

Reprocessing with GANEX: Methodology for Ligand Radiation Tolerance Testing

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ABSTRACT

Results demonstrating the methodology for testing the radiation tolerance of organic ligands are presented. A high activity sealed source was used to irradiate samples which were sequentially removed and analysed using a sensitive mass spectrometer. The degradation of a candidate ligand for a new reprocessing process "GANEX" was found to be around 50% after 567 kGy exposure to gamma from Cs-137.

1 INTRODUCTION

Generation IV nuclear power plants are being designed to operate for longer and to achieve higher fuel burn ups, extracting more energy from uranium fuel. Along with many safety and efficiency advantages, the new reactors will produce spent fuel with higher overall activity and this creates challenges for the back end of the fuel cycle. Whilst in the UK there are no plans to reprocess fuel, some countries are seeking to close the fuel cycle to recycle constituents of irradiated fuel that can be re-used, an admirable aim.

Traditional reprocessing is achieved through the PUREX process, which separates: uranium and plutonium (for re-use as Mixed Oxide fuel); fission products (to be immobilised in a vitrified form); and the minor actinides (also vitrified). The proposed GANEX process (Group Actinide Extraction) offers potential improvements by enabling the recovery of the minor actinides separate from the fission products, and these minor actinides can be subsequently used again as fuel in a reactor. The two advantages of this are: a) increased electrical energy extraction per kg extracted ore; and b) reduced high activity waste volume requiring geological disposal; and c) the predominate radionuclides present in the eventual waste form have far shorter half lives than the minor actinides which have been burnt.

In the GANEX process which shown in Figure 1, irradiated fuel is dissolved in nitric acid and organic ligands are used to carry out the extraction, two of particular interest are DMDOHEMA and TODGA. Together they make up the GANEX mixture, which is dissolved in an organic solvent such as n-Dodecane or kerosene. Whilst it is well-known that these ligands are effective at extracting minor actinides, their suitability for the process under extremely radioactive conditions is not yet well-understood.

- N,N,N',N'-Tetraoctyl Diglycolamide (TODGA).
- N,N'-Dimethyl,N,N'-dioctylhexylethoxymalonamide (DMDOHEMA).

The current work supports the adoption of the new GANEX process by developing a methodology for measuring the effects of intense radiation on the organic ligand molecules used for GANEX, and in this paper we present DMDOHEMA as an example of the results possible.

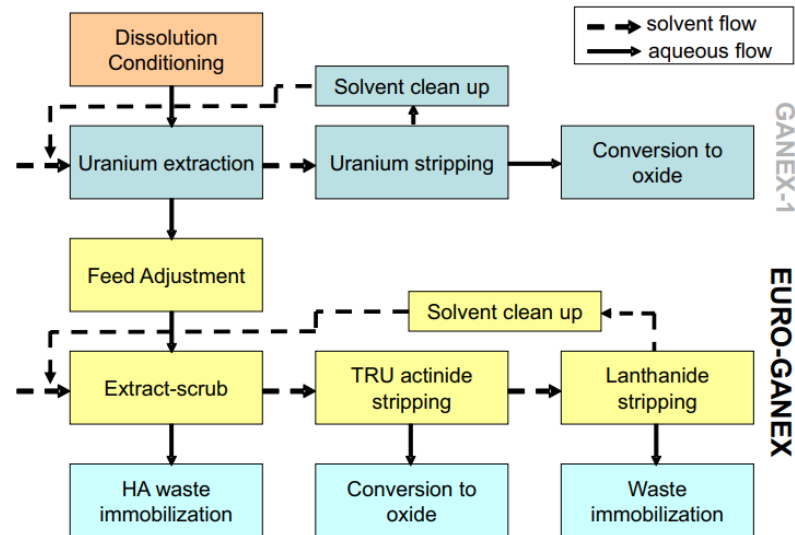


Figure 1: Schematic of the GANEX process, according to [1].

2 METHODOLOGY

2.1 Sample production

During this work, samples of the two organic ligands DMDOHEMA and TODGA were irradiated using a 51.7 TBq caesium-137 source, inside the chamber showed in Figure 2.



Figure 2: Gamma-irradiator chamber.

Quantification of the absorbed dose by samples was carried out to follow the progression of degradation as a function of gamma-dose, and this was carried out using the diamond radiation detector system, whose miniature size enabled close dosimeter placement to the samples. The system was developed at the University of Bristol for the purposes of measuring

real-time high dose rates remotely (Figure 3). It has been calibrated using accurately determined dose rates of collimated caesium-137 and cobalt-60, and has successfully been used on the Sellafield site [2], as well as for experimental purposes using high-activity sealed sources [3].



Figure 3: Diamond radiation detector system developed at the University of Bristol.

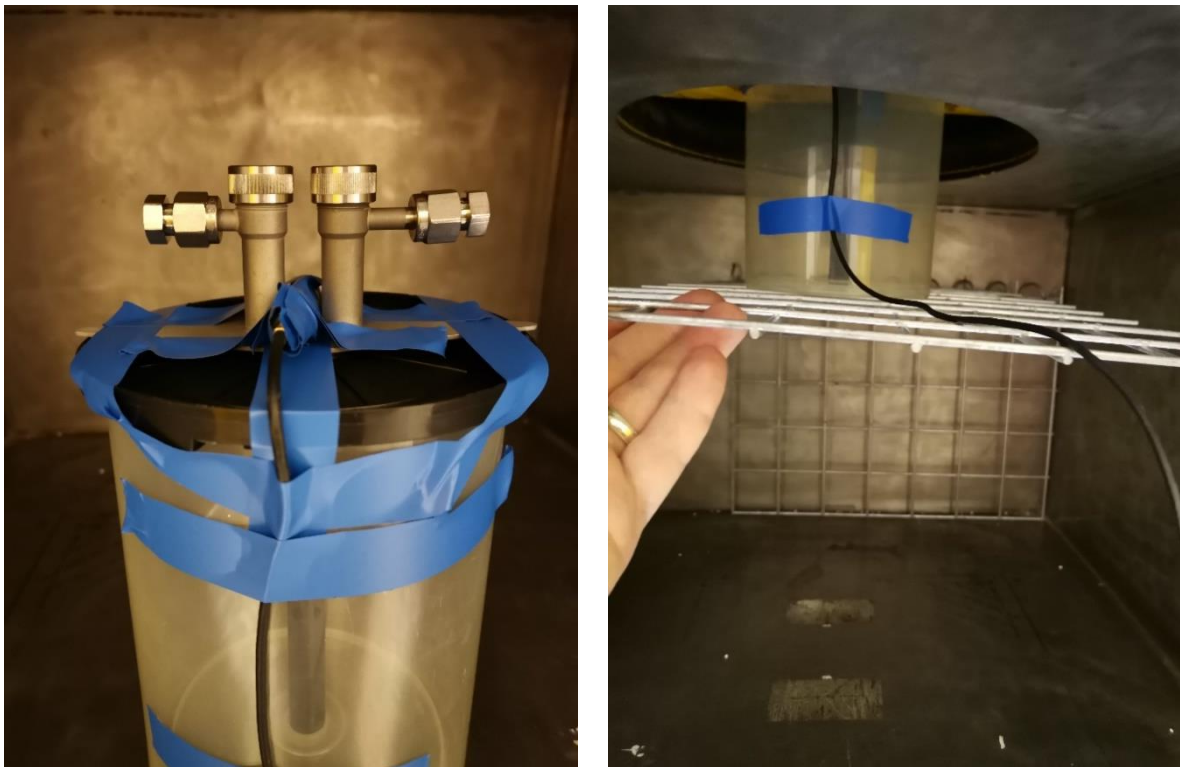


Figure 4: (left) Sample vials placed on the radiation stand; (right) Inserted into position for high dose rate exposure.

These mixtures were positioned inside the irradiator to maximise total dose as far as practical, and this exposure was measured at a rate of 1711 Gy/hr. At intervals, samples of a few 10s of μL were taken to be analysed using gas chromatography mass spectrometry. The remainder of the 2 mL solution was returned to the irradiator chamber for further gamma-exposure, and so a large number of samples were produced spanning several hundred kGy.

The exposures were carried out over several weeks, with sampling taking place at intervals to produce a range of samples exposed at the same dose rate for varying lengths of time, i.e. with different absorbed doses. The total volume of solution irradiated was 2 mL. n-dodecane was used to dilute to 0.5 M DMDOHEMA to match that of the GANEX process.

2.2 Sample analysis

The samples generated by the irradiation part of the study were analysed by ultra-high performance liquid chromatography mass spectrometry (UHPLC-MS). UHPLC [4] is a technique that allows for the spatial separation of mixtures in solution. The separation is achieved by introducing the liquid sample into a continuous flow of solvent that runs through a column packed with a stationary phase which interacts with the individual components of the mixture to different degrees depending on their individual polarities, steric bulk and overall size.

In this case, reverse phase separation was achieved using a column packed with bonded C18 hydrocarbon, resulting in the analytes being separated mostly by their polarity – the most polar having fewer interactions and, thus, traveling through the column faster. Secondary size and steric effects also result in larger components travelling more slowly through the column.

The UHPLC system is then connected to a mass spectrometer using electrospray ionisation (ESI) [5] and Orbitrap mass analysis [6]. This means that the components of the mixture are ionised and separated by the mass spectrometer in real-time with the chromatographic separation as they elute from the column. This results in a chromatogram with time on the x-axis and intensity on the y-axis.

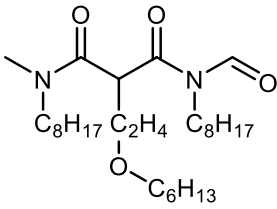
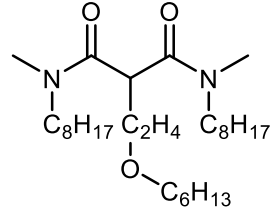
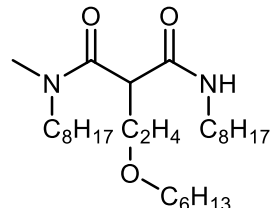
As components leave the column, they produce a signal in the mass spectrometer that is recorded as a peak in the chromatogram. The area under the peak is directly relatable to the concentration of that component in the original mixture (assuming no reaction, loss or alteration occurs during UHPLC separation or during ionisation). As mass spectrometry is used as the detection system, mass spectra are continuously recorded so that by selecting a peak it is possible to visualise the mass spectra and, thus, obtain the molecular weight of the component.

3 RESULTS AND DISCUSSION

In this paper we present the results from the DMDOHEMA exposures as an example of the capability we have developed. The two main mechanisms of radiolytic degradation of DMDOHEMA are demethylation and oxidation to aldehyde, as shown in Table 1. The evolution of these molecules as time (and dose) progresses is shown in Figure 5. The largest dose accrued was 567 kGy, at which point there was around 50% of the DMDOHEMA molecule remaining. The 50% degraded DMDOHEMA was made up of 40% two dominant species and around 10% other degradation mechanisms.

For use in a viable commercial process, it is important for the DMDOHEMA to be sufficiently available for sufficient time to carry out separations, so the required radiation tolerance should be considered and specified.

Table 1: Dominant degradation products evolved by radiolytic degradation of DMDOHEMA under intense gamma exposure.

	$C_{29}H_{56}N_2O_4$	$[M+H]^+$ 497.4312 (0.20) $[M+Na]^+$ 519.4127 (0.96)	5-25 %	Oxidation to aldehyde. Four intense isomers, eight low intensity isomers.
	$C_{29}H_{58}N_2O_3$	$[M+H]^+$ 483.4518 (0.41) $[M+Na]^+$ 505.4334 (1.19)	78-50 %	Undegraded DMDOHEMA.
	$C_{28}H_{56}N_2O_3$	$[M+H]^+$ 469.4361 (0.64) $[M+Na]^+$ 491.4174 (1.83)	8-15 %	Demethylation. Two isomers.

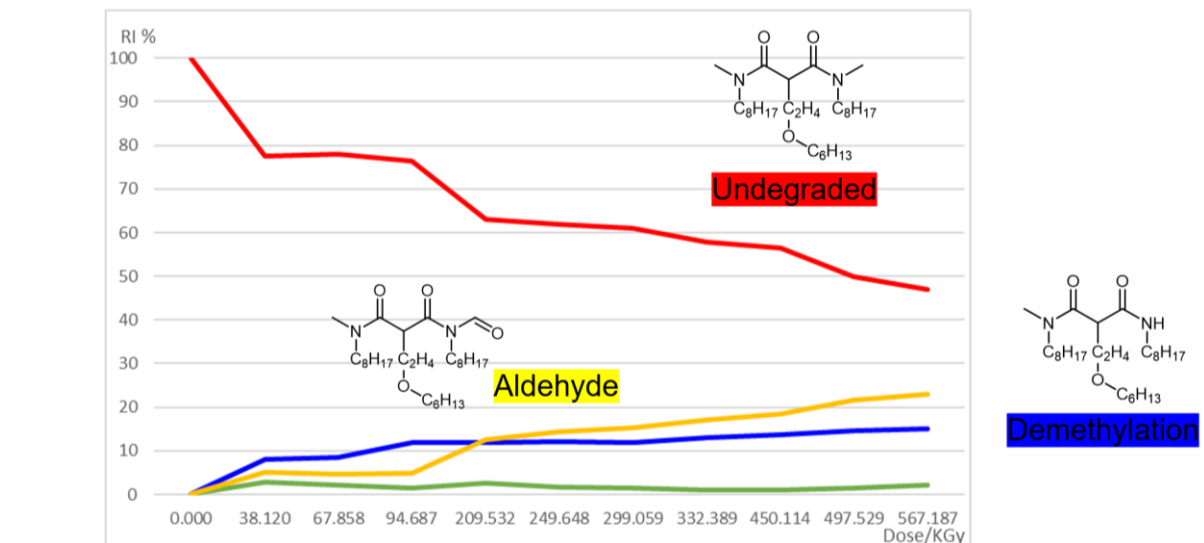


Figure 5: Dose-resolved degradation of DMDOHEMA and the main products

The data collected demonstrates the technique of exposing samples and sequentially analysing them using a sensitive mass spectrometer can offer useful insights into the availability of the organic ligand needed for the reprocessing in the GANEX process. This methodology can be further improved with an online mass spectrometer measurement, and can be applied to other organic species of interest to the GANEX and other proposed reprocessing schemes.

4 CONCLUSION

A methodology has been developed to carry out controlled gamma exposures to simulate conditions predicted in “GANEX” reprocessing. This has demonstrated that one of the

important organic molecules, DMDOHEMA, was 50% degraded after an exposure dose of 567 kGy.

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