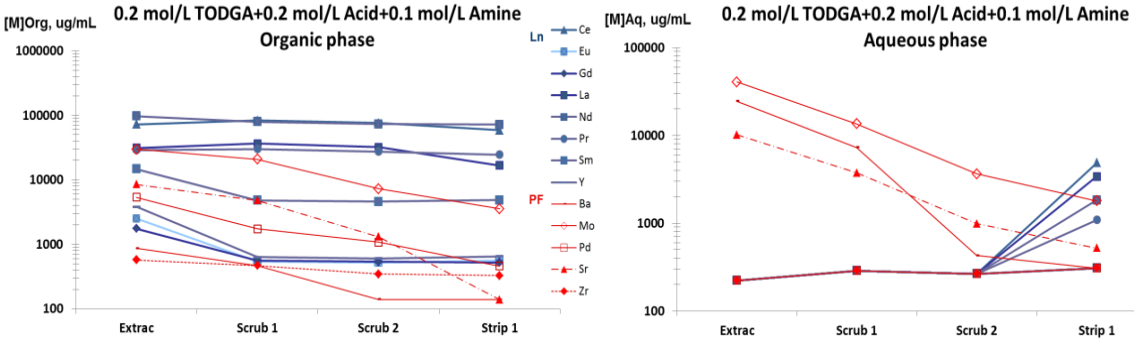
Figure 9 shows the concentration of the Ln and FP in the organic and aqueous phases along the experiment (extraction, scrubbing and stripping steps) for the mixture 0.2 mol/L TODGA + 0.2 mol/L DOA + 0.2 mol/L

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DODGAA. Similar behaviour was observed for the rest of mixtures tested. In general, it can be said that all Ln are slightly more extracted by TODGA alone than for any of mixtures that were checked. However, there are differences related to FP such as Ba, Sr, Pd and Zr depending on the presence or absence of DOGAA and/or DOA.



a)



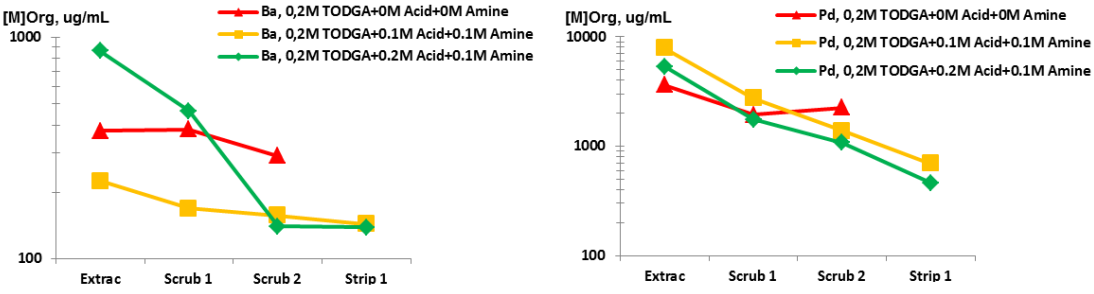
b)

Figure 9. Ln and FP concentrations (µg/mL) obtained with a) 0.2 mol/L TODGA and b) the mixture 0.2 mol/L TODGA + 0.2 mol/L Acid + 0.1 mol/L Amine: a) after the extraction at 4 mol/L HNO_3, b) two scrubbing steps (3 mol/L HNO_3) and c) stripping (0.5 mol/L HNO_3).

Figure 10 shows the profile of each of these FP along the back-extraction experiment for the different mixtures. FP back-extraction is favoured by the presence of both DCs (DOA and DODGAA), especially for those that were initially more extracted, such as Ba and Pd.

In these experiments An were not used, but it is known that DODGAA extracts An even at low nitric acid concentration [9]. Therefore, the presence of these two main DCs could also affect the An back-extraction.

a) b)



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c) d)

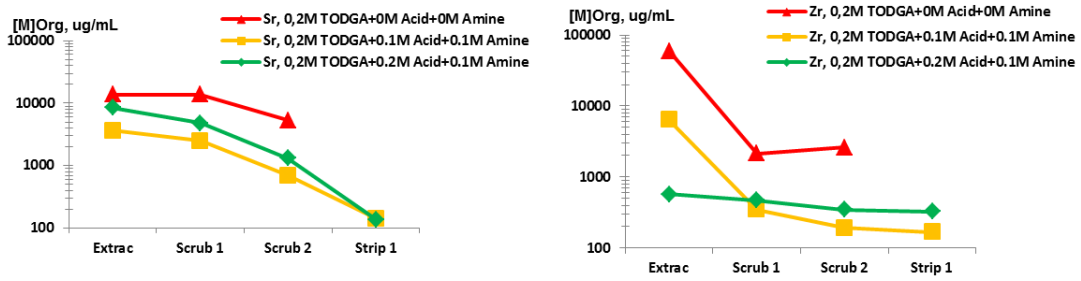


Figure 10. FP (a) Ba, b) Pd, c) Sr, d) Zr) concentration at each stage obtained with TODGA and TODGA+ Acid (0.1 mol/L or 0.2 mol/L) + amine (0.1 mol/L): after the extraction at 4 mol/L HNO_3, two scrubbing steps (3 mol/L HNO_3) and stripping (0.5 mol/L HNO_3).

INFLUENCE OF DODGAA AND DOA ON THE BACK-EXTRACTION OF AN AND LN. SOLUBILITY PROBLEMS

In order to explore the behaviour of the system along the An and Ln stripping steps just after FP scrubbing (the blue shaded boxes in Figure 7), the same sample conditions (0.2 mol/L TODGA + 5% octanol in OK plus DODGAA and DOA in increasing concentrations) were contacted with:

a) 0.5 mol/L HNO_3 + 10% simulated HAR solution[3] (1x Scrub. 2)

b) 0.35 mol/L HNO_3 (2x An Strip.).

c) 0.5 mol/L citric acid with NH_3 (1x Ln Strip.)

As in the previous experiment, neither masking nor stripping agents were added to study the real contribution of each DCs. TODGA has also been tested individually under the same experimental conditions for a better comparison. Again, solubility problems have also been observed. In agreement with the previous experiment, increasing concentration of the amine or acid (DOA/DODGAA), increased the probability of third phase formation. Moreover, crystals gels or third phase formation were observed for all samples where their concentration was 0.4 mol/L for any of them (Table 2). Therefore, D values obtained at those concentrations were rejected for the analysis of the extraction results.

[3] In case of any of the metals contained in a HAR solution (besides Lanthanides) have passed the scrubbing step it is necessary to know the behaviour of these two degradation compounds at these conditions of acidity.

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Table 2. Sample compositions and their behaviour during each step (ESS) of experiments carried out with TODGA and TODGA/DOA/DOGAA mixtures at 0.5 mol/L HNO_3 (Amine = DOA and Acid =DODGAA).

0.2M TODGA +		0.1M Amine	0.2M Amine	0.4M Amine
0.1M Acid	Pre-equil.	(N)	(N)	(TP)
	Scrub. 2	(N)	(N)	(C,TP)
	An Strip. 1	(C)	(C)	(G)
	An Strip. 1´	(C,TP)	(C,TP)	(G)
	Ln Strip.	(N)	(G,TP)	(G)
0.2M Acid	Pre-equil.	(N)	(N)	(N)
	Scrub. 2	(N)	(N)	(N)
	An Strip. 1	(N)	(N)	(G)
	An Strip. 1´	(N)	(N)	(G)
	Ln Strip.	(N)	(G,TP)	(G)
0.4M Acid	Pre-equil.	(N)	(N)	(N)
	Scrub. 2	(G)	(N)	(G)
	An Strip. 1	(G)	(G)	(G)
	An Strip. 1´	(C,TP)	(TP)	(G)
	Ln Strip.	(TP)	(G)	(G)

Scrub. 2 (0.5 mol/L HNO_3), **An Strip. 1** (0.35 mol/L HNO_3), **An Strip. 1´** (0.35 mol/L HNO_3) and **Ln Strip.** (0.5 mol/L citric acid)

(N) Normal, (TP) third phase, (C) crystals, (G) gelled

Figure 11 shows the distribution ratios of Ln and FP obtained by the original TODGA solvent (in black) and TODGA/DOA/DODGAA solvents from a HAR solution at 0.5 mol/L HNO_3. Effects on FP extraction observed at 0.5 mol/L HNO_3 are similar to those observed at 4 mol/L acid concentration. Zr and Pd extraction are the most affected by the presence of DODGAA or DOA (blue, green or red lines, depending on their concentrations), showing a decrease in Zr extraction, meanwhile Pd increases with all mixtures tested. Therefore, in case of problems with masking agent used during Ln/An extraction, an accumulation of DOA and/or DOGAA would increase Pd extraction. Figure 11 also shows that Lns are better extracted in the organic phase during the scrubbing at 0.5 mol/L HNO_3 with the presence of any amount of DODGAA or DOA. Therefore, all these results point out to more complicated recovering of Ln and An when the studied DCs are present.

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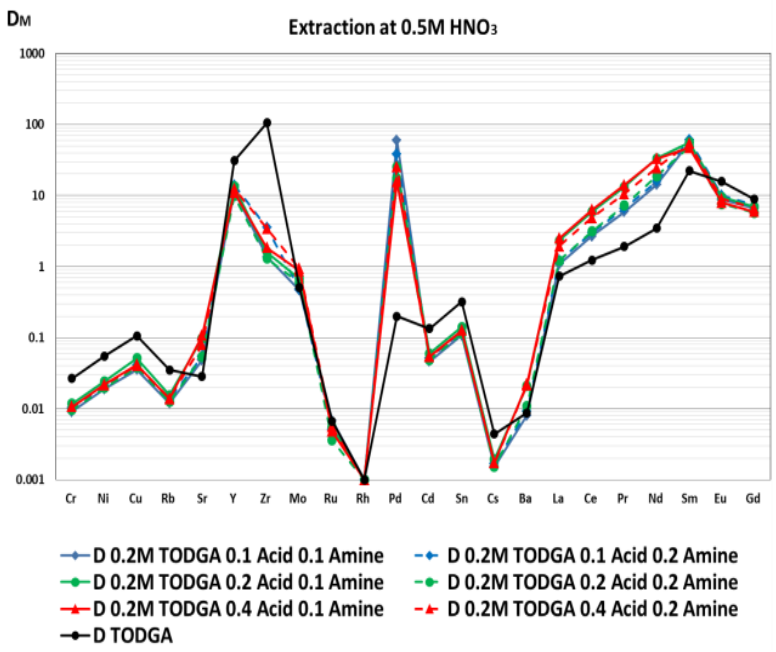


Figure 11. Ln and FP extraction by TODGA solvents with increasing concentrations of DOGAA and DOA from 10% HAR simulated solution at 0.5 mol/L HNO_3.

Figure 12 shows the experiment performed to simulate Ln recovery. Particularly, the concentration of the Ln in the organic phase along stripping steps from a loaded organic phase containing TODGA is followed with increasing concentrations of DOGAA and DOA. During An stripping (at 0.35 mol/ HNO_3), Ln should be kept in the organic phase, therefore, only in presence of a high accumulation of DOA and DOGAA (0.4 mol/L) the extraction of Ln (Eu, Y, Gd and Sm) would be affected. However, during Ln stripping (at 0.5 mol/L citric acid with NH_3), effects can be observed just with lower concentrations of DCs in the organic phase. Most likely it will be necessary to add a higher number of Ln stripping stages than used for the original performance of the process.

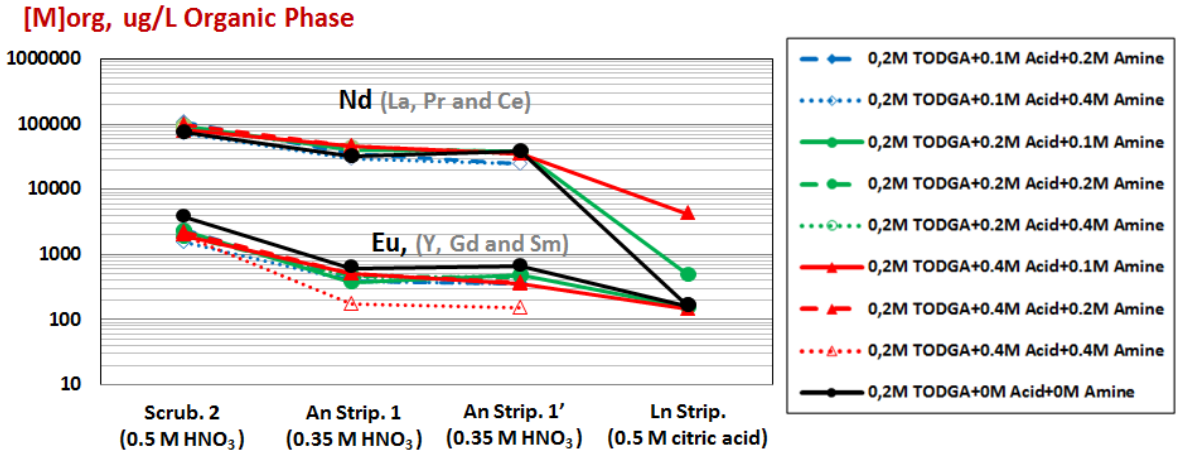


Figure 12. Ln concentration in the organic phase after the corresponding stripping stage from a loaded TODGA solvent (Scrub. 2). Scrub. 2 organics: (TODGA+ Acid + amine (0.1 mol/L or 0.2 mol/L each). Scrub. 2 aqueous: 10% HAR solution at 0.5 mol/L HNO_3.

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RECYCLING OF TODGA BASED SOLVENTS

Based on the previous results, to continue with the study of the most detrimental TODGA DCs and the development of strategies for a successful recycling of TODGA based solvents, three levels of experiments have been designed. First, the removal of the diglycolamic acid (DODGAA) from the organic phase was studied because of its possible effects over the process. Second, the washing studies were extended to mixtures of DOA and DODGAA and the non-easily removable DOHyA and DOAA. Finally, all the previous results were applied to study the effects over a TODGA solvent that has been irradiated during a dynamic experiment (loop irradiation test).

STUDIES TO REMOVE DODGAA FROM ORGANIC PHASES

As it was mentioned before, diglycolamic acid (DODGAA) (Figure 6) is responsible for precipitation observed after irradiation of the Euro-GANEX organic solvent [1]. It does not significantly affect the extraction of Ln, but extracts moderately some FPs; it will give problems for the quantitative stripping of Ln due to metal coordination via the carboxylate group [13-15]. Moreover, an unexpected high solubility of DODGAA (0.4 mol/L in OK) in the organic diluent was observed, even after contacting the organic phases with nitric acid, most probably due to the presence of TODGA and DOA. Therefore, the removal of this DC from organic phase is one of the challenges of TODGA solvent recyclability.

First of all, due to the nature of DODGAA, experiments started with basic washings from pure kerosene. For that, solutions of increasing DODGAA concentration in OK were pre-equilibrated with different nitric acid concentration as a starting point of the experiments. Alternatively, as the clean-up steps of solvents will be always carried out after the corresponding stripping steps (at diluted nitric acid or 0.5 mol/L citric acid), organic solvents were pre-equilibrated with 4 mol/L, 0.5 mol/L and 0.01 mol/L HNO_3 (Table 3).

Samples in which the concentrations of DODGAA were higher than 0.0063 mol/L showed solubility problems for all pre-equilibrated samples. Therefore, 0.0063 mol/L was chosen as the maximum concentration for the initial basic washing experiments to remove DODGAA from pure kerosene.

Table 3. Solutions of increasing DODGAA concentration in OK contacted with 4 mol/L, 0.5 mol/L or 0.01 mol/L HNO_3.

Solutions	Pre-treatment HNO_3		
	4 mol/L	0.5 mol/L	0.01 mol/L
[frag V] mmol/L in kerosene			
100	---	---	---
50	Third phase	Third phase	Third phase
25	Third phase	Third phase	Third phase
12.5	Soluble*	Soluble*	Soluble*
6.3	Soluble	Soluble	Soluble
3.2	Soluble	Soluble	Soluble
1.6	Soluble	Soluble	Soluble

***It was formed as an initial emulsion that disappeared after centrifugation**

Basic solutions such as 0.2 mol/L Na_2CO_3, NaOH, NH_2OH or NH_4OH were contacted with the corresponding organic phases (1:1 volume org:aq) following the consecutive steps that are shown in Table 4 (washing 1-5). After the first step of the washing sequence, only samples contacted with strong bases such as NaOH 0.2 mol/L (washing called CU3 in Table 4) were free of emulsions or third phase formation. For the following washing steps,

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the third phase was kept with the organic phase. The same previous effects were observed for the following washing steps 2 and 3.

Table 4. Washing sequences of 0.0063 mol/L DODGAA in OK. Contact time 15 min, 1:1 org/aq.

Washing name	Washing steps		
	Step 1	Step 2	Step 3
1 (CU-1)	0.2 mol/L Na_2CO_3	0.2 mol/L Na_2CO_3	0.2 mol/L Na_2CO_3
2 (CU-2)	0.2 mol/L Na_2CO_3	0.01 mol/L HNO_3	0.2 mol/L Na_2CO_3
3 (CU-3)	0.2 mol/L NaOH	0.2 mol/L NaOH	0.2 mol/L NaOH
4 (CU-4)	0.2 mol/L NH_2OH	0.2 mol/L NH_2OH	0.2 mol/L NH_2OH
5 (CU-5)	0.2 mol/L NH_4OH	0.2 mol/L NH_4OH	0.2 mol/L NH_4OH

The concentration of DODGAA by HPLC-MS in the organic and aqueous phases after each washing step were determined. Third phases were avoided for HPLC-MS quantitative analysis, so consequently problems with mass balance had to be account for. The evolution of the concentration of DODGAA after each washing step in the organic and aqueous phase along the experiments is shown in Figure 13a and Figure 13b, respectively.

In Figure 13a, it can be seen that washings using NaOH and NH_2OH can reduce drastically the concentration of DODGAA in the organic phase just after the first step. Nevertheless, when NH_2OH was used (CU4 Org, purple colour) the relevant reduction of the concentration of the DODGAA in the organic phase is not the consequence of DODGAA migration to the aqueous phase but due to an important third phase formation. Washing sequences started with Na_2CO_3 (CU-1 and CU-2) produced important third phase formations, and after acid washing gave place to a turbid aqueous phase (step 2 of CU-2: aq. phase quantified as homogeneous phase). Therefore, the use of a strong base such as NaOH seems to be the most efficient for removal of DODGAA but other possibilities with Na_2CO_3 HNO_3/Na_2CO_3 should be further explored.

a) b)

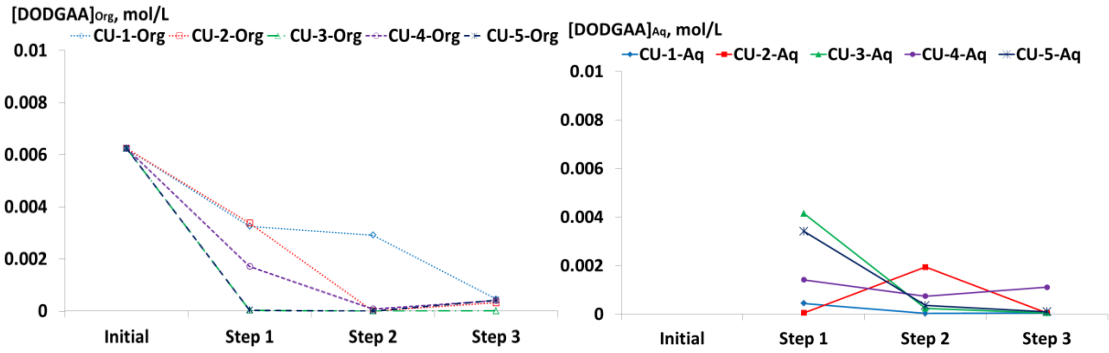


Figure 13. DODGAA concentration (mol/L) in the a) organic and b) aqueous phases in the initial solution, in pure kerosene, and after each of the three steps of washing, with 5 different clean-up agents (CU-1: 0.2 mol/L of 3x Na_2CO_3, CU-2: 0.2 mol/L of Na_2CO_3/0.01 mol/L HNO_3/ 0.2 mol/L of Na_2CO_3, CU-3: 0.2 mol/L of 3x NaOH, CU-4: 0.2 mol/L of 3x NH_2OH, CU-5: 0.2 mol/L of 3x NH_4OH).

ACIDIC AND BASIC WASHINGS OF A MIXTURE OF MAIN TODGA DCS

In this section, washing experiments to remove the most detrimental DCs (DOA and DODGAA) with non-easily removable DCs such as DOHyA and DOAA have been performed. Figure 14 shows the structure of all DCs investigated in these studies. Similar experiments for different compositions of the organic phases than

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presented before have been carried out. On the one hand, mixtures of the acid DODGAA and the amine DOA have been explored, to try to remove both of them (DODGAA by basic washing CU-1 – CU-5 and DOA by acid washing CU-6). On the other hand, it has been explored how these washing steps affect the two main TODGA DCs, DC XII (DOHyA) and DC XIII (DOAA), which are more prone to accumulation because they are not easily removable.



Figure 14. Structure of diglycolamic acid (DODGAA or DC V), dioctylamine (DOA or DC VII), 2-hydroxyl-*N,N*-dioctylacetamide (DOHyA or DC XII) and *N,N*-dioctylacetamide (DOAA or DC XIII).

Table 5. Sequences of steps used for the different clean-up of the mixtures of DCs. Contact time 30 min, 1:1 org/aq.

Clean Up name	Washing steps		
	Step 1	Step 2	Step 3
1 (CU-1)	0.2 mol/L Na_2CO_3	0.2 mol/L Na_2CO_3	0.2 mol/L Na_2CO_3
2 (CU-2)	0.2 mol/L Na_2CO_3	0.01 mol/L HNO_3	0.2 mol/L Na_2CO_3
3 (CU-3)	0.2 mol/L NaOH	0.2 mol/L NaOH	0.2 mol/L NaOH
4 (CU-4)	0.2 mol/L NH_2OH	0.2 mol/L NH_2OH	0.2 mol/L NH_2OH
5 (CU-5)	0.2 mol/L NH_4OH	0.2 mol/L NH_4OH	0.2 mol/L NH_4OH
6 (CU-6)	0.01 mol/L HNO_3	0.01 mol/L HNO_3	0.01 mol/L HNO_3

For these experiments, two mixtures of DCs were prepared and contacted with the sequence of aqueous washing shown in:

a) Six solutions of 0.1 mol/L of DODGAA and 0.1 mol/L of DOA in OK.[4]

b) Six solutions of 0.1 mol/L of DOHyA and 0.1 mol/L of DOAA in OK.

The evolution of the washing experiments was monitored by quantitative HPLC-MS analysis of all DCs in the organic phase as well as in the aqueous phase. However, the results of the samples type a) cannot be shown due to problems during the analysis. Regarding the effect of these washing steps over a mixture of XII and XIII, in Figure 15 (solution type b), it is represented the initial concentration of each DCs in the organic phase and final concentration after the corresponding washing sequences. As it can be expected, the concentrations of both DCs, XII and XIII, remain almost invariable in the organic phase and no third phase formation was observed in any case (Figure 15b). Therefore, although these two DCs would not be removed with the cleaning strategy, its accumulation will not affect to the normal performance of clean-up.

[4] Initially, the experiment was carried out with 0.2 mol/L but third phase was formed in all cases just after the contact with the aqueous washing phase.

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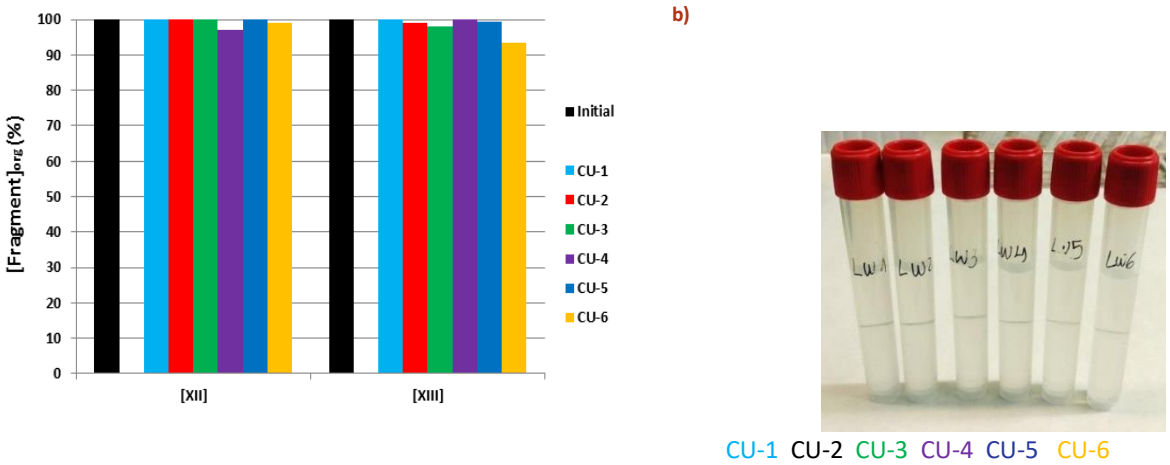


Figure 15. a) DOHyA and DOAA concentrations in the organic phase of: initial organic solution, and after the third steps of washing, with 6 different clean-up agents (CU-1: 0.2 mol/L of 3x Na_2CO_3, CU-2: 0.2 mol/L of Na_2CO_3/0.01 mol/L HNO_3/ 0.2 mol/L of Na_2CO_3, CU-3: 0.2 mol/L of 3x NaOH, CU-4: 0.2 mol/L of 3x NH_2OH, CU-5: 0.2 mol/L of 3x NH_4OH, CU-6: 0.01 mol/L of 3x HNO_3). b) Vials of 0.1M DOHyA and 0.1M DOAA after the third washing step with different clean-up agents.

Another possibility to remove difficult DCs would be a selective distillation as is done in the La Hague plant for the PUREX process [16-18]. However, because of the boiling point of kerosene, only the smallest DCs seem to be candidates for selective distillation. Figure 16a shows a boiling points range of the components of a degraded TODGA solvent and Figure 16b shows the schematic degradation pathways that give rise to the smallest DCs such XXII and XXIII. Therefore, considering DCs XII (DOHyA) and XIII (DOAA) will be accumulated but also degraded into XXII and XXIII, and that DC XXII is able to extract some FPs [12, 13], the distillation of DCs such XXII and XXIII could be considered.

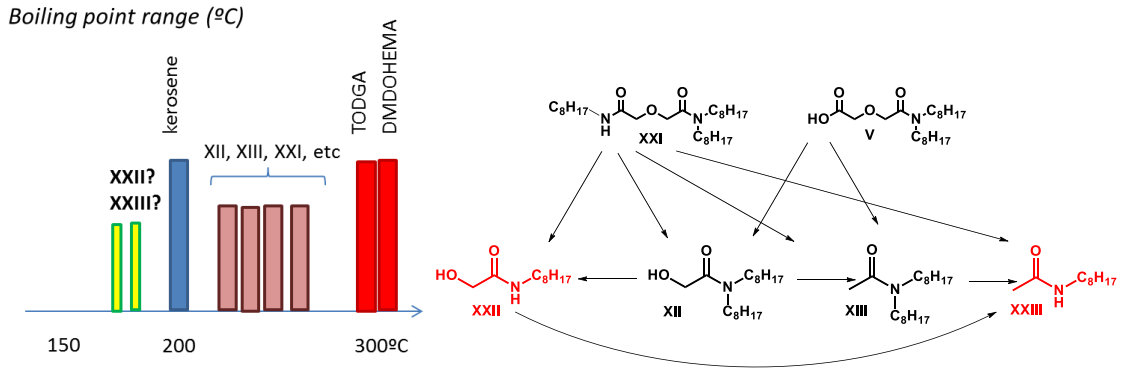


Figure 16. a) Schematic representation of boiling point range of TODGA, DMDHOEMA, kerosene and some of DCs; b) Example of degradation of DCs like XXI and V into smaller ones XXII and XXIII.

ACIDIC AND BASIC WASHINGS AFTER IRRADIATION TEST LOOP OF TODGA-BASED SOLVENTS

In this section, all the previous results have been applied to study the effects of acid and basic washing over TODGA solvents that have been irradiated during a dynamic experiment (loop irradiation test) carried out at Náyade facility. Particularly, the two biphasic systems irradiated were TODGA/HNO_3 [19] and TODGA-DMDOHEMA/HNO_3 (Euro-GANEX) [8].

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The aim of these washing studies was to explore how the washing sequences studied previously could affect removal of the other DCs present in the irradiated TODGA-based solvent. For that, the same six washings sequences studied before (CU-1, CU-2, CU-3, CU-4, CU-5 and CU-6) have been applied to the two different organic solvents. In Table 6 are shown the composition of the aqueous phase of the different sequence steps and the corresponding photograph taken during the experiment. As it can be seen, especially the stronger basic washings gave rise to third phases formation or turbidity (* and **, respectively for CU-1, CU-2, CU-3 and CU-5 washings) for TODGA system. Nevertheless, in the Euro-GANEX system, third phase formation is less than expected, most probably due to a phase modifier as DMDOHEMA is present. The concentration of the clean-up agent was selected based on the literature [20-24]. However, most of these samples formed third phase, therefore, the concentration of clean-up agents could be reduced. Moreover, and contrary to some work [25] we observed that the introduction of a HNO_3 washing step between the two Na_2CO_3 steps (CU-2) is not useful at all to avoid that third phase formation.

Table 6. Pictures of irradiated TODGA and Euro-GANEX samples after the first, second and third washing steps with the 6 different clean-up agents (CU-1: 0.2 mol/L of 3x Na_2CO_3, CU-2: 0.2 mol/L of Na_2CO_3/0.01 mol/L HNO_3/ 0.2 mol/L of Na_2CO_3, CU-3: 0.2 mol/L of 3x NaOH, CU-4: 0.2 mol/L of 3x NH_2OH, CU-5: 0.2 mol/L of 3x NH_4OH, CU-6: 0.01 mol/L of 3x HNO_3).

*** Third phase formation, ** org/aq phase turbidity**

	Initial TODGA (0.1M TODGA in OK) irradiated to 405kGy			Initial GANEX (0.2M TODGA+0.5M DMDOHEMA in OK) irradiated to 540kGy		
	1st washing Step	2nd washing Step	3th washing Step	1st washing Step	2nd washing Step	3th washing Step
CU-1 3x 0.2M Na_2CO_3	Initial + 0.2M Na_2CO_3	Org1+ 0.2M Na_2CO_3	Org2+ 0.2MNa_2CO_3	Initial+ 0.2M Na_2CO_3	Org1+ 0.2M Na_2CO_3	Org2+ 0.2MNa_2CO_3
	 *	 *, **	 **	 *		
CU-2 0.2M Na_2CO_3 0.01M HNO_3 0.2M Na_2CO_3	Initial+ 0.2M Na_2CO_3	Org1+ 0.01M HNO_3	Org2+ 0.2M Na_2CO_3	Initial+ 0.2M Na_2CO_3	Org1+ 0.01M HNO_3	Org2+ 0.2M Na_2CO_3
	 *	 *, **	 **	 *	 *, **	 *
CU-3 3x 0.2M NaOH	Initial+ 0.2M NaOH	Org1+ 0.2M NaOH	Org2+ 0.2MNaOH	Initial+ 0.2M NaOH	Org1+ 0.2M NaOH	Org2+ 0.2MNaOH
	 *	 *	 *	 *	 *	 **

CU-4 3x 0.2M NH_2OH	Initial+ 0.2M NH_2OH	Org1+ 0.2M NH_2OH	Org2+ 0.2MNH_2OH	Initial+ 0.2M NH_2OH	Org1+ 0.2M NH_2OH	Org2+ 0.2MNH_2OH
						
CU-5 3x 0.2M NH_4OH	Initial+ 0.2M NH_4OH	Org1+ 0.2M NH_4OH	Org2+ 0.2MNH_4OH	Initial+ 0.2M NH_4OH	Org1+ 0.2M NH_4OH	Org2+ 0.2MNH_4OH
	*, **	*, **	*, **			
CU-6 3x 0.01M HNO_3	Initial+ 0.01M HNO_3	Org1+ 0.01M HNO_3	Org2+ 0.01M HNO_3	Initial+ 0.01M HNO_3	Org1+ 0.01M HNO_3	Org2+ 0.01M HNO_3
						

TODGA/HNO_3 SYSTEM

The original organic phase was 0.1 mol/L TODGA in OK, which was irradiated at Náyade facility in contact with 0.5 mol/L HNO_3, with continuous mixing and recirculation (up to an absorbed dose of 405 kGy; dose rate of ^{60}Co sources 44.72 kGy/h; real absorbed dose rate of 3.35 kGy/h). This study is part of work developed within task 1 of WP5, and it was reported in CIEMAT HYPAR-05 [19].

The quantitative analysis by HPLC-MS of TODGA and its DCs in the original irradiated solvent and after the corresponding washing sequences was carried out. Although, third phases were included in the following washing steps to try to eliminate them, for HPLC-MS quantitative analysis they were rejected to evaluate the real transference from the organic to the aqueous phase; therefore, mass balance inconsistencies are expected.

The concentration of TODGA and some of its DCs in the initial and final organic phases are shown in Figure 17. The concentration of the other DCs are not shown as they were lower than the detection limit (DCs XXII and XXIII) or really low and were not influenced by the steps (DCs XIII and XX).

As expected, from the third phase photographs in Table 6 (particularly when basic clean up agents are used: CU-1, CU-2, CU-3 and CU-5) no good mass balance results were obtained, for example, there are important variations in TODGA concentrations (in Figure 17). It is highlighted how the dioctylamine (DC VII, DOA) is not efficiently removed with acid washing, nor the acid (DODGAA/V) by weak basic washing, therefore, it should be necessary to increment the number of steps, alternate acid/basic washings or even look for other clean-up agents. As it was observed individually for XII and XIII, their concentrations remain almost invariable in the organic phase,

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therefore, as these two DCs would not be removed with this cleaning strategy, its accumulation would affect the normal performance of the process.

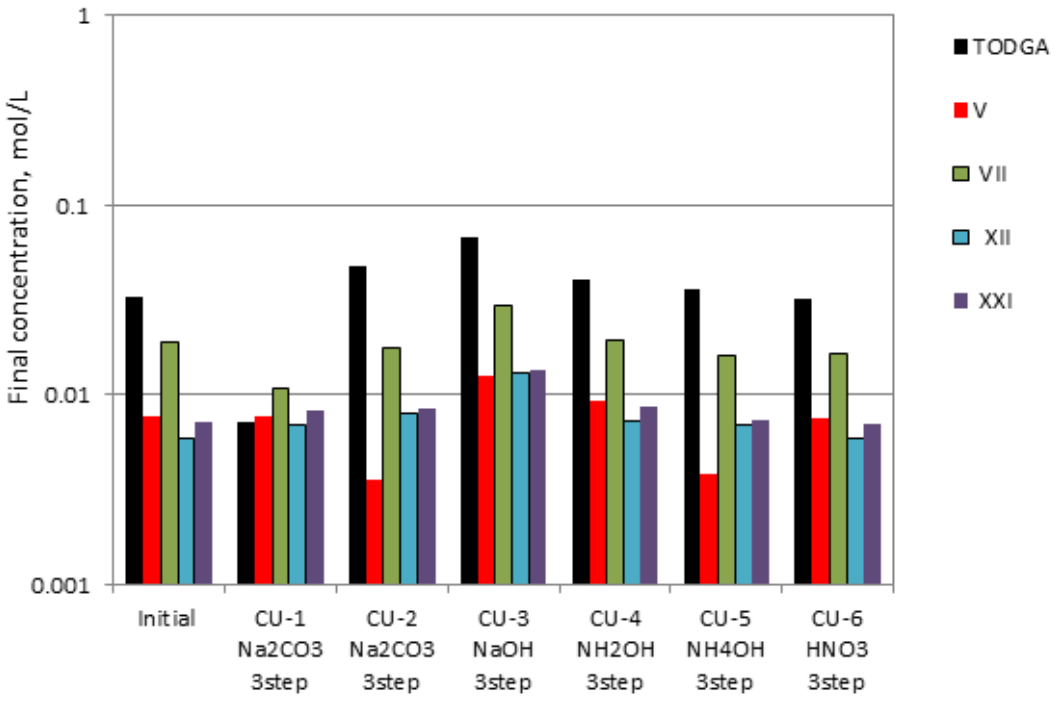


Figure 17. HPLC-MS quantitative analysis of TODGA and its DCs (V, VII, XII and XXI) in the organic phase irradiated in the test loop in contact with 5 mol/L HNO_3 up to 405 kGy (initial) and after third steps of washing with the 6 different clean-up agents (CU-1: 0.2 mol/L of 3x Na_2CO_3, CU-2: 0.2 mol/L of Na_2CO_3/0.01 mol/L HNO_3/ 0.2 mol/L of Na_2CO_3, CU-3: 0.2 mol/L of 3x NaOH, CU-4: 0.2 mol/L of 3x NH_2OH, CU-5: 0.2 mol/L of 3x NH_4OH, CU-6: 0.01 mol/L of 3x HNO_3).

TODGA-DMDOHEMA/HNO_3 (EURO-GANEX) SYSTEM

The original organic phase was 0.2 mol/L TODGA+ 0.5 mol/L DMDOHEMA in OK, which was irradiated at Náyade facility simulating the two main steps of the EURO-GANEX process, the An + Ln co-extraction and TRU stripping (dose rate of ^{60}Co sources 44.72 kGy/h; real absorbed dose rate of 3.35 kGy/h). Between these two steps, scrubbing was introduced using lower nitric acid concentration to remove other elements as FP co-extracted and to adjust the acidity for the next step. More details about that experiment are shown in CIEMAT HYPAR 7 [8].

The samples employed for the washing experiments correspond to an organic phase irradiated up to 540 kGy in two steps: first up to 500 kGy in contact with 5 mol/L HNO_3 and after that, another 40 kGy irradiated in contact with 0.018 mol/L SO_3-Ph-BTP in 0.5 mol/L HNO_3.

Figure 18 shows the quantification of TODGA, DMDOHEMA and TODGA DCs by HPLC-MS for samples irradiated at 540 kGy. Only the main TODGA DCs were quantified (DODGAA/V, DOA/VII, XII and XXI, VII, XII, XIII, XX) but some of them are not shown as they were lower than the detection limit (DCs XXII and XXIII) or really low and were not influenced by the washing steps (DCs XIII and XX). It has to be considered that third phases were again avoided for quantitative analysis, thus mass balance could be affected. In general, the TODGA and DMDOHEMA concentration keeps relatively constant in the Euro-GANEX mixture after all the different washes tested. If these

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results are compared to those obtained for TODGA/HNO_3 system, in which important variations in concentrations were observed due to third phase formation, a lower variation was observed now. This result could be explained by the absence or less third phase formation, mainly due to the presence of DMDOHEMA. Under the irradiation test loop conditions, the majority DCs are DOA/VII, XII and XXI, as it can be seen in Figure 18, and unfortunately its concentrations keep relatively constant after all washing steps. On the one hand, although DC DOA/VII concentration is reduced, it is not completely removed, which should be taken into account and not overlooked. And on the other hand, the acid DODGAA/V, which another of the problematic DCs, is only washed with the stronger basic washing agents. Therefore, the accumulation of these DCs; amine (VII or DOA), acid (V or DODGAA), and again XII and XIII would be very problematic; thus, online monitoring of their formation could be useful alongside the running experiment. Further washing strategies should be explored for these DCs (increasing the number of washing steps, alternating acid and basic washing agents, changing to distillation or other clean-up techniques, etc.).

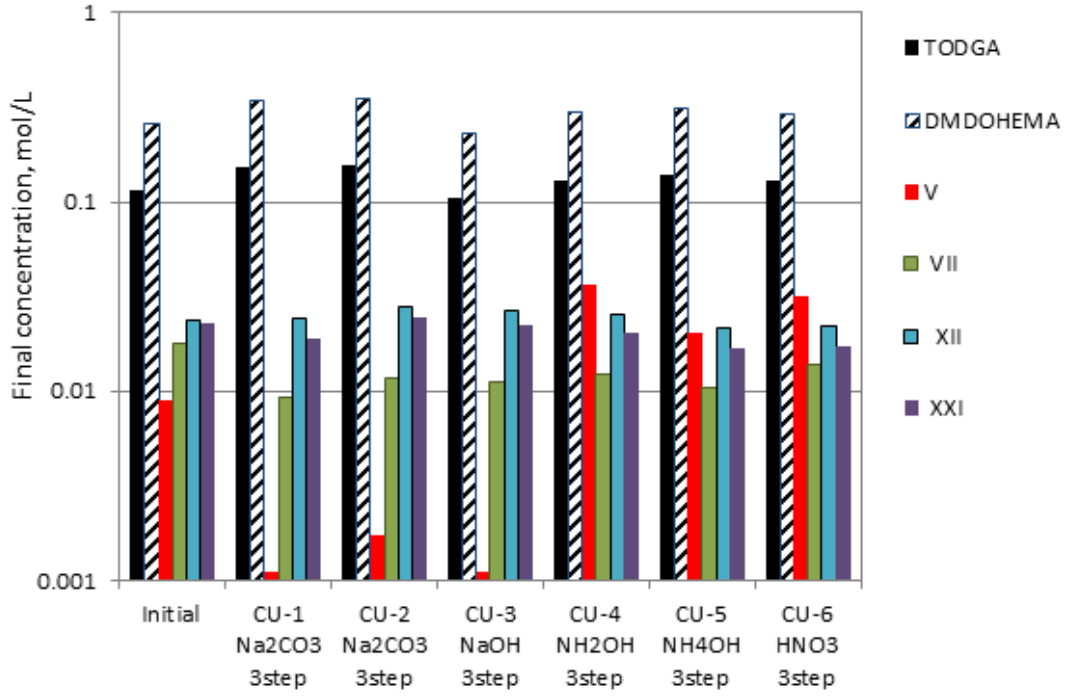


Figure 18. HPLC-MS quantitative analysis of TODGA, DMDOHEMA and TODGA DCs (V, VII, XII and XXI) in the Euro-GANEX solvent irradiated in the test loop up to 540 kGy (initial, solvent from WP5 of this HYPAR) and its final concentrations after third steps of washing with the 6 different clean-up agents (CU-1: 0.2 mol/L of 3x Na_2CO_3, CU-2: 0.2 mol/L of Na_2CO_3/0.01 mol/L HNO_3/ 0.2 mol/L of Na_2CO_3, CU-3: 0.2 mol/L of 3x NaOH, CU-4: 0.2 mol/L of 3x NH_2OH, CU-5: 0.2 mol/L of 3x NH_4OH, CU-6: 0.01 mol/L of 3x HNO_3).

In this regard, the colour variations of samples is also striking (if it is compared between the three right columns to those of the left in Table 6). The colour variation may be due to both: the different system compositions and/or the presence of the metals coming from the stainless steel reactor corrosion during the irradiation loop (explained in more detail in WP5 of CIEMAT HYPAR 7, [8]). For that reason, a quantitative and semi-quantitative analysis by ICP-MS of these degraded GANEX samples has been performed.

The concentration of the main metals which is made of the 316 stainless steel (Fe, Ni, Cr and Mo) in the initial and the final organic phases after the three consecutive washing steps is shown in Figure 19. It can be seen that Ni does not vary greatly throughout the test. Both the Cr and Mo are removed from the organic phase with the

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basic washes. However, CU-4 and CU-6, although they eliminate part of the Cr, the Mo is still present in the final organic phase. And indeed, the orange colour is mainly due to the presence of Fe, whose concentration is especially high in the most coloured solutions (CU-1, CU-2 and CU-3), being its concentration even higher than in the initial one, which is again attributed to the formation of an abundant third phase.

From these results, we have seen that the alternation of acid and basics washing steps could be useful to avoid acids and amines DCs, and also to remove all the metals extracted into the organic phase due to the reactor corrosion during the irradiation loop.

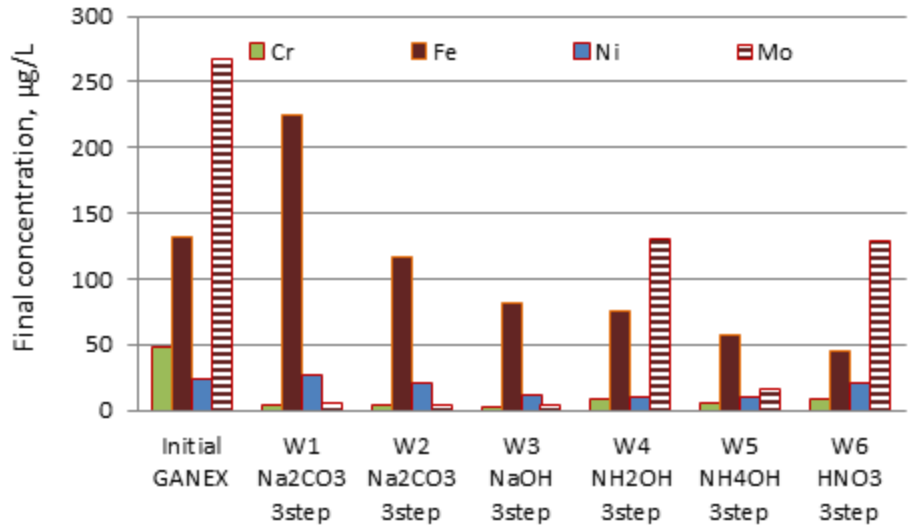


Figure 19. Evolution of the concentration of 316 stainless steel corrosion products: Fe, Cr, Ni and Mo in different GANEX samples irradiated at 540 kGy in the irradiation test loop with 5 mol/L HNO_3 after the third steps of washing with 6 different clean-up agents (CU-1: 0.2 mol/L of 3x Na_2CO_3, CU-2: 0.2 mol/L of Na_2CO_3/0.01 mol/L HNO_3/ 0.2 mol/L of Na_2CO_3, CU-3: 0.2 mol/L of 3x NaOH, CU-4: 0.2 mol/L of 3x NH_2OH, CU-5: 0.2 mol/L of 3x NH_4OH, CU-6: 0.01 mol/L of 3x HNO_3).

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FISSION PRODUCT RETENTION IN SOLVENT

INTRODUCTION

TODGA (*N*,*N*,*N'*,*N'*-tetraoctyl-diglycolamide, Figure 20) is known to co-extract some unwanted fission and corrosion products together with the trivalent lanthanides (Ln(III)) and actinides (An(III)), namely Sr, Zr, Mo, Ru, and Pd. Ruthenium and zirconium extraction with TODGA are especially difficult, as these elements are difficult to back-extract during a counter-current process using the usual scrubbing steps. Therefore, they need to be removed during solvent washing steps. Ruthenium speciation seems to be of utter importance as some Ru complexes are extractable others are not.[1]

Scrubbing of co-extracted fission and corrosion products from a loaded TODGA-based solvent was tested using hydrophilic complexants. An overview of the used complexants is shown in Table 7. The loaded TODGA solvent used was an old solution from the last H_4TPAEN centrifugal contactor test, which was not completely used. It consists of 0.2 mol L^{-1} TODGA + 5%$_{vol.}$ *n*-octanol in TPH (hydrogenated tetrapropene).

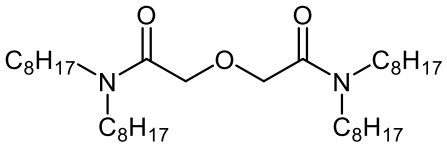
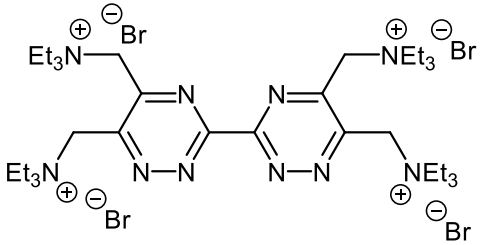
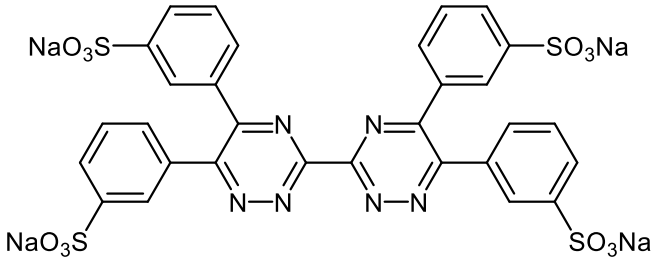
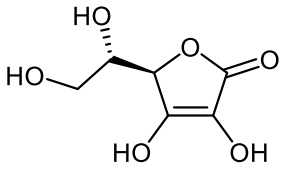


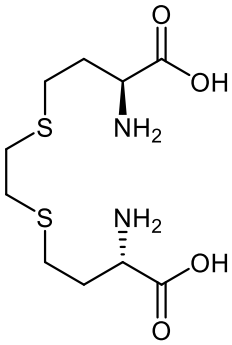
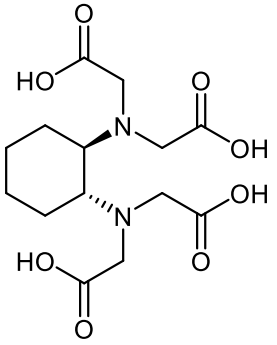
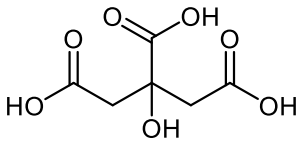
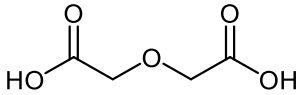
Figure 20. Chemical structure of TODGA.

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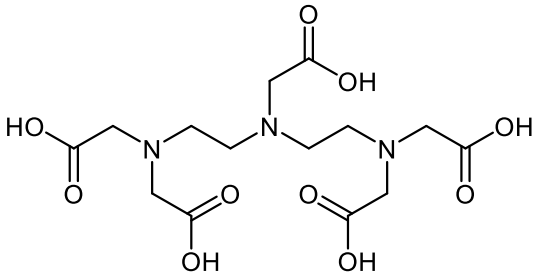
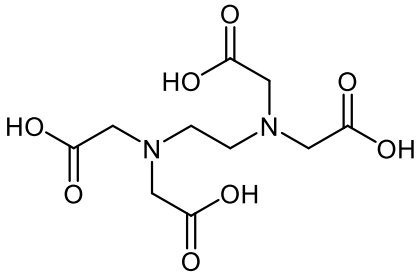
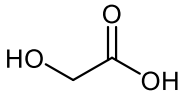
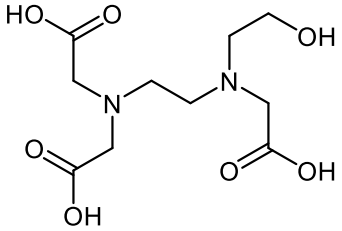
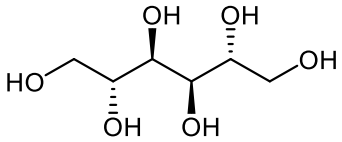
Table 7. Overview of tested hydrophilic complexants and their chemical structure.

Complexant (acronym)	Full chemical name	Chemical structure
$(CH_2NEt_3X)_2BT$	3,3'-Bis-1,2,4-triazine-5,5',6,6'-tetrayltetrakis(*N*,*N*,*N*-triethylmethanaminium) tetrabromide	
$(PhSO_3Na)_2BT$	Tetrasodium 3,3',3'',3'''-[3,3'-bis-1,2,4-triazine-5,5',6,6'-tetrayl]tetrabenzenesulfonate	
Ascorbic acid	*L*-Ascorbic acid	

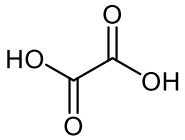
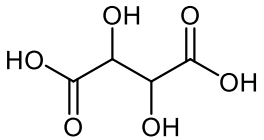
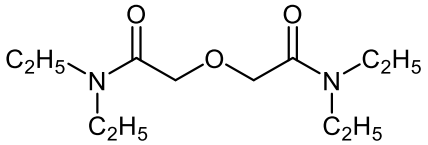
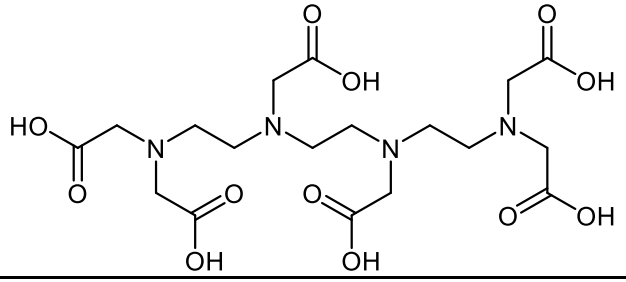
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Bimet	(2*S*,2'*S*)-4,4'-(Ethane-1,2-diyl-bis(sulfanediyl))-bis(2-aminobutanoic acid)	
CDTA	*trans*-1,2-Diaminocyclohexane-*N*,*N*,*N*',*N*'-tetraacetic acid	
Citric acid	2-Hydroxypropane-1,2,3-tricarboxylic acid	
Diglycolic acid	2-(Carboxymethyloxy)-acetic acid	

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DTPA	Diethylenetriamine *N*,*N*,*N'*,*N''*,*N''*-pentaacetic acid	
EDTA	Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid	
Glycolic acid	2-Hydroxyethanoic acid	
HEDTA	*N*-(2-Hydroxyethyl)-ethylenediamine-*N*,*N'*,*N'*-triacetic acid	
Mannitol	*D*-mannitol	
$NaNO_2$	Sodium nitrite	$NaNO_2$

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Oxalic acid	Oxalic acid	
Tartaric acid	2,3-Dihydroxysuccinic acid	
TEDGA	*N*,*N*,*N'*,*N'*-Tetraethyl-diglycolamide	
TTHA	Triethylenetetramine-*N*,*N*,*N'*,*N''*,*N'''*,*N'''*-hexaacetic acid,	

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RESULTS AND DISCUSSION

SOLUBILITY ISSUES

All hydrophilic complexants were first tried to dissolve in 0.0001 (pH 4) and 0.1 mol L^{-1} HNO_3 in 0.1 mol L^{-1} concentration. Some hydrophilic complexants were not soluble under these conditions, namely DTPA, TTHA, CDTA, and bimet.

DTPA dissolved at 0.05 mol L^{-1} concentration in 0.1 mol L^{-1} HNO_3.

TTHA dissolved at 0.1 mol L^{-1} concentration in 1 mol L^{-1} HNO_3.

CDTA was tried to solubilize at 0.025 mol L^{-1} concentration in 1 mol L^{-1} HNO_3, but did not fully dissolve.

CDTA and bimet suspensions were centrifuged and the clear supernatants were used in solvent extraction experiments. The exact concentrations of the complexants in these experiments is unknown.

$(CH_2NEt_3X)_2BT$ and $(PhSO_3Na)_2BT$ were used in 0.01 mol L^{-1} concentration.

SOLVENT EXTRACTION TESTS

The hydrophilic complexants were tested in solvent extraction tests using the loaded TODGA solvent. Table 8 shows an overview of the experimental conditions and denotes experiments in which a precipitation was observed.

Figure 21 and Figure 22 show the distribution ratios *D* as a function of the experiment no. as given in Table 8 for Am and Eu, as well as Ru, Pd, Zr, Mo, and Sr, respectively.

The results show that the HNO_3 concentration has a major influence on the An(III) and Ln(III) distribution ratios, as would be expected from the TODGA extraction behavior.[2-3] The hydrophilic complexants TEDGA, HEDTA, EDTA, diglycolic acid, citric acid, tartaric acid, glycolic acid, ascorbic acid, oxalic acid, mannitol, DTPA, $(CH_2NEt_3X)_2BT$, $(PhSO_3Na)_2BT$ and $NaNO_2$ gave Am distribution ratios <1 (in that order with ascending values). A similar order is observed for the Ln(III), but with generally higher distribution ratios.

The hydrophilic complexants or HNO_3 concentration did not show much of an influence on Ru, Pd, Zr, Mo, and Sr. Their distribution ratios remained mostly high. Diglycolic acid showed a decrease of Mo and Sr distribution ratios <1 at 0.1 mol L^{-1} HNO_3 concentration, but not at ph 4. Mannitol showed the opposite: Decrease of Mo and Sr distribution ratios <1 at pH 4 vs. 0.1 mol L^{-1} HNO_3 concentration. Zirconium distribution ratios were slightly influenced by oxalic acid. This was expected, as oxalic acid was used for Zr complexation in previous process demonstrations.[4-5] However, we observed some precipitation and a bad mass balance in these experiments and the results should therefore be handled with care. Ruthenium extraction was not influenced by any of the hydrophilic complexants tested.

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Table 8. Overview of experimental conditions.

Experiment no.	Complexant (acronym)	Complexant concentration [mol L^{-1}]	HNO_3 concentration [mol L^{-1}]	Comment
1	$(CH_2NEt_3X)_2BT$	0.01	0.1	
2	$(CH_2NEt_3X)_2BT$	0.01	0.0001	
3	$(PhSO_3Na)_2BT$	0.01	0.1	Precipitate, bad mass balance
4	$(PhSO_3Na)_2BT$	0.01	0.0001	Precipitate, bad mass balance
5	Ascorbic acid	0.1	0.1	
6	Ascorbic acid	0.1	0.0001	
7	Bimet	<0.1*	0.1	
8	CDTA	<0.025*	1.0	
9	Citric acid	0.1	0.1	
10	Citric acid	0.1	0.0001	
11	Diglycolic acid	0.1	0.1	
12	Diglycolic acid	0.1	0.0001	
13	DTPA	0.05	0.1	
14	EDTA	0.1	0.1	
15	EDTA	0.1	0.0001	Fine precipitate, mass balance not too bad
16	Glycolic acid	0.1	0.1	
17	Glycolic acid	0.1	0.0001	
18	HEDTA	0.1	0.1	
19	HEDTA	0.1	0.0001	
20	Mannitol	0.1	0.1	
21	Mannitol	0.1	0.0001	
22	$NaNO_2$	0.1	0.1	
23	$NaNO_2$	0.1	0.0001	
24	Oxalic acid	0.1	0.1	Precipitate, bad mass balance
25	Oxalic acid	0.1	0.0001	Precipitate, bad mass balance
26	Tartaric acid	0.1	0.1	
27	Tartaric acid	0.1	0.0001	
28	TEDGA	0.1	0.1	
29	TEDGA	0.1	0.0001	
30	TTHA	0.1	1.0	

*CDTA and bimet were not fully dissolved. The suspensions were centrifuged and the clear supernatants were used in solvent extraction experiments.

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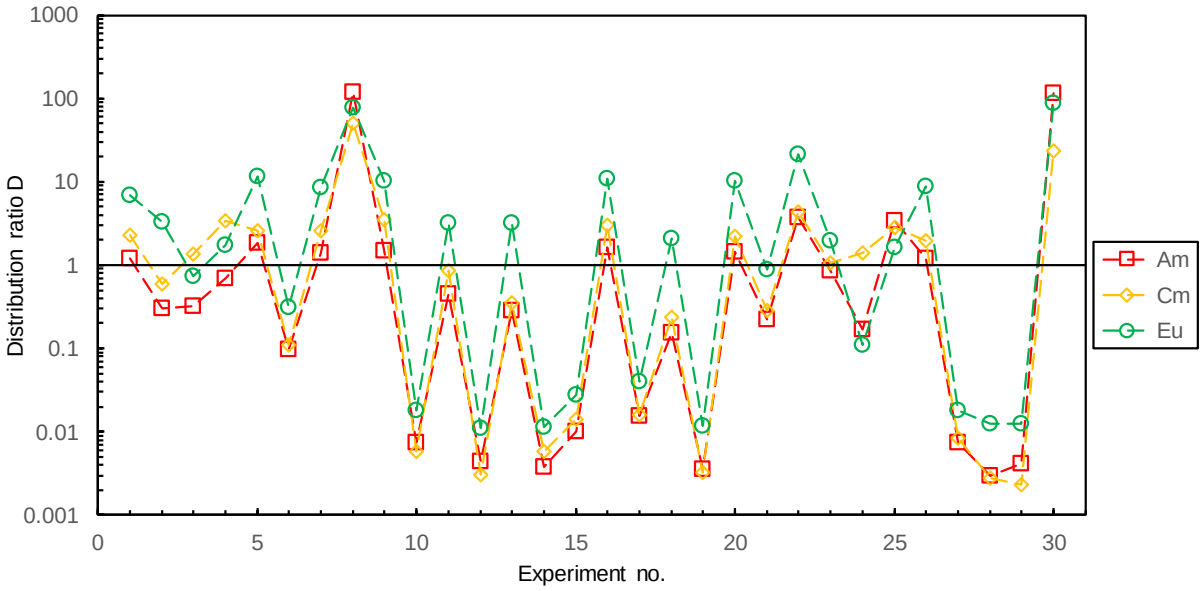


Figure 21. Distribution ratio *D* as a function of the experiment no. as given in Table 8. Am and Eu data calculated from Am-241 and Eu-152 gamma spectrometry, Cm data calculated from the Cm-244 alpha spectrometry.

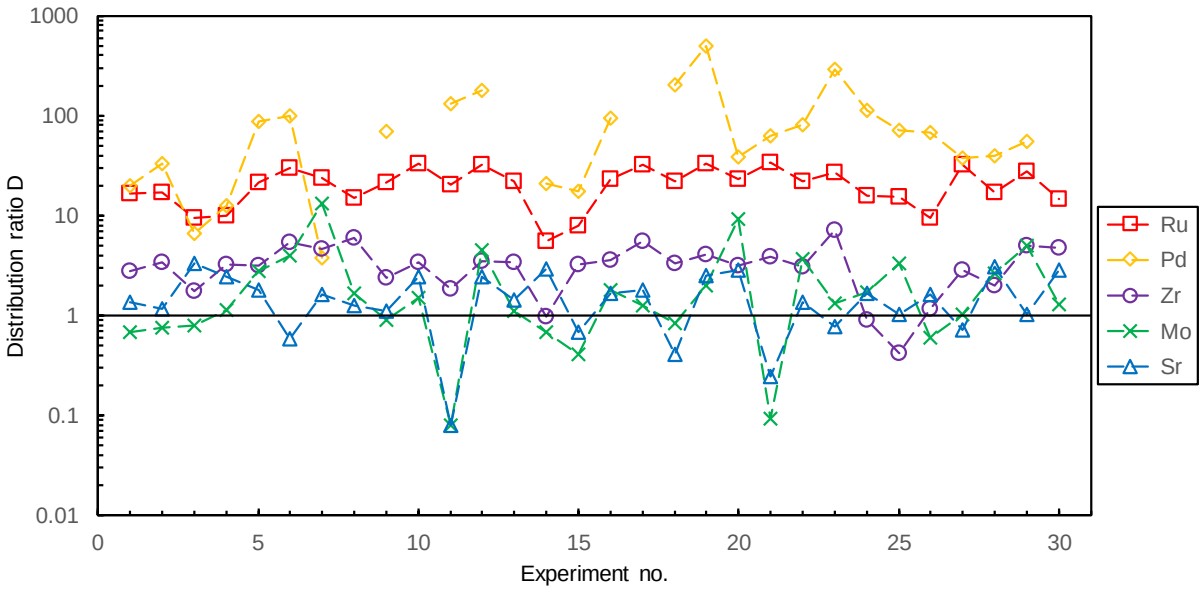


Figure 22. Distribution ratio *D* as a function of the experiment no. as given in Table 8. Ru, Pd, Zr, Mo, and Sr data calculated from ICP-MS measurements. For missing data points the distribution ratio *D* could not be calculated, as the aq. phase concentration was below the detection limit (the *D* value is >500).

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CONCLUSIONS

The back-extraction of problematic fission products (e.g. Ru) from a loaded TODGA solvent was studied using different hydrophilic complexants. However, no complexant was found to work better than those already known.

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DEVELOPMENT OF A SOLVENT DOSE MODEL

INTRODUCTION

A lot of work has been performed to measure hydrogen G values and dose coefficients for TODGA and malonamide-based solvent systems [2] [3]. However, there has long been a missing link in understanding what doses are likely to be found in the actual process and, therefore, the overall effect of irradiations. Gaining an understanding of expected doses and, therefore, degradation would then provide an understanding of the operational limits under which aqueous reprocessing is no longer viable, with respect to radiolytic degradation and hydrogen hazard, for the reprocessing of spent nuclear fuel and where alternative (pyro) processes are required. The radiation dose during the process will be heavily dependent on the burn up, cooling time, original fuel composition and dissolution parameters of the fuel.

As previous work within European funded projects has provided a flow sheet based on the EURO-GANEX process this was chosen as a starting point to build an Excel based model that can predict the expected doses to the solvent phase during aqueous reprocessing [4]. Excel was chosen as a simple method of building the model as it is expected that all GENIORS partners have access to it. The model has been designed to provide approximate doses resulting from α, β and γ radiation to guide further experimentation. For example, this will help understand the maximum dose to solvents that need to be investigated to evaluate degradation effects. This should allow interpretation of the applicability of results to an industrial process, rather than focussing solely on evaluating the dose required for a chemical effect to be observed. Therefore, this model has been designed to estimate the total dose that the solvent receives during the solvent extraction process. It has been designed to use a FISPIN output file (an industry-standard computer modelling software that yields a total inventory of fuel from a knowledge of its original content, burn-up and cooling) as an input but could be adapted for alternative fuel inventory calculations.

The workbook is used to calculate an estimate for the dose received by the Euro-GANEX solvent (0.2 M TODGA, 0.5 M DMDOHEMA in OK) during the second cycle of the Euro-GANEX process. It is in this second cycle where the separation of the Fission Product (FP), Actinide (An) and Lanthanide (Ln) species occurs (the majority of the uranium (U) has been separated in the first cycle of the process). Fortunately, extensive work has been undertaken on the process in terms of flow rate and mass flow modelling. The previously issued gPROMS flowsheet details the amount of various fluids and the masses of various radionuclides throughout the system [4]. The gPROMS flowsheet model is the basis for the flowsheeted radionuclide concentrations and material mass balance inputs for this spreadsheet and has been used to scale further FISPIN data.

A 5-year cooled FISPIN with ~220 nuclides was used as the basis for the gProms model. From this, radionuclides were either assigned to a species (e.g. An, Ln, FPs etc) or neglected. This was adequate for the original purposes for which it was used. Unfortunately, this is not adequate for a full dose model. Many of the species that were viewed as of low significance from a chemical separation perspective are important when considering their dose contribution. Additionally, there is a desire to understand the effect of using fuel with much shorter cooling or higher burn up. Therefore, this dose model must account for many more radionuclides, which may have decayed away during cooling or been ignored in the previous model. For this reason, this model assigns every radionuclide to an appropriate species stream that is tracked through the flowsheet, thereby capturing its contribution to the total dose.

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One should refer to the notes within the spreadsheet itself for a more detailed description of the process and working assumptions but below is a brief outline of how the spreadsheet is structured:

- User inputs a FISPIN in the 'Input Sheet'.
- Radionuclides in the FISPIN are automatically assigned to a specific species stream as previously defined in the gProms model.
  The mass of each species from the user FISPIN is compared with the gProms FISPIN species mass to obtain a ratio for that species, *e.g. user FISPIN has 50 kg of Pu, gProms FISPIN has 40 kg of Pu – ratio of 5:4 Pu – ratio = 1.25*
- The masses from each stage of the flow sheet from the gProms model are then multiplied by this ratio to scale the total metal content of the solvent to the new FISPIN.
- The mass of a nuclide in a species is calculated from the abundances in the user FISPIN, e.g. if there is 75% Pu239 and 25% Pu241 in the user FISPIN we assume this same ratio at all stages in the process.
- The original flow sheet is scaled, firstly to account for the change in species mass between each FISPIN and then to account for the isotopic abundances in each species.
- Once each stage of the process has an assumed isotopic inventory, it is possible to calculate a dose at each point, albeit with the following conservative assumptions.

ASSUMPTIONS

- The solvent inventory in the gProms model is able to contact/be loaded with an increased/decreased loading of any species depending on user inputted FISPIN, *e.g. a heavier Pu loading will not affect the volumes of Aq or Solvent and will not change extraction capability (D values).*
- The ratio of isotopes/nuclides within a species stream does not change throughout the process, e.g. if we start with a FISPIN with 75% Pu239 and 25% Pu241 for the Pu species, we expect this ratio to be true throughout the sheet.
- We assume that the decay of the nuclides is subject to the data found in ICRP 107 (where it is not available there it was obtained from databases of NPL) [5], [6]. This includes the decay energies, branching ratios and the half-lives/specific activities. One should note that the branching ratios were obtained from ICRP 107 and manually transcribed. These have been formally checked for consistency, but this is a potential source of error. Unfortunately, it was not possible to obtain all the photon branching ratios. It has, therefore, been necessary to normalise all γ branching to 100% wherever ICRP 107 has a photon energy ≠ 0. This represents a clear pessimism in the model. This combined dataset is available in the 'data sheet' – first table.
- Certain nuclides that decay into short-lived daughter nuclides have been modified within the ICRP 107 library. These have been chosen based on their non-negligible mass in the FISPIN and the total time spent in the system. To account for these sequential decays, the energy of the daughter decay has simply been added to that of the parent decay. This was necessary as otherwise the dose contribution from the short-lived daughter(s) would not be included due to their low abundances in the input FISPIN. A description of this can be found in the 'Species and Special Decays' sheet.
- Any energy contribution from processes that do not form a pure α, β or γ emission have been neglected. This includes neutron emission, proton emission, spontaneous fission, cluster decay, double α decay etc. These are assumed to be of low significance due to the small branching ratios and small masses of nuclides that undergo such transformations.

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- During the species separation within a contactor bank, a discrete jump between one stream and another is assumed. This could be modified to be more gradual over multiple contactors/banks but was done this way for simplicity, e.*g. in the TRU Extract stage a FP loaded aqueous phase and a clean solvent is assumed on one side of this separation contactor and on the other side there is an aqueous phase loaded with the entire contents of the FISPIN that have made it to the separations plant and an organic loaded with An and Ln.*
- The contactors that have been used are those that are commercially available from the CINC website [7]. The occupancy time for these has been calculated using the flow rates and the volume of the contactor.
- The effect of water within the flowsheet has been neglected from both the aqueous and organic phases. Water is used to dilute the HNO_3 at various points but has been omitted for simplicity. Instead, the total aqueous flow is assumed to be HNO_3.
- α, β and γ absorption rates for each stage are outlined below.

GENERAL DOSE METHOD

The doses for each contactor in each stage in the workbook are calculated using the following method:

- The nuclide inventory of the contactor $\dot{m}_i$ (kg/d), specific activity of nuclides SA_i (Bq/g) and residence time t_{Rd} (days) are used to find the total activity expected in the contactor in 1 occupancy time (1 residence time).

$$A(Bq) = \sum_{Nuclides\ =i} SA_i \times 1000 \times (\dot{m}_i \times t_{Rd})$$

- The mass of solvent present in the contactor in 1 occupancy time is determined using the mass flow of solvent to the contactor $\dot{m}_s$ (kg/d) and the residence time t_{Rd} (days)

$$Mass\ of\ Solvent = \dot{m}_s \times t_{Rd}$$

- The number of decays in the solvent (Decays/kg) is determined using the above. Note, as Bq is decays per second, the residence time must be used in seconds t_{Rs} (seconds):

$$Decays/kg = \frac{A(Bq) \times t_{Rs}}{\dot{m}_s \times t_{Rd}}$$

$$Decays/kg = \frac{t_{Rs} \times (\sum_{Nuclides\ =i} SA_i \times 1000 \times (\dot{m}_i \times t_{Rd}))}{\dot{m}_s \times t_{Rd}}$$

- This assumes that all decays occur in the solvent - a deeply flawed assumption for some stages of the 2nd cycle of the Euro-GANEX process. Hence, we must add a factor to partition the decay energy between the aqueous and organic phase.

One should note that the branching ratios BR_{xi} and emission energies E_{xi} (J) are isotope dependent but the absorption terms φ_x are common for each emitted particle species.

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The exact nature of the absorption terms φ_x are outlined in the assumptions for α, β and γ dose, which follows in subsequent sections. φ_x is defined as:

$$\varphi_x = \left\{ \begin{array}{c} \varphi_\alpha = 1_{for\ alpha\ in\ solvent}\ ;\ 0_{otherwise} \\ \varphi_\beta = \dfrac{\dot{m}_{solvent\ in\ stage}}{\left(\dot{m}_{solvent\ in\ stage} + \dot{m}_{aqueous\ in\ stage}\right)} \\ \varphi_\gamma = \dfrac{\mathbb{G} \times \dot{m}_{solvent\ in\ stage}}{\left(\dot{m}_{solvent\ in\ stage} + \dot{m}_{aqueous\ in\ stage}\right)} \end{array} \right\}$$

$$\mathbb{G} = geometric\ gamma\ factor\ which\ accounts\ for\ attenuation\ in\ fluid\ and\ escape\ from\ contactor$$

Therefore, for each contactor, *j*, the dose (J/kg) to the solvent phase is:

$$Dose_j = \frac{t_{Rs} \times \sum_{Nuclides\ =i}\left\{(1000\ SA_i)(\dot{m}_i t_{Rd})(BR_{\alpha i}E_{\alpha i}\varphi_\alpha + BR_{\beta i}E_{\beta i}\varphi_\beta + BR_{\gamma i}E_{\gamma i}\varphi_\gamma)\right\}}{\dot{m}_s t_{Rd}}$$

As there are multiple contactors with different inventories within each stage, and several stages make up the system, it is necessary to sum up doses for each contactor to obtain a total dose. The absorption terms are dependent on the stage and contactor (or more correctly, contactor inventory) so have been expressed as functions of these variables in the expression for total dose below:

$$Dose_{TOTAL} = \sum_j \left(\frac{t_{Rs} \sum_i \left\{(1000\ SA_i)(\dot{m}_i t_{Rd})(BR_{\alpha i}E_{\alpha i}\varphi_\alpha + BR_{\beta i}E_{\beta i}\varphi_\beta + BR_{\gamma i}E_{\gamma i}\varphi_\gamma)\right\}}{\dot{m}_s t_{Rd}} \right)_j$$

$$Where: \quad \begin{array}{l} (i)\ is\ an\ index\ of\ all\ nuclides \\ (j)\ is\ an\ index\ over\ all\ contactors\ in\ a\ stage \end{array}$$

α DOSE TO SOLVENT

The α dose is assumed to be 100% of the α particles emitted by a radionuclide dissolved within the solvent. This approximation is justified based on the very short range of α particles in fluids and is conservative in the present context. Ehmann and Vance suggests that for a 5.5 MeV α particle, the range is approximately 48 µm in water [8].

$$range\ (mg\ cm^{-2}) = 0.173\ E^{3/2}A^{1/3}$$

Where E is in the energy of the α particle and A is the (average) atomic mass number of the medium. The range in mg/cm^2 is divided by the density to give a range in cm.

Using the same method and equation as above the ranges for a 5.5 MeV α particle are as follows:

- TODGA – 48.89 µm
- OK – 53.92 µm

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- HNO_3 – 36.19 µm
- DMDOHEMA – 49.20 µm

The 'Alpha Ranges' sheet of the workbook determines the average α particle energy for each stage of the process (and each stream within that stage). This is then used along with the chemical composition of the fluids to deduce an average range in the solvent for each stage. Previous studies with centrifugal contactor systems have established that the solvent bubbles are approx. 40–70 µm in diameter. This is of a similar magnitude to the range of the α particles in each stage of the process [9]. This allows us to make the pessimistic assumption that for an α particle emitted in a solvent phase, all energy is transferred to the solvent. In reality, the expected range of the particles in the solvent is usually larger than the radius of the solvent bubble so some energy will escape. Likewise, energy deposition resulting from an α particle traversing from solvent to aqueous back to solvent (bubble to bubble) is assumed to be negligible because the range of the α particle is so short.

For any α emitting nuclei that are assumed to not be in the solvent (e.g. the small amount that escapes with the FP waste) the assumed α dose to solvent is 0. It should be noted that the effects of water and process additives, AHA, BTP and CDTA, have been neglected here.

β DOSE TO SOLVENT

As the range of the β particles is much greater than that of the α particles, the previous assumption of 100% absorption would be too conservative. Instead, the range corresponding to the average β energy deposited during each stage of the process has been determined. The absorption process is similar to the process alluded to for α radiation. One key difference is that the range-energy relation for β was not calculated. Instead, the NIST eStar web application was utilised [10].

The eStar web application takes a chemical formula and density for a user inputted material and calculates the expected range of β particles at a variety of energies. The underpinning mathematics of this application can essentially be thought of as a modified Bethe equation. Unfortunately, the eStar application does not account for the molecular form of species only the atomic components. TODGA and DMDOHEMA are very specifically structured molecules (as opposed to amorphous solids) and, hence, the eStar data for these may be somewhat in error where it does not account for polarizability, electronegativity and other molecular properties. However, the values for HNO_3, H_2O and OK (assumed to be dodecane) are likely to be a good approximation due to the relative simplicity of the molecules. The output of this analysis is that the expected β ranges for each stage are above 550 µm. This is significantly larger than the size of the solvent bubbles (40-70 µm) found in contactor trials [9].

Therefore, the β dose is partitioned between both solvent and aqueous phases since the β particles can traverse many bubbles of solvent without being completely absorbed. For ease (and lack of further assumptions) the energy deposition can hence be assumed to be proportional to the mass of solvent in a stage divided by the total mass of solvent and aqueous in a stage. It should be noted that the effect of H_2O has been neglected here.

γ DOSE TO SOLVENT

Unlike the α and β cases previously discussed, γ radiation is deeply penetrating and will travel through large amounts of matter. Consequently, for γ radiation it is necessary to calculate the amount of energy that escapes the contactor.

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The geometry of the contactor is complex and the fluid inside forms an annulus around the edge. In an ideal case, the γ dose assessment in a contactor would be calculated numerically. In principle, this could be performed using established modelling codes if the full contactor structure was defined. However, this is computationally demanding. Therefore, for the present purposes a simple approximation is considered appropriate and fit-for-purpose for a user-friendly Excel solution.

In this approximation the contactor is treated as an equivalent sphere of the same volume as the contactor. This simplification is displayed graphically below in Figure 23. In this approximation the dose from γ rays emitted from any single point should be calculated as the integral over the solid angle range of the exponential attenuation of gamma rays to the surface of the sphere. However, an analytical solution is not possible. Consequently, a further simplification is made by evaluating the average path length from a point distance *x* from the origin to the surface of a sphere; see Appendix. The average path $\bar{r}$ calculated for *x*=*R*/2 is taken to be reasonably representative for all fluid in the contactor.

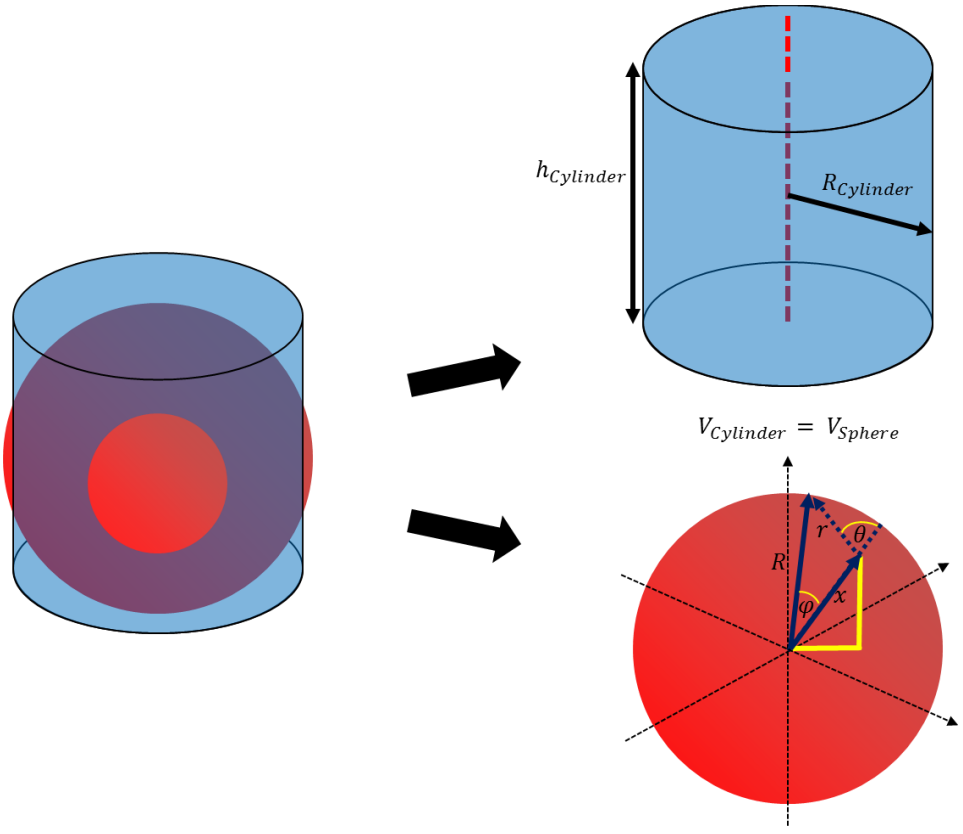


Figure 23: The cylindrical to spherical geometry approximation.

Using this assumption, an estimate for γ absorption is calculated assuming:

$$I = I_0 e^{-\mu_{Lin}\bar{r}} = I_0 e^{-\frac{\mu\bar{r}}{\rho}}$$

Where I_0 is the initial intensity, I is the intensity after traversing a distance $\bar{r}$, μ is the mass attenuation coefficient and ρ is the density of the medium.

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Each stage must be considered separately because each stage will have a different average γ energy and a different fluid inventory (amounts of solvent and aqueous).

Since the materials are known, as is the average γ energy for each stage, the linear attenuation coefficient 'μ_{Lin}' can be determined:

$$\mu_{Lin_{\bar{E}_\gamma}} = \sum_{i=fluids} \mu_{Lin;i_{\bar{E}_\gamma}} \left(\frac{m_{i\ in\ stage}}{m_{total\ in\ stage}}\right)$$

$$\mu_{Lin_{\bar{E}_\gamma}} = \sum_{i=fluids} \frac{\mu_{i_{\bar{E}_\gamma}}}{\rho_i}\left(\frac{m_{i\ in\ stage}}{m_{total\ in\ stage}}\right)$$

$$\mu_{Lin_{\bar{E}_\gamma}} = \sum_{i=fluids} \left(\frac{1}{\rho_i}\right)\left(\frac{m_{i\ in\ stage}}{m_{total\ in\ stage}}\right) \sum_{j=elements} \mu_{j_{\bar{E}_\gamma}} \left(\frac{A_j}{A_{Molecule}}\right)$$

$$\mu_{Lin_{\bar{E}_\gamma}} = \sum_{i=fluids} \left\{\left(\frac{\mu_{C;i_{\bar{E}_\gamma}} A_C}{A_{Molecule}}\right) + \left(\frac{\mu_{N;i_{\bar{E}_\gamma}} A_N}{A_{Molecule}}\right) + \left(\frac{\mu_{O;i_{\bar{E}_\gamma}} A_O}{A_{Molecule}}\right) + \left(\frac{\mu_{H;i_{\bar{E}_\gamma}} A_H}{A_{Molecule}}\right)\right\} \left(\frac{1}{\rho_i}\right) \left(\frac{m_{i\ in\ stage}}{m_{total\ in\ stage}}\right)$$

As can be seen, the mass attenuation coefficient for each element is first weighted by the atomic mass fraction of that element within the molecule (e.g. carbon in TODGA). The sum of these terms gives the effective total molecular mass attenuation coefficient for each molecule (i.e. HNO_3, TODGA, OK…). Next the total molecular mass attenuation coefficient is divided by the fluid density to give rise to a total molecular linear attenuation coefficient. This term is further weighted for each fluid by the mass of that fluid in the current stage of the system. The sum of these weighted linear attenuation coefficients gives a total effective linear attenuation coefficient for the stage of the process. This linear attenuation coefficient for all of the contents of the stage can then be used to calculate the absorption:

$$Absorption = \left(1 - \frac{I}{I_0}\right) = \left(1 - e^{-\mu_{Lin_{\bar{E}_\gamma}} \bar{r}}\right)$$

Since the absorption goes into both aqueous and solvent, only a fraction of this absorbed γ energy will be deposited in the solvent. This is assumed to be proportional to the mass fraction of the solvent in the stage.

$$Absorption\ (solvent) = \left(\frac{m_{solvent}}{m_{solvent} + m_{aqueous}}\right)\left(1 - e^{-\mu_{Lin_{\bar{E}_\gamma}} \bar{r}}\right)$$

USING THE MODEL

The model itself has been commented throughout to guide the user in obtaining information from it. There is an 'intro' sheet that provides much of the information provided below and in the first instance the user is advised to go and use the model and run test cases, altering the allowed parameters. The model is devised so that the user can input information in Cells that have no shading. Information and notes are provided in boxes shaded in yellow. For the most part the user should only need to use the 'data input' sheet with all other sheets performing calculations and providing the user information about those calculations. Where the information is in blue shaded cells it relates to α radiation, where it is red it relates to β radiation and where it is green it relates to γ radiation.

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In its simplest form the user simply pastes a FISPIN in to the 'data input' sheet and is provided a dose per pass through the flowsheet. This dose is broken down in to the various components, α, β and γ and the section of the flowsheet that it originates from. However, there are quite a few variables that the user can alter to adjust the flowsheet and understand the effect of certain variables.

FUEL HISTORY

The initial FISPIN input parameters clearly have a large effect on the dose received by the solvent. This input is defined by the initial fuel make-up, burn-up, cooling time and dissolution parameters. Once the FISPIN model has been evaluated for the chosen fuel type, history and cooling all the user must do is copy the predicted fuel composition (isotopes and masses) in to the allowed part of the 'input sheet'. For example, the data should take the form of:

H 1	0.0106362
H 2	0.0076935
H 3	0.12626

That is, the element symbol and actual isotope in the first column and the mass present in grams per tonne of fuel in the second column. The sheet will report any issues, such as the inclusion of 'TOTALS', which the user must remove.

FLOWSHEET SETUP

The model should initially be setup with the number of stages for each section of the flowsheet that were used in the gProms model. However, this can be changed by altering the values in column "T" of the 'input sheet'. Changing these values will change the amount of dose the solvent absorbs. Likewise, it is possible to change the contactor where the separation actually occurs, this again will change the absorbed dose. Altering these parameters will also change the visual display of the relevant section of the flowsheet.

CONTACTOR PARAMETERS

It is also possible to change the type of contactor that is used for the separation process. This has a marked effect on all flow rates and γ absorption across the flowsheet. The options that are available are all commercially available contactors from CINC Industries [7].

POTENTIAL FUTURE IMPROVEMENTS

There are many possible optimisations and improvements to the workbook. These have been separated in to themes indicating the type of improvement they provide. It should be noted that there are likely other possible improvements, these are simply those that have been identified during the design process.

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MODEL/INFORMATION INPUT

- The change in stream contents over the separation within a contactor bank should be treated more gradually. In the current workbook there is an abrupt change from one stream to another at the point where the loaded solvent is added to the system. This is a relatively simple improvement once the correct profile for mixing is understood. One can simply assign a multiplier to the parameters in the relevant cells, e. g. “BB7” on the data sheet following the process outlined here:

=IF('Input Sheet'!U$15="FP Loaded Aq",$AT12*'Input Sheet'!$BD7,

IF('Input Sheet'!U$15="HM Loaded Solvent",$AT12*('Input Sheet'!$AU7+'Input Sheet'!$BA7+'Input Sheet'!$AX7+'Input Sheet'!$BG7),

IF('Input Sheet'!U$15="FP Separation Stage",$AT12*'Input Sheet'!$BD7*multiplying function which dictates mixing,"Error")))

+ Additional stages and relevant multiplied parameters.

- The spreadsheet can be further developed to account for those problematic dissolved metals that undergo a complex route through the system. For example, Sr can be recycled between the TRU Extract and TRU Scrub stages, thereby increasing its concentration above expected feed levels and depositing energy whilst it does this. Hence, the total dose from these problematic elements is likely to be underestimated. The fact that the overall dose from all species in a single pass is of the order of kGy it is likely that even if this were treated more explicitly it would not increase the overall dose that much.
- The workbook does not account for any hold-up in the process and hence dose whilst the solvent is stationary in tanks, traversing in pipes between stages, etc. The workbook essentially models the process as a system of contactors with no breaks in between. Once again, these additional steps could be added as additional stages in the ‘data sheet’.
- The branching ratio for γ energies would be a very beneficial data set to have. Currently, the ratio is normalised to 100% whenever an isotope has a photon energy in ICRP 107. This is likely a large over-estimation in γ dose since the dose is linearly proportional to the branching ratio for each nuclide.

CALCULATION IMPROVEMENTS

- The α, β and γ dose absorption could be evaluated in a more sophisticated way:
  - The α dose could be partitioned between the solvent and aqueous phase with further knowledge of bubble properties, size distribution and micelle extractant-metal micelle formation and location within the bubbles.
  - The β and γ attenuation by the fluid could be determined experimentally using a simple attenuation apparatus. This would provide a better understanding of the absorption and range of the radiation in the mixed fluid.
  - The β/γ attenuation could be handled a little more rigorously by ‘binning’ energy ranges and calculating individual path lengths and weighting them by the incidence rate as opposed to averaging over all as has been done here.

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- The γ ray dose in the contactor could be calculated much more rigorously. The spherical approximation used is an adequate first estimate, but a more rigorous model could be designed in software such as MicroShield or by Monte Carlo simulation to better understand the full effect of the contactor geometry.
- Each individual contactor is assumed to have no effect on any other i.e. where a γ ray escapes a contactor it is lost to the system and does not then enter adjacent contactors. This could be accounted for when undertaking the above Modelling for γ ray dose.

MODEL EXTENSION

- The spreadsheet could be altered to provide a degradation estimate (using G-values/dose coefficient to understand a loss of extractant or build-up of degradation products including hydrogen) for the solvent. It is possible that these degradation products could inhibit the operation of the system – the workbook does not account for this.

FINAL REMARKS

This model has been produced to guide further research, discussion and plans around next generation fuel cycles. It is by no means perfect. It is designed to provide indicative values/orders of magnitude of absorbed dose to an organic phase during the recycling of spent nuclear fuel. It was written by a single individual over a few months to help provide information to guide further work. The underlying model has been through a formal checking and approval process within NNL but the values it produces should be used as indicative only due to the large number of assumptions and approximations involved. However, the aim of producing the model was that it might go some way towards answering the questions:

- What dose matters?
- What dose will the solvent experience in reprocessing?

In a next generation reprocessing plant:

- What solvent management strategy do you need to account for:
  - Loss of extractant,
  - Build-up of degradation products and,
- What is a reasonable solvent inventory to hold in a plant?

It begins to provide some answers to these questions (see next section) and with careful use will help guide further work in the field and planning of R&D for next generation fuel cycles.

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PRELIMINARY ASSESSMENT OF SOLVENT DOSE IN EURO-GANEX FLOWSHEET

A preliminary assessment of the radiation dose to the solvent in the EURO-GANEX flowsheet has been carried out using the model described in the previous section. The intention of this assessment is to provide an estimate of the dose to the solvent for a single pass through the flowsheet and the total accumulated dose for a period of extended operation, in order to allow the extent of solvent degradation in the process to be estimated.

REFERENCE FISPIN

It is not possible to define a typical fuel composition for a fast reactor fuel due to the variation in GenIV reactor and fuel types that may be employed. The final composition of any reactor fuel will vary greatly, depending on a range of factors, including:

- Initial enrichment
- Other TRU isotopes
- Burn-up – Typically > 80GWd/te for fast reactors but possibly double this value (150 GWd/te)
- Irradiation time sequence
- Loading position in the reactor
- Power rating
- Decay storage

Consequently, a reference FISPIN for a GenIV gas cooled reactor was proposed under the ACSEPT project [1] to provide a basis for defining feed compositions of the chemical separation processes under development. This reference FISPIN was simply intended to provide key features of a fast reactor type fuel i. e. greater Pu content, higher minor actinide content and high heat loading, for comparison with a typical LWR fuel. The FISPIN was generated for a theoretical MOX fuel for a gas cooled fast reactor. The reactor was assumed to be loaded with MOX fuel composed of two different types for the inner and outer core zones, which had differing actinide content and Pu isotopic composition. The mass loading ratio of the inner:outer fuel in the reactor was approximately 2:3. The Pu + Am content of the fuel was 14% and 18% for the inner and outer fuel respectively. The initial uranium enrichment of the fuel was 0.7% (i. e. natural) and the fuel was subjected to an average burnup of ~90 GWd/t.

FISPINS were generated for this fuel composition based on cooling times of 1 to 10 years after discharge from the reactor. These FISPINS have been used as the basis for evaluating the dose accumulated by the solvent in the concept EURO-GANEX flowsheet.

FLOWSHEET

The accumulated solvent dose is based upon the concept EURO-GANEX flowsheet (Figure 24) [2]. This flowsheet has been scaled to provide a total fuel throughput of 5 te/d[5]. It is assumed that the first GANEX cycle has removed

[5] Note: the 5 te/d throughput has been selected to enable easy comparisons with commercial scale thermal oxide reprocessing plants rather than based on the likely throughput for a FR fleet and fuel cycle. Effects of throughput and other parameters can be analysed by future modelling studies.

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the bulk of the uranium from the feed and that the raffinate from the first cycle has been conditioned to provide the active feed to the EURO-GANEX flowsheet.

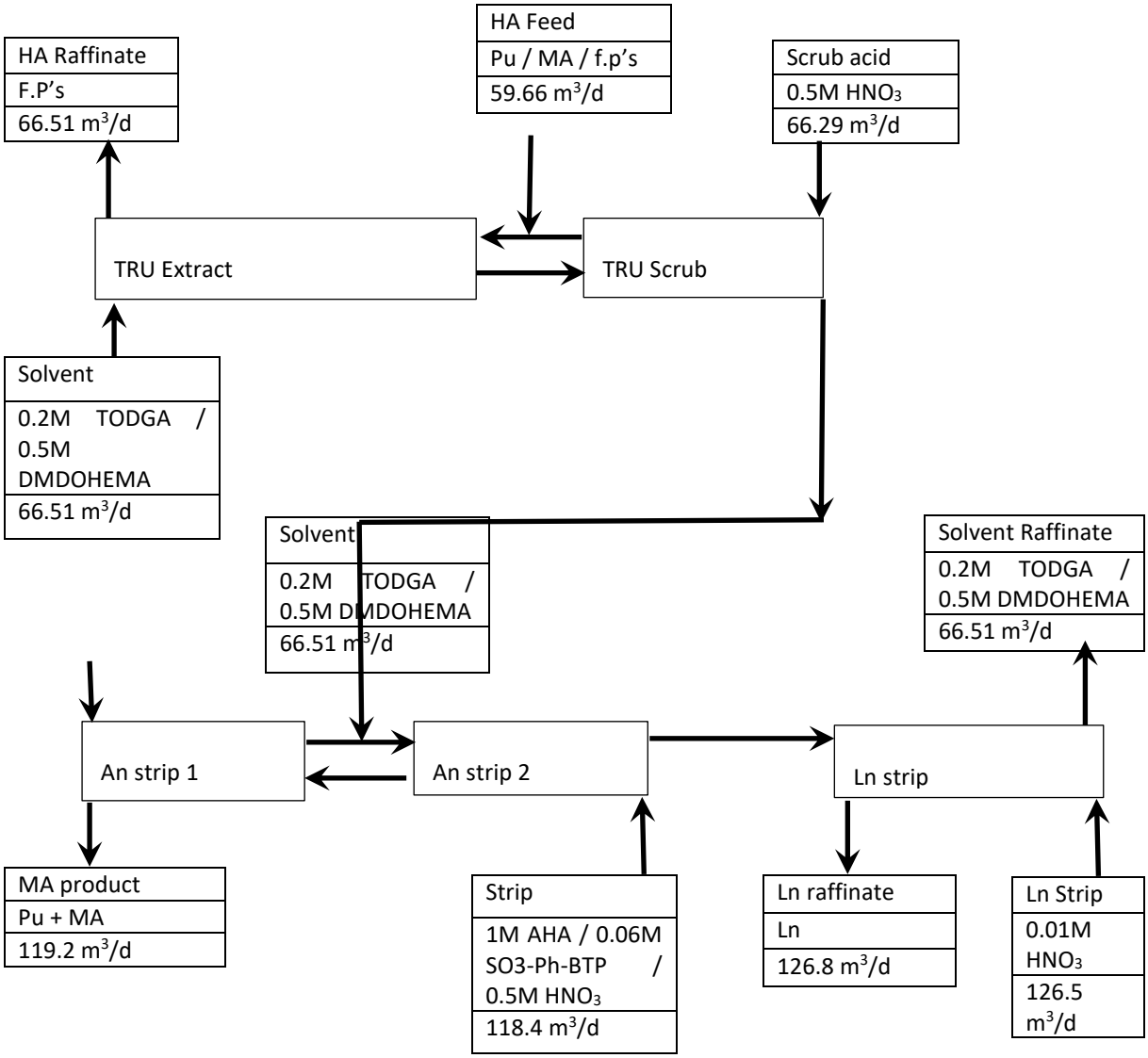


Figure 24. Outline of concept EURO-GANEX flowsheet for a process operating at 5te/d HM

ASSUMPTIONS

The calculation of the solvent dose in the EURO-GANEX process was based on a number of assumptions, which are summarised below:

Centrifugal contactors:

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- The size of contactors was selected based on the assumption that the total flow rate (aqueous + organic feeds) through the contactor is up to 50 % of the maximum throughput. Consequently, the CINC V16 centrifugal contactors (40cm diameter rotor) were used as the basis for determination of residence time in the contactors.
- The volume of the aqueous and solvent inside each contactor assumed to be equivalent to the S/A ratio of the feed flow rates.
- The hold-up volume in contactors calculated based on the manufacturers data for the filling volume. In this case the data from CINC V16 (40cm diameter) contactors was used.

Flowsheet and process assumptions:

- It was assumed that the number of stages in the flowsheet were based on the concept GANEX flowsheet: TRU extract (12 stages), TRU scrub (4 stages), An strip 1 (6 stages), An strip 2 (6 stages) and Ln strip (4 stages)
- The flow rates are based upon the concept EURO-GANEX flowsheet operating with a throughput of 5 te/d HM (U+Pu).
- Assumed that maximum solvent loading of ~ 10 g/l is employed for the process. Use of a higher loading would reduce the solvent volume / flow rate required.
- The total volume of solvent in the process, based upon the number of contactors and hold up volume of each stage, is approximately 1 m^3.
- The extraction and backwashing of species from the solvent is assumed to occur at single stage within the bank of contactors. This is not entirely correct as the concentration profile across the contactors will change across several stages. However, this assumption simplifies the calculations and allows estimation of the solvent dose.
- The dose model does not take account of recycle in the contactors and the concentration in the solvent phase is assumed to remain constant after extraction. This is reasonable for the majority of species, except Np, Sr and Fe, that are known to recycle within the extract-scrub section.
- The dose was calculated for a single pass of the solvent through the flowsheet.

Alpha radiation

- It was assumed that all the energy from alpha decay of species present in the solvent will be absorbed by the solvent phase. The range of alpha particles in the solvent phase was estimated to be within the range of the droplet size, 40 to 70 microns , measured in the contactors [3].

Beta radiation

- It was assumed that there was no loss of beta radiation from the contactor (i.e. all beta energy absorbed in aqueous and solvent phase)
- The proportion of the beta energy absorbed was assumed to be directly proportional to the mass fraction of solvent phase present in the contactor.

Gamma radiation

- It was assumed that the proportion of gamma energy that escaped from the contactor was estimated based upon a weighted average of the gamma energy present in the contactor and the average distance to the surface of a sphere of equivalent volume to the contactor.

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- The gamma radiation from adjacent contactors was not included in the estimate.
- Proportion of absorbed gamma dose to the solvent was assumed to be directly proportional to the mass fraction of solvent present in the contactor.

RESULTS AND DISCUSSION

There are a number of factors that will have an impact upon the accumulated dose to the solvent in the process, including:

- Fission product inventory of the fuel
- Fuel cooling time
- Pu (and MA/Ln) loading of the solvent phase
- Residence time in the contactors (which is a function of flow rate, contactor hold-up volume and total number of contactors in each section of the flowsheet).
- Inventory of the solvent in the process.

An initial assessment of the dose to the solvent in the EURO-GANEX process was carried out to consider the effect of fuel cooling times of 1, 2 5 and 10 years upon the dose received by the solvent for a single pass through the flowsheet. Table 9 summarises the data for the solvent dose, due to alpha, beta and gamma radiation in each section of the flowsheet.

Unsurprisingly, the majority of dose to the solvent occurs in the TRU extract and scrub contactors, due to the presence of the beta/gamma emitting fission products in the aqueous phase and the extraction of the alpha emitters (Pu and minor actinides) in the solvent phase. Therefore, modifications of the TRU extract/scrub section of the flowsheet, such as increasing Pu and MA loading of the solvent or factors that affect residence time (flowrate, size of contactors, number of stages), would have a significant impact upon the radiation dose to the solvent in the process. The beta/gamma dose to the solvent in the latter stages of the flowsheet (An strip and Ln strip) is primarily due to the presence of the lanthanides. The results also show that there is no contribution from alpha radiation to the solvent dose in An strip1. This is due to the assumption the Pu and minor actinides are present in the aqueous phase, after being stripped from the solvent, and that the corresponding dose due to alpha radiation will be absorbed entirely by the aqueous phase. In reality, there is likely to be a contribution to the solvent dose from alpha emitters present in the aqueous phase and this is an area that requires further refinement. It should also be noted that the model assumes instantaneous transfer from aqueous phase to organic phase in the extract contactors and vice versa for the backwash contactors. In reality, the concentration profile for a species across a block of contactors would be more gradual and this is another area that requires further refinement of the model.

The model results indicate that, for these flowsheet parameters, the expected radiation dose to the solvent for a single pass through the process decreases from approximately 340 Gy for 1 year cooled fuel to 127 Gy for 10 year cooled fuel. Obviously, this is dependent upon the FISPIN data used, flowsheet conditions (Pu loading of the solvent / flowrates) and process parameters (size and number of contactor stages).

Although this gives the expected dose to the solvent for a single pass through the flowsheet, it is not sufficient to assess the extent of solvent degradation within the process and the impact that this may have upon the management and recycle of the solvent. In this case, it is also necessary to consider both the solvent inventory of the process and a period of extended operation.

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Table 9. Estimated radiation dose to solvent in EURO-GANEX process (for a single pass through the flowsheet)

Cooling time	Stage	Alpha Dose (Gy)	Beta Dose (Gy)	Gamma Dose (Gy)	Total (Gy)
1 yr	TRU Extract	48.65	47.65	12.57	108.86
	TRU Scrub	140.41	41.38	2.20	183.99
	An Strip 2	19.80	18.15	0.92	38.87
	An Strip 1	0.00	0.20	0.04	0.24
	Ln Strip	0.03	5.75	0.27	6.05
	Total	208.89	113.12	15.99	338.00
2 yr	TRU Extract	33.63	25.36	9.24	68.23
	TRU Scrub	97.06	17.52	1.38	115.96
	An Strip 2	13.69	7.65	0.57	21.91
	An Strip 1	0.00	0.18	0.03	0.21
	Ln Strip	0.02	2.42	0.17	2.61
	Total	144.41	53.13	11.38	208.92
5 yr	TRU Extract	28.81	6.77	6.09	41.67
	TRU Scrub	83.14	1.77	0.72	85.63
	An Strip 2	11.73	0.72	0.29	12.74
	An Strip 1	0.00	0.15	0.03	0.18
	Ln Strip	0.02	0.22	0.08	0.33
	Total	123.70	9.63	7.21	140.54
10 yr	TRU Extract	27.36	3.82	4.54	35.72
	TRU Scrub	78.96	0.34	0.47	79.77
	An Strip 2	11.14	0.11	0.18	11.43
	An Strip 1	0.00	0.12	0.04	0.15
	Ln Strip	0.02	0.03	0.05	0.10
	Total	117.48	4.42	5.28	127.18

The total solvent inventory in the process will have an impact upon the accumulated dose to the solvent as it will determine the frequency with which the solvent is recycled through the flowsheet each day. The total hold-up volume of solvent in the centrifugal contactors used for the solvent dose calculations is approximately 1 m^3. As the total flowrate of solvent in the concept EURO-GANEX flowsheet is approximately 126 m^3/d there is scope to operate the process with a solvent inventory substantially less than 126 m^3. This may be desirable when considering the cost of the extractants required for the process. However, for a conventional separations plant used for fuel reprocessing, the total solvent inventory is generally equivalent to 1 day of operations at 5 te/d throughput. Therefore, for the purpose of this assessment a solvent inventory range of 10 m^3 to 126 m^3 was considered.

In order to determine the impact of accumulated radiation dose upon the extent of solvent degradation in the process a period of extended operation was also considered. The concept design for the EURO-GANEX flowsheet was based upon the assumption that the process will operate for a total of 200 days (24 hours per day) within a

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1 year period. This is equivalent to a plant with a 1000 te/yr capacity and is consistent with the design basis for conventional thermal oxide reprocessing plants.

Table 10 summarises the total solvent dose calculated for 1 year of operation (assuming 200 operational days per year) with fuel cooling times from 1 to 10 years and for a solvent inventory of 10, 50 and 126 m^3. For a process operated with a smaller solvent inventory this will obviously increase the frequency which it is recycled through the flowsheet and leads to a higher accumulated dose. For example, a solvent inventory of 10m^3 would lead to the solvent being cycled through the flowsheet > 12 times in a single day (based on a solvent requirement of 126 m^3/d in the concept design flowsheet).

Table 10. Summary of total accumulated solvent dose for a single pass through the flowsheet and for 1 year of operation

Solvent inventory / m^3		10	50	126
Cooling time	Dose for single pass through process	Accumulated dose for 1 year of operation		
yr	kGy	kGy	kGy	kGy
1	0.338	852	170	68
2	0.209	526	105	42
5	0.141	354	71	28
10	0.127	320	64	25

(Note: total accumulated dose for 1 year based on 200 operating days)

Figure 25 shows the increase in accumulated dose to the solvent over a period of 200 days for a 1 year cooled fuel with a process solvent inventory of 10, 50 and 126m^3. Based on the model calculations the total accumulated solvent dose for the concept EURO-GANEX flowsheet during 1 year of operation would be expected to be between 68 to 852 kGy per year for a 1 year cooled fast reactor fuel.

There is a contribution from alpha, beta and gamma radiation to the total solvent dose. Each radiation type can have a different effect on the radiolysis and this is normally attributed to the linear energy transfer (LET) rate. A higher LET causes more ionisation events in close proximity, which increases the likelihood of recombination reactions rather than secondary ionisation events. Alpha radiation has the highest LET, followed by beta and finally gamma. Therefore, gamma radiation tends to produce greater degradation so will represent a worst case scenario relative to a mixed radiation source. The change in the concentration of a species for a given absorbed dose can be calculated based on the G-value. The G-value represents the change in the number of molecules per unit of energy absorbed, typically this can be expressed as number of molecules per 100eV or $\mu mol.J^{-1}$. However, the G-value is often not constant across the dose range due to the occurrence of multiple competing reactions. Consequently, the use of a dose constant (d), has been suggested [4] to account for this variation where the dose constant is defined as:

$$[C] = [C_0].\exp^{(-d.D)}$$

Where C_0 is the initial concentration and C is the concentration of the species for the absorbed dose, D. Sugo et al. [5] has reported dose constants of 2.2×10^{-6} Gy^{-1} for TODGA and 1.2×10^{-6} Gy^{-1} for DMDOHEMA. The predicted solvent dose was used in conjunction with the dose constants for TODGA and DMDOHEMA to consider the effect upon the degradation of TODGA and DMDOHEMA in the flowsheet over time.

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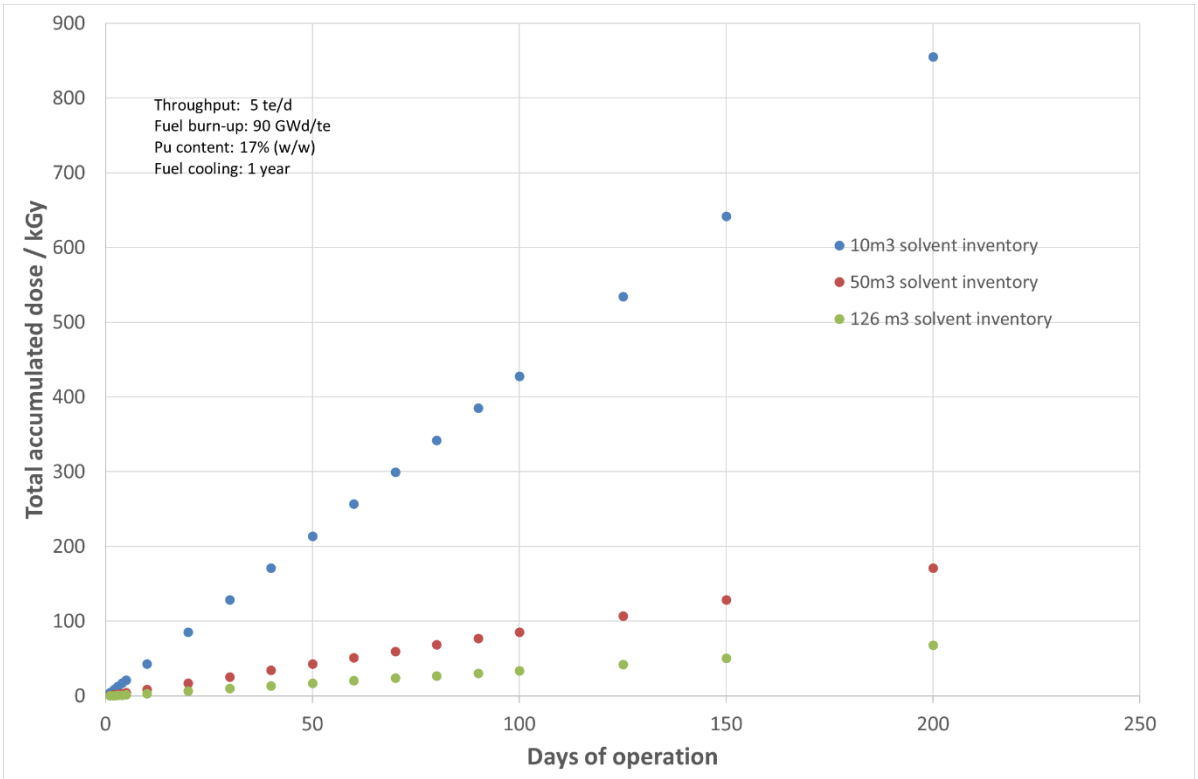


Figure 25. Impact of solvent inventory upon total accumulated solvent dose

Figure 26 and Figure 27 present the predicted change in the concentration of TODGA and DMDOHEMA respectively, at various fuel cooling times and with a solvent inventory of 50 m^3 in the process assuming that there is no addition of fresh solvent to the process. Table 11 summarises the predicted concentration of TODGA / DMDOHEMA present in the EURO-GANEX flowsheet after 1 day and 200 days of operation, assuming that no action is taken to correct the composition.

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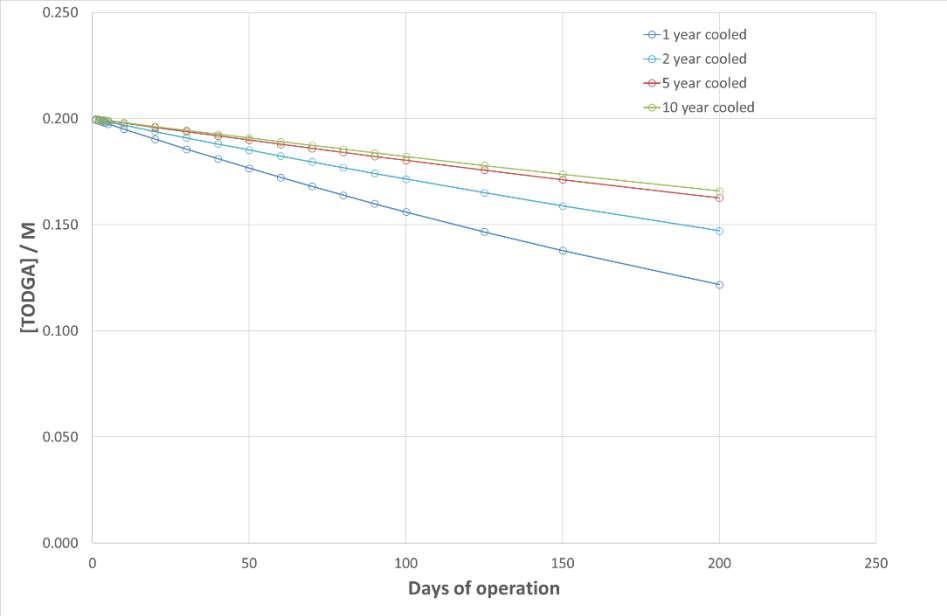


Figure 26. Predicted degradation of TODGA in EURO-GANEX flowsheet for different fuel cooling times (assumed 50 m³ solvent inventory)

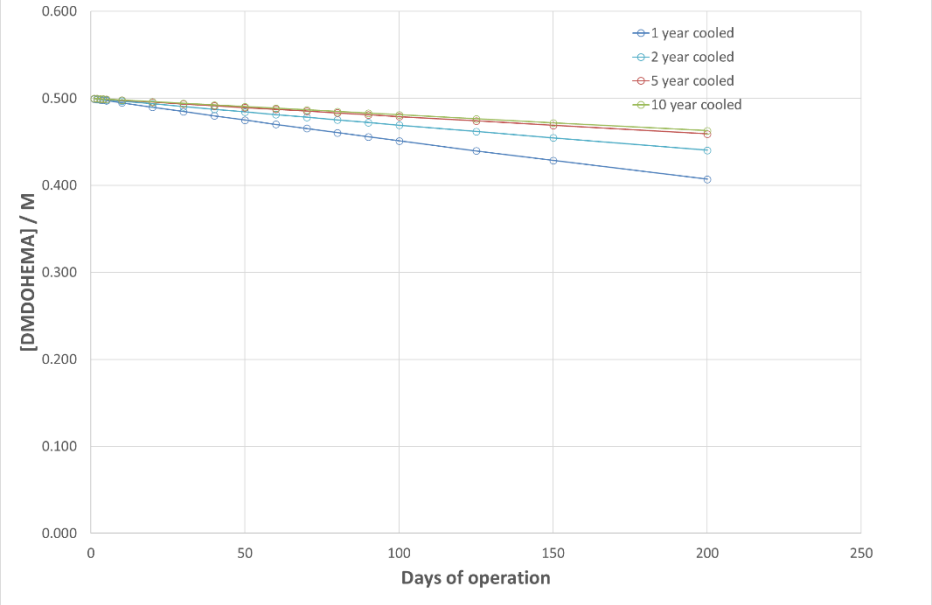


Figure 27. Predicted degradation of DMDOHEMA in EURO-GANEX flowsheet for different fuel cooling times (assumed 50 m³ solvent inventory)

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Table 11. Predicted change in TODGA/DMDOHEMA concentration due to radiolysis in EURO-GANEX flowsheet (based on 50m³ solvent inventory)

	After 1 day		After 200 days	
Fuel cooling time / y	[TODGA] / M	[DMDOHEMA] / M	[TODGA] / M	[DMDOHEMA] / M
1	0.200 (-0.2%)	0.499 (-0.1%)	0.122 (-39%)	0.407 (-18%)
2	0.200 (-0.2%)	0.500 (-0.1%)	0.147 (-26%	0.440 (-12%)
5	0.200 (-0.1%)	0.500 (<-0.1%)	0.163 (-18%)	0.459 (-8%)
10	0.200 (-0.1%)	0.500 (<-0.1%)	0.166 (-17%)	0.463 (-7%)

(Note: figure in parentheses show % decrease in predicted concentration)

The accumulated dose in the process for 1 day of operation results in very little change in the solvent composition (typically < 0.2%). It is expected that this would be corrected by daily additions to the process to maintain the desired solvent composition. An engineering solution to this degradation is to install a small volume daily solvent purge where a small proportion of solvent is removed from the process and replaced with fresh solvent. This maintains the solvent composition and allows gradual replacement of the solvent inventory over a period of time. In addition to providing adjustment of the solvent composition the daily solvent purge also helps to ameliorate the impact of degradation products that are not readily removed by the solvent wash process and gradually accumulate in the solvent over time.

The management of the TODGA/DMDOHEMA composition in the solvent will be relatively simple in the flowsheet. However, it is also necessary to remove degradation products that would otherwise accumulate and interfere with the flowsheet performance. Consequently, it is also relevant to consider the concentration of the TODGA and DMDOHEMA degradation products that would be present due to radiolysis of the solvent from a single pass through the flowsheet. This would allow assessment of the levels of the degradation products present in the solvent feed to any solvent wash / recycle process and also accumulation of degradation products that are not readily removed by the solvent wash.

The primary degradation products for TODGA and DMDOHEMA have been identified and are shown in Figure 28 and Figure 29 respectively.

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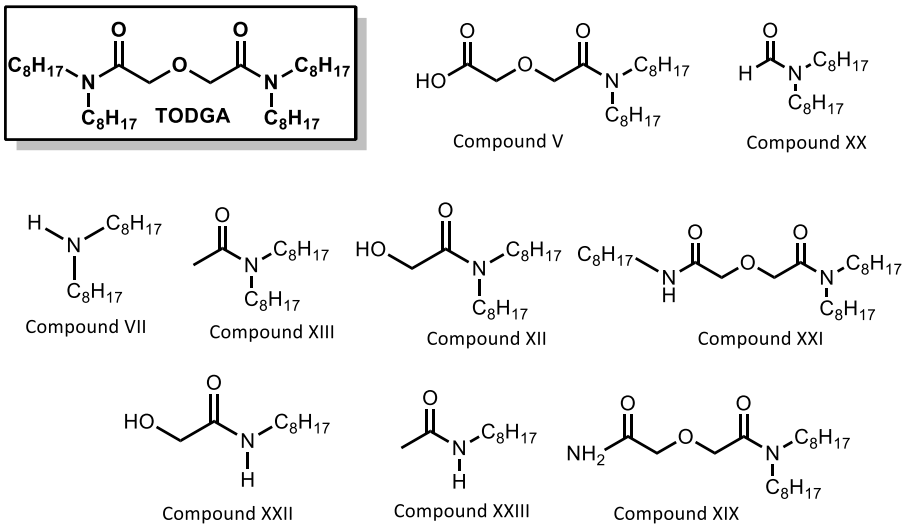


Figure 28. TODGA degradation products

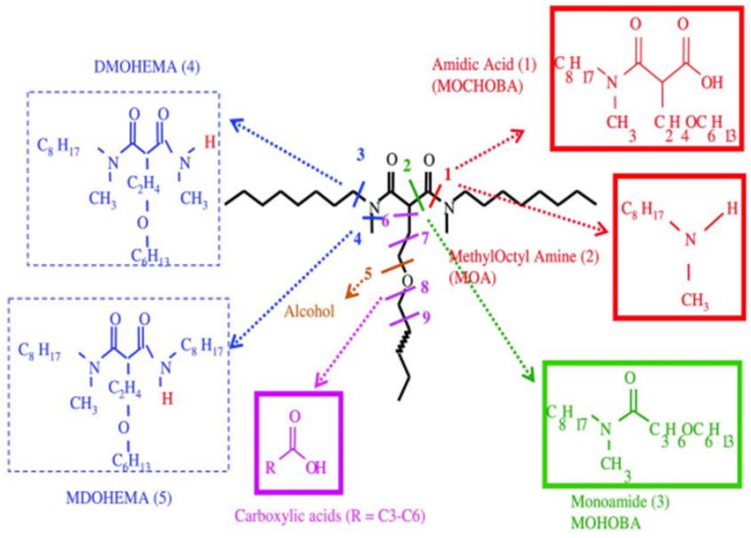


Figure 29. DMDOHEMA degradation products [6]

However, there are no specific G values or dose coefficients for the individual degradation products that can be used to calculate the concentration of these species in the solvent for a given absorbed dose. This is also complicated due to the number of potential degradation products that may be generated and the fact that these species may undergo further radiolysis to produce smaller secondary species. Therefore, the approach has been taken to assess the maximum concentration of these species that may be present based upon the decrease in the TODGA and DMDOHEMA concentration. The decrease in the TODGA and DMDOHEMA concentration due to radiolysis of the solvent was calculated based upon the total accumulated dose for a single pass through the flowsheet and the dose coefficients for TODGA (2.2×10^{-6} Gy^{-1}) and DMDOHEMA (1.2×10^{-6} Gy^{-1}). Table 9 12 summarises the calculated decrease in TODGA / DMDOHEMA concentration arising from solvent radiolysis with fuel cooling times of 1, 2 , 5 and 10 years.

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Table 12. Calculated change in the TODGA / DMDOHEMA concentration for a single pass through the EURO-GANEX flowsheet

Cooling time / y	Accumulated dose for single cycle / Gy	[TODGA] / M	[DMDOHEMA] / M	Δ[TODGA] / M	Δ[DMDOHEMA] / M
1	338.00	0.19985	0.49980	1.48×10^{-4}	2.02×10^{-4}
2	208.92	0.19991	0.49987	9.19×10^{-5}	1.25×10^{-4}
5	140.54	0.19994	0.49982	6.18×10^{-5}	8.43×10^{-4}
10	127.18	0.19994	0.49992	5.59×10^{-5}	7.63×10^{-5}

Although it is not possible to calculate the concentration of individual products this can be used to provide an estimate of the bounding concentration. Thus for TODGA degradation products, such as N,N-dioctyldiglycolamic acid (compound V), only one mole is produced per mole of TODGA that is degraded by radiolysis and for degradation products such as N,N-dioctylamine, 2 moles may be generated per mole of TODGA. Consequently, for 1 year cooled fuel, the maximum concentration for individual degradation products arising from radiolysis of the solvent would be in the range of 1.48×10^{-4} to 2.96×10^{-4}M.

Similarly, the maximum concentration of individual species arising from the degradation of DMDOHEMA in a single solvent extraction cycle can be inferred from the loss of DMDOHEMA from the solvent. Therefore, the upper concentration expected for species such as DHOHEMA and the acid amide in a single pass of the solvent through the process would be 2.02×10^{-4}M, while the maximum possible concentration for species such as MOA would be approximately 4.04×10^{-4}M.

In reality, the concentration for individual species will be lower than this as radiolysis will generate more than a single degradation product. However, the intention is that these values can provide a guide for further supporting work to assess the impact of solvent degradation products upon the process performance and assess the effectiveness of solvent clean-up methods.

CONCLUSIONS

A model created to calculate the dose to the solvent in the concept EURO-GANEX flowsheet has been used to consider the impact of the dose upon the degradation of the extractants, TODGA and DMDOHEMA, over time. This initial assessment has considered the impact of fuel cooling times (from 1 to 10 years) and the total solvent inventory upon the dose to the solvent and the corresponding impact upon the degradation of TODGA and DMDOHEMA.

The dose model results indicate that, for the flowsheet parameters used, the dose to the solvent for a single pass through the flowsheet decreases from 338 Gy for 1 year cooled fuel to 127 Gy for 10 year cooled fuel. Obviously, this will be depend upon factors, such as the fuel FISPIN, flowsheet parameters (Pu and MA loading) and process parameters (size of contactors and residence time).

During operation of the process, factors such as the total solvent inventory will also have an impact upon the total accumulated dose as this will influence the frequency of solvent recycle in the process. The total dose to the solvent for 1 year of operation with 1 year cooled fuel was estimated to be between 68 and 852 kGy for a solvent inventory between 126 m^3 and 10m^3 respectively.

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It is expected that the composition of the solvent can be readily maintained with a small volume daily purge that will allow the concentration of TODGA and DMDOHEMA to be adjusted and maintained within the flowsheet parameters.

An initial assessment of solvent degradation in the EURO-GANEX flowsheet has been carried out to provide an indication of the concentration of degradation products present in the solvent for a single pass through the process and that would subsequently enter the solvent clean-up / solvent wash. For a 1 year cooled fuel the maximum concentration for individual degradation compounds from TODGA and DMDOHEMA was estimated to be in the range of 1.48×10^{-4} to 2.96×10^{-4}M and 2.02×10^{-4} to 4.04×10^{-4}M respectively.

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CONCLUSIONS

Solvent degradation and associated clean up procedures have been reviewed for a range of processes used for spent fuel reprocessing and/or minor actinide partitioning. These include phosphate based reagents, such as TBP, and CHON based solvents. The clean up processes can be divided into (conventional) alkaline washes that introduce salt wastes into the system and more novel salt-free based washing processes. The latter are preferable from the waste management perspective but, whilst promising results have been obtained, significant R&D is still required to identify efficient, effective and safe options.

A review of previous solvent wash studies for the development of the DIAMEX process has shown that the degradation products from DMDOHEMA can be effectively removed using a combination of acid and alkaline washes. MOA can be effectively removed by the low acid scrub within the flowsheet or a low acid wash as part of the solvent wash regime. Alkaline washes using reagents, using NaOH / Na_2CO_3, removed the carboxylic acids and the acid amide from the solvent. Although the monoamide degradation product is not removed by acid or alkaline washes it was proposed that the accumulation of this species can be minimised by the continuous removal of the acid amide which is the precursor in the formation of the monoamide. Consequently, the only major DMDOHEMA degradation products that were considered to accumulate in the solvent were the diamides (MDOHEMA). However, this was not considered to be an issue within the DIAMEX process since the extraction behaviour was similar to that of DMDOHEMA. Therefore, this previous work suggests that the degradation products arising from DMDOHEMA in the EURO-GANEX process should be readily removed by a combination of dilute acid and alkaline washes.

Preliminary studies have been undertaken to evaluate the removal of TODGA degradation products from i-SANEX and EURO-GANEX solvent systems. This has shown that the degradation products from TODGA are more problematic to remove using conventional alkaline wash reagents. Whilst it is possible to successfully remove some acidic degradation products, such as DODGAA, using alkaline wash reagents it was not possible to remove other species, such as DOA, DOHyA or DOAA. Furthermore, testing of the solvent wash procedures using solvent that has been irradiated in the Nayade test loop highlighted some differences between 0.1M TODGA and the EURO-GANEX solvent. The tests with this solvent demonstrated that while DODGAA was removed from the EURO-GANEX solvent using alkaline washes, the same procedure was less effective for removing the degradation product from the 0.1M TODGA solvent. Therefore, further work is required to develop and evaluate solvent clean-up methods to remove TODGA degradation products.

The retention of certain fission products in the solvent presents a potential issue for the cycle and re-use of solvent in a flowsheet. The accumulation of fission products in the solvent may lead to a degradation of decontamination factors in the process and also contribute to an increased dose to the solvent. A range of complexants were assessed to remove fission products from the i-SANEX solvent. This showed that used of an aqueous wash with diglycolic acid or mannitol may provide an option for the removal of Sr and Mo from the solvent, while oxalic acid was suitable for stripping Zr. However, none of the reagents tested were capable of removing Ru or Pd from the solvent. The use of CDTA in the active feed also offers a means of improving the control of Zr and Pd to minimise retention in the solvent by suppressing their extraction.

The use of solid sorbents, such as macroreticular resins, may also provide an alternative option for the removal of problematic fission products from the solvent. Previous work has shown that these have been effective for the removal of fission products from solvent in the PUREX process.

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In the development of processes to clean-up and recycle the solvent it is also relevant to consider the extent of solvent degradation in the process to assess the levels of degradation products that would need to be removed to allow the recycle of the solvent. A solvent dose model has been created to assess the expected dose to the solvent within the EURO-GANEX flowsheet and this has been used to determine the dose to the solvent and the extent of solvent degradation for a single pass through the flowsheet:

- The radiation dose to the solvent in the concept EURO-GANEX process is dependent upon a number of factors including FISPIN (burnup, cooling time), flowsheet parameters (Pu loading, flow rates) and process parameters (number and size of contactors).
- The radiation dose to the solvent for a single pass through the concept EURO-GANEX flowsheet was calculated to be in the range of 338 Gy to 127 Gy for fuel with cooling times of 1 and 10 years respectively.
- The accumulated radiation dose to the solvent for 1 year of operation (200 operating days) was calculated to be in the range of 25 kGy to 852 kGy depending upon the fuel cooling time and the solvent inventory in the process.
- Although it is not possible to calculate the concentration of individual degradation products in the process for a given solvent dose, the loss of TODGA / DMDOHEMA from the solvent was used to provide a bounding concentration for an individual species.
- For a 1 year cooled fuel the maximum concentration for individual degradation compounds from TODGA and DMDOHEMA was estimated to the in the range of 1.48×10^{-4} to 2.96×10^{-4}M and 2.02×10^{-4} to 4.04×10^{-4}M respectively.
- Further testing of solvent clean-up methods should consider using degradation products within the concentration range expected for as single pass through the flowsheet.

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FURTHER WORK

Further development of the solvent dose model is required to provide a flexible model that can be adapted to other flowsheets and allows changes to the process parameters / feeds to assess the impact upon solvent degradation in the process. This would allow assessment of the solvent dose in the i-SANEX process for example.

Further research, development and testing are required to assess options for the removal of degradation products from TODGA (or other diglycolamide) based solvents. This may include:

- Systematic evaluation of reagents for removal of the individual degradation products to assess whether there is a suitable combination of reagents to remove TODGA degradation products. This should also include testing of salt free reagents (such as tetramethyl ammonium hydroxide) to consider options for reducing volumes of waste streams.
- Evaluate solid sorbents for removal of species that are not readily removed by aqueous wash regimes
- Carry out testing using levels of degradation products that would be representative of process conditions (i.e. removal of degradation product after each cycle through the process)

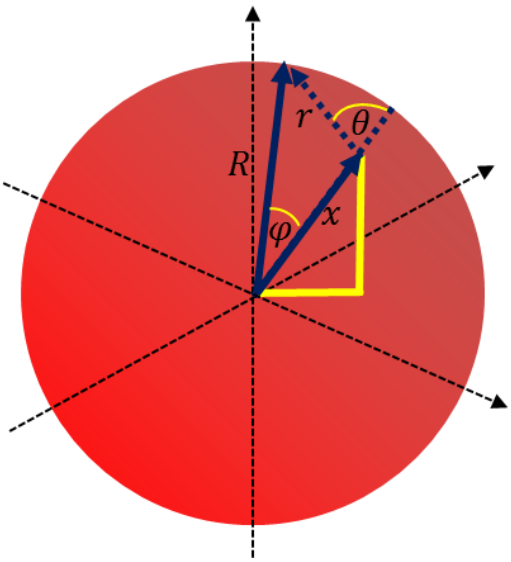
Directions in solvent washing should focus on salt free reagents and process development that reduces the size of the solvent wash cycle plant footprint, i.e. reducing wastes generated, simplifying the process and ensuring process safety whilst meeting solvent quality requirements (these also need to be better defined).

Further tests can be undertaken to assess whether there is a concentration of degradation product that can be tolerated within the process. This would allow further assessment whether the impact of species that are difficult to remove can be mitigated using a low volume solvent purge.

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APPENDICES

Appendix: Average distance to spherical surface from a point inside a sphere.



$$R^2 = x^2 + r^2 - 2xrcos(\theta)$$

$$0 = -R^2 + x^2 + r^2 - 2xrcos(\theta)$$

$$r = \frac{2xcos(\theta) \pm \sqrt{4x^2cos^2(\theta) - 4(x^2 - R^2)}}{2}$$

$$r = xcos(\theta) + \sqrt{x^2cos^2(\theta) - x^2 + R^2}$$

$$r = xcos(\theta) + \sqrt{R^2 - x^2sin^2(\theta)}$$

$$\bar{r} = \frac{1}{4\pi} \int_{sphere} \left(xcos(\theta) + \sqrt{R^2 - x^2sin^2(\theta)}\right)\, d\Omega$$

$$\bar{r} = \frac{1}{4\pi} \int_{sphere} \left(xcos(\theta) + \sqrt{R^2 - x^2sin^2(\theta)}\right)\, \sin(\theta)\, d\phi d\theta$$

$$\bar{r} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \left(xcos(\theta) + \sqrt{R^2 - x^2sin^2(\theta)}\right)\, \sin(\theta)\, d\phi d\theta$$

The $xcos(\theta)$ term cancels as integral of odd function over even limits

$$\bar{r} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \left(\sqrt{R^2 - x^2sin^2(\theta)}\right)\, \sin(\theta)\, d\phi d\theta$$

$$\bar{r} = \frac{2\pi}{4\pi} \int_0^{\pi} \left(\sqrt{R^2 - x^2sin^2(\theta)}\right)\, \sin(\theta)\, d\theta$$

$$\alpha = xcos(\theta)$$

$$\frac{dx}{d\theta} = -x\sin(\theta) \rightarrow d\theta = \frac{dx}{-\sin(\theta)}$$

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$$\bar{r} = \frac{1}{2}\int_{\alpha=-x}^{\alpha=x}\left(\sqrt{R^2 - x^2 + \alpha^2}\right)\sin(\theta)\frac{d\alpha}{-xsin(\theta)}$$

$\sin(\theta)$ cancel

$$\bar{r} = \frac{1}{2x}\int_{-x}^{x}\left(\sqrt{R^2 - x^2 + \alpha^2}\right)\ d\alpha$$

$$\bar{r} = \frac{1}{2x}\int_{-x}^{x}\left(\sqrt{R^2 - x^2 + \alpha^2}\right)\ d\alpha$$

$$\bar{r} = \frac{1}{x}\int_{0}^{x}\left(\sqrt{R^2 - x^2 + \alpha^2}\right)\ d\alpha$$

$$\beta^2 = R^2 - x^2$$

$$\bar{r} = \frac{1}{x}\int_{0}^{x}\left(\sqrt{\beta^2 + \alpha^2}\right)\ d\alpha$$

$$\bar{r} = \frac{1}{x}$$

$$\bar{r} = \frac{1}{x}\left(x\sqrt{x^2 + R^2 - x^2} + (R^2 - x^2)\log\left(x + \sqrt{x^2 + R^2 - x^2}\right) - (R^2 - x^2)log\left(\sqrt{R^2 - x^2}\right)\right)$$

$$\bar{r} = \frac{1}{2x}\left(Rx + (R^2 - x^2)log\left(\frac{R + x}{\sqrt{R^2 - x^2}}\right)\right)$$

$$\bar{r} = \frac{R}{2} + \frac{R^2 - x^2}{2x}log\left(\frac{R + x}{\sqrt{R^2 - x^2}}\right)$$

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