



5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Decomposition studies of aqueous phase ligands used in advanced reprocessing flowsheets

Stacey Reilly^{a*}, Chris Maher^a, Steven Brewer^b, Robin Taylor^a

^aNational Nuclear Laboratory, Central Laboratory, Sellafield, Cumbria, CA20 1PG, UK

^bC-Tech Innovation Limited, Capenhurst, Chester, Cheshire, CH1 6EU, UK

Abstract

Two potential methods for decomposing organic ligands in nitric acid have been studied using acetic acid and diethylenetriaminepentaacetic acid (DTPA) as examples; these methods were oxidation by nitric acid at elevated temperatures (70–110 °C) and electrochemical oxidation, both direct and mediated electrochemical oxidation. Based on total carbon measurements, acetic acid proved to be rather stable against nitric acid oxidation whereas 60–80 % of DTPA was decomposed at 100–110 °C. Electrochemical oxidation methods were generally more effective in decomposing acetic acid and DTPA with mediated electrochemical oxidation using Ag (II) ions the most effective method under the conditions tested, with ~ 80 and > 90 % loss of carbon from acetic acid and DTPA solutions respectively, at ambient temperature in 6 M HNO₃.

© 2016 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of ATALANTE 2016

Keywords: process safety; decomposition; ligands; oxidation; electrochemistry

1. Introduction

Various advanced reprocessing flowsheets are being developed internationally as potential solutions to recycling uranium, plutonium and the minor actinides as part of a future closed nuclear fuel cycle. Closing the fuel cycle offers some significant potential benefits; notably the reduction in the long term radiotoxicity and thermal output of waste destined for disposal in a geological disposal facility and maximizing the energy potential of uranium supplies. The development of more efficient reprocessing flowsheets can thus benefit the overall fuel cycle economics, public perception and the sustainability of nuclear energy production.¹

The safety of actinide separation processes (SACSESS) project, funded by the European Union's 7th Framework Programme, addresses process safety issues associated with advanced reprocessing and minor actinide partitioning flowsheets. One of the components of this project is the investigation of downstream effects of processing nitrate product solutions containing aqueous phase (hydrophilic) ligands that have been used to back-extract actinides from organic phases in the core separation processes.

* Corresponding author. Tel.: +441967 79262.

E-mail address: stacey.reilly@nnl.co.uk

Abbreviations

AHA	Acetohydroxamic acid
BDD	Boron doped diamond
CEA-GANEX	Commissariat à l'énergie atomique – grouped actinide extraction
DEO	Direct electrochemical oxidation
DIAMEX	Diamide extraction
DTPA	Diethylenetriaminepentaacetic acid
EDTA	Ethylenediaminetetraacetic acid
EURO-GANEX	European grouped actinide extraction
GANEX	Grouped actinide extraction
HEDTA	(2-hydroxyethyl)-ethylenediaminetriacetic acid
IEM	Ion exchange membrane
i-SANEX	Innovative- selective actinide extraction
MEO	Mediated electrochemical oxidation
MMO	Mixed metal oxide
OML	Oxalate mother liquor
PUREX	Plutonium uranium redox extraction
SACSESS	Safety of actinide separation processes
TALSPEAK	Trivalent actinide-lanthanide separation by phosphorus reagent extraction from aqueous complexes

Generally, actinide ions exhibit an affinity for hard oxygen donor ligands but, compared to the chemically similar lanthanide ions, trivalent actinides also have an enhanced affinity for molecules with soft bases such as nitrogen¹. Therefore, many of the novel actinide separation processes that are currently being developed are based on selective actinide back-extraction (or stripping) from the loaded organic phase using polyaminocarboxylic acids or similar derivatives. For instance, the European grouped actinide extraction (EURO-GANEX) flowsheet uses acetohydroxamic acid (AHA) to strip neptunium and plutonium²; AHA has also been proposed for use in advanced plutonium uranium redox extraction (PUREX) processes³. Diethylenetriaminepentaacetic acid (DTPA) is used in the trivalent actinide-lanthanide separation by phosphorus reagent extraction from aqueous complexes (TALSPEAK) process⁴ and thus is so well-established that it can practically be considered as the reference molecule for aqueous phase complexation of trivalent actinide ions. The similar ligand, (2-hydroxyethyl)-ethylenediaminetriacetic acid (HEDTA) is employed in the Commissariat à l'énergie atomique – grouped actinide extraction (CEA-GANEX) process with a citric acid buffer to selectively strip the trivalent actinides^{2,5}.

As these organic species are complexants, it is important to understand if they can be decomposed as their presence could be problematic in other areas of the reprocessing plant. It is possible that they may interfere with the product finishing process, for example, by increasing losses of actinides to the mother liquor in the oxalic acid precipitation stage or adversely affecting the quality of the oxide product on conversion. It would also be detrimental for the ligands to survive as there would be a risk of them remaining complexed to the radionuclides and travelling to areas of plant that are not equipped to deal with their presence; for example, if the oxalate mother liquor (OML) is recycled to the head end of the process or travelling in waste streams and interfering with the effluent abatement process. Therefore, there may be a requirement for an additional process stage that decomposes these complexants, and as such the total carbon content, to inconsequential levels.

Here we report the results from two methods of organic destruction using acetic acid and DTPA as example ligands, both of which can be seen in figure 1. As mentioned previously, DTPA is used in numerous advanced reprocessing flowsheets and is a typical example of this class of complexants. Acetic acid is not directly used in the processes; however, it is a probable decomposition product for AHA and other ligands used in the advanced reprocessing flowsheets. As acetic acid is known to be quite stable towards oxidation, it is a good test molecule for the potential applicability of the different methods for decomposition of organics.

One of the methods we have investigated is electrochemical oxidation, which has been previously studied⁶⁻⁸ as an approach to destroy organic compounds such as ethylenediaminetetraacetic acid (EDTA)⁹. The application uses conventional flow electrolysis cells to oxidise organic species to carbon dioxide and water. Two electrochemical approaches have been tested, direct electrochemical oxidation (DEO) and mediated electrochemical oxidation (MEO). DEO at a boron doped diamond (BDD) electrode permits oxidation by absorption of the organics onto the electrode surface and by the generation of highly oxidising hydroxyl radicals. These mechanisms for oxidation also occur during MEO, but generation at the anode of highly oxidising ions such cerium (IV), cobalt (III) or silver (II) increases, for most applications, the rate and efficiency of oxidation. The use of mediators reduces the impact of mass transport at the anode on the reaction kinetics and therefore flow optimization within the electrochemical cell is less critical than when DEO is used. The metal ions are catalytic, they are reduced by the oxidation process and the electrochemical cell re-oxidises the ion, allowing it to be recycled in the process⁹.

Download English Version:

<https://daneshyari.com/en/article/4910975>

Download Persian Version:

<https://daneshyari.com/article/4910975>

[Daneshyari.com](https://daneshyari.com)