

Institution: University of Reading
Unit of Assessment: 8 Chemistry
Title of case study: Development of New Chemical Methods for Waste Management in Future Nuclear Fuel Cycles
<p>1. Summary of the impact</p> <p>The research groups of Professor Laurence Harwood and Dr Michael Hudson (now retired) at the University of Reading have developed new and highly selective extractants for spent and reprocessed nuclear fuels. These novel extractants remove specifically the components in nuclear waste that have the highest levels of long-term radioactivity. The extracted components (minor actinides) may subsequently be converted – “transmuted” – into elements with greatly reduced radioactivity. Storage times for high-level nuclear waste can thus be reduced by a factor of a thousand, typically from 300,000 to 300 years. This significant advance in the management of nuclear waste means that next-generation nuclear power production will be safer, more economical and more sustainable, as well as increasing the wider acceptance of nuclear power as a viable alternative to fossil fuels. The newly-developed extractants are now available commercially through TechnoComm Ltd.</p>
<p>2. Underpinning research</p> <p>Much of the uranium and plutonium in spent nuclear fuel can be recovered and re-used for power generation. However, 3% of the residual waste from current nuclear fuel cycles is extremely radiotoxic and must be stored for some 300,000 years before it can be considered safe. This long-term radiotoxicity arises from the presence of <i>highly</i> radioactive minor actinides (americium, curium and neptunium), though these constitute less than 0.1% of the spent fuel. If these active components can be separated from the accompanying lanthanides, they can be converted to short-lived or non-fissile elements by neutron bombardment, a process known as “transmutation”, in the next generation of nuclear reactors (“Generation IV”). Such reactors are due for deployment between 2020 and 2030 and represent major advances in sustainability, safety, resilience and economics. Transmutation of the minor actinides will reduce waste-storage times a thousand-fold, to only some 300 years. However, separation of the minor actinides from the accompanying lanthanides is essential for transmutation to succeed, as the lanthanides preferentially absorb neutrons in the reactor, so acting as “neutron poisons”.</p> <p>The challenge of separating very similar chemical species in nuclear waste is made even more difficult by the operating conditions under which it must be carried out: strong radioactive flux and extreme acidity. In 2003, it was shown by researchers at the University of Reading, working with the French Atomic Energy Commission, that bis(triazinyl)-pyridine ligands (BTPs) can selectively extract minor actinides from lanthanides, with a selectivity of around 30:1. However, while these BTPs provided good selectivity under laboratory conditions, they proved unstable under the conditions experienced during nuclear waste reprocessing.[1]</p> <p>Building on this discovery, University of Reading researchers then went on to develop <i>stable</i> extractant molecules that can separate the minor actinides from the chemically very similar lanthanides in nuclear waste. Since 2000, Dr M. J. Hudson (Lecturer/Reader 1972–2005), Dr C. E. Boucher (Ph.D. student, 2000–2003), Dr T. A. Youngs (Ph.D. student, 2000–2004), Dr M. R. St. J. Foreman (PDRA, 2001–2007), Dr F. W. Lewis (PDRA, 2008–2012) Dr A. W. Smith (PDRA, 2013 – present) and Prof. L. M. Harwood (Professor of Organic Chemistry, 1995 – present) have carried out this research.</p> <p>The research undertaken at the University of Reading has led to the design and synthesis of a new series of selective extractants. The first of these, dubbed CyMe4BTP was shown to be stable under typical nuclear reprocessing conditions (high radioactive flux and acidity) and, moreover, showed an unexpectedly high minor-actinide selectivity of 5000:1 relative to lanthanides.[2] Subsequent research by the group led to a second-generation ligand, CyMe4BTBP, which achieved the desired minor-actinide separation from actual downstream reprocessing waste [3], enabling the establishment of Europe’s first practical Separation of Actinides and Extraction (SANEX) process. Finally, a third-generation ligand, CyMe4BTPhen, has most recently been developed, which is structurally pre-organised and shows considerably faster rates of extraction.</p>

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The new ligand achieves high levels of extraction in only 15 minutes, as opposed to several hours for CyMe4BTBP, whilst maintaining stability and selectivity.[4]

The work at Reading University has been funded by the European Union through four programmes (PARTNEW, 2000–2003; EUROPART, 2004–2007; ACSEPT, 2008–2012; and SACCESS, 2013–2015), with combined budgets of over €22M, and involving more than 30 research institutes throughout Europe and leading European nuclear-research centres (Commissariat à l'Énergie Atomique, Marcoule, France; National Nuclear Laboratory, Sellafield, UK; Karlsruhe Institute of Technology, Karlsruhe, Germany).

3. References to the research

Key outputs include one Patent Cooperation Treaty (PCT) application and five papers published in internationally renowned, peer-reviewed journals. As further indication of the “quality” of these publications, the number of times each paper has been cited is given in parentheses (retrieved from *Scifinder* on 23/10/13):

[1]. M. J. Hudson *et al.*, "The coordination chemistry of 1,2,4-triazinyl bipyridines with lanthanide(III) elements – implications for the partitioning of americium(III)", *Dalton Trans.*, 1675 (2003). DOI: 10.1039/b301178j. (Cited 42 times).

[2]. M. J. Hudson *et al.*, "New Bis-triazinyl Pyridines for Americium(III) Extraction", *New J. Chem.* 8, 1171 (2006). DOI: 10.1039/B514108G. (Cited 79 times).

[3]. L. M. Harwood *et al.*, "The Separation of Americium(III) from Europium(III) by Two New 6,6'-Bis(triazinyl)-2,2'-bipyridines in Different Diluents", *Solvent Extr. Ion Exch.* 29, 551 (2011). DOI:10.1080/10496475.2011.556989.

[4]. F. W. Lewis *et al.*, "Highly Efficient Separation of Actinides from Lanthanides by a Phenanthroline-Derived Bis-Triazine Ligand", *J. Am. Chem. Soc.* 133, 6950 (2011). DOI: 10.1021/ja203378m. (Cited 36 times). *This paper was accompanied by an article in Chemistry World News on the Royal Society of Chemistry website* (www.rsc.org/chemistryworld/News/2011/August/09081101.asp)

[5]. L. M. Harwood, M. J. Hudson and F. Lewis (co-inventors), "Synthesis of Ligands for use in Actinide Extraction", PCT application number WO2001/077081 (2011); <http://www.google.com/patents/US20120264935>.

[6]. F. W. Lewis *et al.*, "Synthesis and Evaluation of Lipophilic BTBP Ligands for An/Ln Separations in Nuclear Waste Treatment: Effect of Alkyl Substitution on Extraction Properties and Implications for Ligand Design", *Eur. J. Org. Chem.* 8, 1509 (2012). DOI: 10.1002/ejoc.201101576. (Cited 7 times).

Grants: (i) M. J. Hudson, PARTNEW, European Union, 2000-2003, £216,000. (ii) M. J. Hudson, EUROPART, European Union, 2004-2006, £214,000. (iii) L. M. Harwood, ACSEPT, European Union, 2009-2011, £265,000. (iv) L. M. Harwood, MBase, EPSRC, 2010-2014, £149,000. (v) L. M. Harwood, SACCESS, European Union, 2013-2015, £149,000.

4. Details of the impact

The UK government is committed to delivering a mixture of energy sources that will provide a secure, affordable, low-carbon supply of electricity in the future. Given finite fossil-fuel resources, the pressing need to reduce carbon emissions worldwide and the inadequacy of alternative means of electricity generation, such as wind and wave power, nuclear power represents a major viable source of electricity. In 2012, nuclear energy accounted for 19% of electricity supply (Digest of UK Energy Statistics 2013, Department of Energy and Climate Change). Given the UK's target of reducing emissions of greenhouse gases to 20% of their 1990 levels, by 2050, nuclear energy is expected to become increasingly important. By 2050, up to 49% of the UK's electricity generation could be provided by nuclear power (House of Lords report on Nuclear Research and Development Capabilities, 2011).

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The UK currently has about 4.7 million cubic metres of nuclear waste, of which 1000 cubic metres is classified as high-level radioactive waste (Radioactive Wastes in the UK, 2010 Inventory, Nuclear Decommissioning Authority). This will grow as the UK invests in new nuclear build. The UK, along with France, currently reprocesses its spent nuclear fuel to recover unused uranium and plutonium, which can then be used again as fuel. The residual waste contains highly radioactive minor actinides (americium, curium and neptunium) as well as corrosion products and non-radioactive fission products such as lanthanides. Whilst comprising less than 0.1% of the mass of the spent fuel, the minor actinides constitute the major long-term hazard, posing extreme, long-term storage problems. They emit highly penetrating gamma-radiation and generate large amounts of heat, requiring deep geological storage for more than 300,000 years. Reducing this nuclear-waste burden would make nuclear power far more sustainable. One approach to this is through the development of strategies to separate (partition) and inactivate (transmute) the highly radioactive minor actinides.

The group in Reading developed the CyMe4BTP ligand during the PARTNEW programme (2000 – 2003, budget €2.2M, 10 partners) and this led to the EUROPART (budget €6M, 26 partners) and ACSEPT programmes (budget €9M, 34 partners). During these programmes, further research at Reading led to the discovery of the CyMe4BTBP and CyMe4BTPhen ligands. Within EUROPART and ACSEPT, partner organisations including the French Atomic Energy Commission were involved in assessing the minor-actinide selectivity of the ligands and in measuring their rates of actinide extraction, stripping qualities, solvent loading and hydrolytic and radiolytic stability. The European Commission continues to support this work through the SACSESS programme (€5.5M, 24 partners).[a] The ligands developed at Reading have been shown to be highly selective for extraction of the minor actinides (relative to the lanthanides), and they also exhibit significant stability under the extremely radioactive and highly acidic reprocessing conditions. Furthermore – and crucially in terms of impact – the CyMe4BTBP ligand has been shown by workers at the European Commission's Joint Nuclear Research Centre in Germany to effectively “clean up” real nuclear reprocessing waste.[b]

The success of the work to develop selective extractants has impacted on French nuclear policy, as noted in the "National Plan for Management of Radioactive Materials and Nuclear Waste 2013-2015" where it is stated (p. 214) in Section 4.2. "Separation of minor actinides":

"Research has led to the development of specific extractants and methods of separation, successfully tested on the laboratory scale for each process considered: extraction of Americium (EXAM), extraction of Americium and Curium (SANEX) and group extraction of all actinides (GANEX)". "In the period 2013-2015 a full scale experiment should be pursued, from the extraction of several kg of spent fuel obtained from actual, current processing operations, right through to the production of pure pellets of Americium dioxide, AmO₂. This experiment will test, across several nuclear laboratories, the sequence of the various unit operations (separation, isolation, conversion to oxide, pellet fabrication), and also various related operations including the management of effluents and by-products."[c]

For use in an industrial setting, these ligands need to be synthesised on a tonne scale. The Reading group has developed a scalable synthesis of the CyMe4-diketone, a key precursor to all of the ligands, demonstrating for the first time the potential for large-scale industrial production of these compounds. This led to the filing of a patent [d] and the licensing of intellectual property in this patent from the University of Reading to TechnoComm Ltd, a company specialising in technology commercialisation in the chemical sciences.[e] The CyMe4-BTP, CyMe4BTBP and CyMe4-BTPhen ligands are now manufactured and sold by TechnoComm Ltd.[f] These ligands have been purchased for process evaluation by leading national and international nuclear centres such as the NNL (UK), the European Commission Joint Research Centre (Germany), and the Idaho and Oak Ridge National Laboratories (USA), demonstrating that these organisations recognise the potential of the new compounds for effectively treating nuclear waste.

Funding to develop a full-scale industrial process for separating minor actinides from nuclear reprocessing waste awaits EU approval. However, the demonstration that CyMe4BTBP shows excellent efficiency and selectivity for the minor actinides on real nuclear reprocessing waste has provided first proof of concept for industrial scale chemical partitioning of the minor actinides and demonstrates the potential to revolutionise nuclear waste management. Not only does it promise to

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dramatically reduce the levels of radiotoxicity and waste-heat production, but it also paves the way to more efficient use of geological nuclear-waste repositories. This will help to make nuclear power more sustainable, strengthening its role as a genuine alternative to fossil fuels and helping the UK government to meet its 2050 greenhouse-gas emission targets. Reading's position within UK partitioning and transmutation capability has been recognised in a report by the Select Committee on Science and Technology.[g]

5. Sources to corroborate the impact

[a]. Chef de Project (SACSESS), Commissariat à l'Énergie Atomique, Marcoule. (information on budgets and partners involved in the PARTNEW, EUROPART, ACSEPT and SACSESS consortia). (Contact details provided separately)

[b]. D. Magnusson *et al*, "Demonstration of a SANEX process in centrifugal contactors using the CyMe4-BTBP molecule on a genuine fuel solution", *Solvent Extraction and Ion Exchange*, 27, 97, (2009). DOI:10.1080/07366290802672204.

[c] Translated from "Plan national de gestion des matières et des déchets radioactifs 2013-2015", Le ministère de l'Ecologie, du Développement durable et de l'Energie, Paris, 2013.

See: <http://www.developpement-durable.gouv.fr/Publication-du-Plan-National-de.html>

[d]. L.M. Harwood, M. J. Hudson and F. Lewis, GB 09 22 588.9, 2010; WO2001/077-81, 2011.

[e]. Contact: CEO of TechnoComm Ltd. (<http://www.technocomm.co.uk>). Full details of purchasing establishments and quantities sold are commercially sensitive.

[f]. Technocomm Ltd <http://www.technocomm.co.uk/page15.html>

[g]. Oral and written evidence to the Select Committee on Science and Technology "Inquiry on Nuclear Research and Development Capabilities" 24 May 2011, page 190.

See: <http://www.parliament.uk/business/committees/>