

Solvent Extraction Research and Development in the U.S. Fuel Cycle Program

International Solvent Extraction Conference

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October 2011

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance



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SOLVENT EXTRACTION RESEARCH AND DEVELOPMENT IN THE U.S. FUEL CYCLE PROGRAM

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ABSTRACT

Treatment or processing of used nuclear fuel to recycle uranium and plutonium has historically been accomplished using the well known PUREX process. The PUREX process has been used on an industrial scale for over 60 years in the nuclear industry. Research is underway to develop advanced separation methods for the recovery of other used fuel components, such as the minor actinides (Np, Am, Cm) for possible transmutation in fast spectrum reactors, or other constituents (e.g., Cs, Sr, transition metals, lanthanides) to help facilitate effective waste management options. This paper will provide an overview of new solvent extraction processes developed for advanced nuclear fuel cycles, and summarise recent experimental results. This will include the utilisation of new extractants for selective separation of target metals and new processes developed to selectively recover one or more elements from used fuel.

INTRODUCTION

The United States is currently re-evaluating its strategy to managing the nation's used nuclear fuel and nuclear waste. Some strategies include separation technologies that could enable greater uranium resource utility as well as waste management benefits from transmuting long-lived actinides. The United States Department of Energy has been researching advanced separation methods for the transuranium actinides, primarily plutonium, neptunium, americium and curium from the rest of the used fuel constituents. A number of solvent extraction technologies have been recently studied and demonstrated in laboratory-scale experiments. The current research focus in the U.S. has shifted from flowsheet testing and demonstration, to a longer-term research effort involving a deeper understanding of separation fundamentals.

Solvent extraction has played a very significant role in used nuclear fuel reprocessing, beginning in the early 1950s with the use of solvent extraction to recover uranium and plutonium for national weapons programs. Solvent extraction, in the form of the well known PUREX process (plutonium-uranium reduction-extraction), has been practiced at industrial scale in the nuclear industry for over 6 decades. New solvent extraction technologies have been under investigation for decades, and recently a new solvent extraction process has started in the U.S. for the separation of caesium from high level waste stored at the Savannah River Site in South Carolina. Other solvent extraction processes are being investigated for recovery of uranium (without separating plutonium), co-extraction of uranium and plutonium, minor actinides (Np, Am, Cm) and some fission products (e.g., Cs and Sr).

URANIUM/PLUTONIUM SEPARATION

New methods to extract uranium from the dissolved used fuel solution by one of two selective solvent extraction processes, employing the well-known extractant tri-*n*-butyl phosphate (TBP) in normal paraffin hydrocarbon (NPH) diluents have been investigated. The first process, called the Uranium Extraction (UREX) process, uses acetohydroxamic acid (AHA) to reduce plutonium in the acidic feed solution to the trivalent state, and to form inextractable complexes of plutonium and neptunium, preventing TBP from extracting them [1]. Both uranium and technetium are extracted into the TBP-bearing solvent along with other minor extractable species, which are subsequently scrubbed from the solvent. After stripping both metals from the solvent, technetium is separated from the uranium by passing the solution through an anion exchange column.

The UREX process has been studied extensively for the past decade, including a number of flowsheet demonstration tests in small-scale centrifugal contactors using spent light water reactor fuel [2,3]. Results of the demonstration tests were very promising, and indicate that the process may be a viable technology for treating spent nuclear fuel.

The second potential process for uranium separation is referred to as the co-decontamination process, as both uranium and plutonium are simultaneously extracted from the dissolved spent nuclear fuel. In this process, the valence of neptunium is adjusted from (V) to either (IV) or (VI). Uranium, technetium, plutonium and neptunium are all extracted into a TBP/NPH solvent. Most other extracted species are subsequently scrubbed from the solvent using a high-nitric acid scrub. Extracted zirconium will not scrub out of the solvent in a high-acid scrub, therefore an additional low nitric acid (~0.6 M) scrub is utilized to remove zirconium from the solvent. Plutonium and neptunium are stripped from the solvent in dilute nitric acid containing AHA. This strip product must be scrubbed with a sufficient concentration of nitric acid to re-extract any uranium or technetium in the plutonium/neptunium strip product. Following the Pu/Np strip, uranium and technetium are stripped in 0.01 M nitric acid. Technetium is removed from the uranium product by an anion exchange column.

The primary difference between the codecontamination process and the UREX process is that plutonium and neptunium are separated from the other TRU's and fission products in the codecontamination process. This separation is advantageous if the plutonium and neptunium are to be recycled for transmutation. The codecontamination process also requires a relatively high nitric acid concentration in the feed (~ 3 M), which may improve spent fuel dissolution efficiency and dissolver solution stability. The codecontamination process was successfully tested used nuclear fuel feed in a hot cell facility at Oak Ridge National Laboratory [4].

Similar approaches to uranium plutonium coextraction have been developed in France (COEX[®]) and the UK (NUEX) where uranium and plutonium are coextracted and stripped and do not produce a pure plutonium stream. This approach is more similar to the classical PUREX process chemistry but with modified uranium and plutonium stripping sections. The ratios of plutonium and uranium in the U/Pu product can be adjusted to meet process and safeguards constraints.

AMERICIUM AND CURIUM SEPARATION

Americium is the primary heat source term for a geologic repository in the 1000-3000 year time frame. Curium, with mostly short lived isotopes does not contribute significantly to the heat source term of a repository. Separating and transmuting americium is desired to reduce the heat source to the repository, but because of the chemical similarity of americium and curium, their separation

from each other is a very difficult approach. Therefore, research into separating americium and curium from the trivalent lanthanides, as well as separating americium from curium and the lanthanides are both active research topics. Specific areas of research are focused on developing a more robust one-step An/Ln separation process, developing a broad operating envelope of An/Ln separation processes through better fundamental understanding, developing a viable method to separate Am from Cm and Ln and establishing a strong scientific basis for future process selection. The primary benefit of this research is expected to be a significant simplification of fuel recycle methods, resulting in overall improvement in economics and increased acceptability of the nuclear fuel cycle.

One of the underlying aspects of developing a one-step An/Ln separation process as well as developing a broad operating envelope and scientific basis, is to understand the competing factors in current separation processes such as the TALSPEAK process [5]. This process, and related processes such as the SANEX process [6], rely on the strong complexation of actinides and lanthanides by an organic extractant such as di-2-ethylhexylphosphoric acid (HDEHP), and the complexation of the actinides in the aqueous phase by another complexant such as diethylenetriaminepentaacetic acid (DTPA), in the presence of a buffer such as lactic acid. It is expected that as a greater understanding of the TALSPEAK chemistry is developed, this knowledge will translate to other An/Ln separation chemistry applications (such as alternative extractants) as well.

Purposeful manipulation of ternary metal complexes in the aqueous phase in a TALSPEAK-type extraction system is another avenue of research being investigated to effect Am/Cm selectivity. Research into appropriately sized aqueous complexants has shown some promise in fitting the secondary ligand in the open coordination site, making complexation more favorable for the slightly larger Am (III) cation.

Another approach to a simplified An (III) separation is the combining of the extractants of the TRUEX and TALSPEAK processes. The hypothesis being explored is that the combined extractant would extract An (III) and Ln (III) elements in nitric acid with selective stripping of An (III) occurring in a buffered, complexant solution. Preliminary results indicate that it may be feasible to combine extractants to effectively separate An (III) and Ln (III), although there is still much work to determine if this approach is robust enough for industrial application.

Molecular modeling is being employed to identify and select targets for synthesis of soft-donor ligands in the bis(dithiophosphinic) acid family. This effort is focused on identifying ligands that are designed for optimal Am(III) binding, and therefore provide some selectivity for Am over Cm and the lanthanides, as well as having greater chemical stability than current ligands in this class.

The above methods seek to identify ligands or ligand systems that selectively complex Am (III) in the presence of Ln (III). In a different approach, selective extraction of Am (V) or (VI) from Cm (III) and Ln (III) has been demonstrated in organic solvents [7]. The greatest challenge with this approach is being able to hold the Am in the higher oxidation state long enough to extract it. Another approach would be to extract Am (III) with Cm (III) and Ln (III) in a TRUEX-like extractant, and then selectively strip Am (V) from the loaded solvent. A third approach would be to utilize an actinyl-selective complexant that would stabilize Am in the penta- or hexavalent state.

Understanding the fundamental properties of separation processes is a major effort of the FCR&D program. A key activity that supports the minor actinide separation activities is developing an understanding of the thermodynamic and kinetic behavior of the trivalent actinides and lanthanides

in the TALSPEAK process using microcalorimetry, fluorescence and conventional spectrophotometric techniques, radiochemical techniques, and stopped flow kinetics. This work builds on recently developed methodologies and will focus on a) studying the behavior of the fundamental thermodynamic parameters ΔG° , ΔH° and ΔS° in relation to changes in the extraction media; b) characterization of the solution chemistry parameters for the actinides and lanthanides within the operational envelope of the TALSPEAK process. It is envisaged that the results of these studies will be useful in improving the TALSPEAK process and/or provide a useful starting point for the development of alternative Am/Cm separation methods.

Another key area of research is the area of radiation chemistry. Radiation chemistry may adversely affect the separations process in a number of ways. In addition to direct radiation damage, the formation of free radicals in solution may also damage organic solvents indirectly [8]. Gamma and alpha radiolysis are of particular interest, as well as understanding radiolysis mechanisms needed to develop predictive tools/models. In the past, most work involved performing solvent extraction experiments on irradiated solvents. Today, a more fundamental chemical investigation includes steady state radiolysis and identification of decomposition products as well as pulse radiolysis to understand the kinetics of free radical reactions with solutes. These data will be important in the overall development of any separation process in the presence of high radiation fields that exist in used nuclear fuel.

CAESIUM AND STRONTIUM SEPARATION

Two technologies have been developed for the concurrent separation of caesium and strontium from the raffinate resulting from the UREX or codecontamination process. The first process utilizes chlorinated cobalt dicarbollide (CCD) and polyethylene glycol (PEG) in a phenyltrifluoromethyl sulfone diluent [9]. The CCD/PEG process is most efficient when the feed is < 1 M nitric acid; therefore, it can be used directly on the UREX process raffinate or on the codecontamination process raffinate, after an acid recovery process. Caesium and strontium, along with any barium or rubidium present, are extracted into the solvent. A 3 M nitric acid scrub is used to remove any trace actinides present in the solvent. Caesium and strontium are effectively stripped using a guanidine carbonate/ diethylenetriamine pentaacetic acid strip solution. Recent results indicate that a new, regenerable strip reagent, based on methylamine carbonate would significantly reduce the amount of organics in the caesium/strontium strip product and greatly simplify subsequent solidification operations [10]. The cesium and strontium strip product may be solidified in a number of ways, namely sorption onto a zeolite-type matrix, mineralization by steam reforming, calcination, etc.

This process has been demonstrated in countercurrent flowsheet tests using both simulated and actual UREX and codecontamination flowsheet raffinates. Both tests demonstrated removal efficiencies for caesium and strontium of ~99% or greater, which is more than sufficient to eliminate cesium and strontium as main contributors to the short term heat load to the repository.

The second technology for the separation of caesium and strontium is based on a combined solvent containing two extractants 4',4',(5')-Di-(t-butylidicyclo-hexano)-18-crown-6 (DtBu18C6) and Calix[4]arene-bis-(tert-octylbenzo-crown-6) (BOBCalixC6) combined with a phase modifier- 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB) in a branched aliphatic hydrocarbon diluent (Isopar[®] L). This solvent composition was based on the Strontium Extraction (SREX) process developed at Argonne National Laboratory and the Caustic Side Solvent Extraction

(CSSX) process developed at Oak Ridge National Laboratory (for alkaline waste)[11,12]. A simple combination of the two solvents produced unacceptable extraction results; however, it was found that the Cs-7SB modifier used in the CSSX process had a synergistic effect on the extraction of strontium. Therefore, the modifier used in the SREX process (TBP) was not needed in the new combined solvent. Flowsheet testing of this Cs/Sr extraction process has been completed and results indicate that the process is effective at selectively extracting caesium and strontium from UREX or co-decontamination raffinates and that the caesium and strontium can be stripped from the solvent using dilute nitric acid [4,13]. Recent improvements include the development of a new calixarene extractant to replace the BOBCalixC6 extractant. The new extractant 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy) calix[4]arenebenzocrown-6, or MaxCalix has a much higher solubility in the diluents, allowing the process to utilize an extractant concentration of 0.2 M rather than the concentration of the BOBCalix that was limited to 0.007 M. This allows for much higher distribution ratios and greater separation efficiency of caesium in the process. This extractant was also recently adapted as the reference extractant by the Savannah River Site for testing in the Modular Caustic Side Solvent Extraction Unit (MCU) using high-level radioactive tank waste.

SUMMARY

The DOE Fuel Cycle Research and Development Separations program is investigating a number of solvent extraction technologies to enable recycle of used nuclear fuel for both resource utilization and waste management purposes. The research program spans the breadth of fundamental research into thermodynamic and kinetics of extraction processes to demonstration of process flowsheets. The current emphasis of the program is in a longer-term science-based research effort.

REFERENCES

1. **Laidler, J. J.; Bresee, J. C.** (2004) *The U.S. Advanced Fuel Cycle Initiative: Development of Separation Technologies*, Proceedings of Advances for Nuclear Fuel Cycles (ATALANTE 2004), Nimes, France
2. **Vandegrift, G. F.; Regalbuto, M. C.; Pereira, C.; Bakel, A. J.; Aase, S. B.; Bowers, D. L.; Byrnes, J. P.; Clark, M. A.; Emery, J. W.; Falkenberg, J. R.; Hafenrichter, L. D.; Leonard, R. A.; Quigley, K. J.; Vander Pol, M. H.; Laidler, J. J.** (2005) *Lab-Scale Demonstration of the UREX+2 Process using Spent Nuclear Fuel*, Proceedings of Waste Management '05, Tucson, AZ, USA
3. **Pereira, C., Vandegrift, G. F., Regalbuto, M. C., Bakel, A. J., and Laidler, J. J.** (2007) *A Summary of the Lab-Scale Demonstrations of UREX+ Processes at Argonne National Laboratory*, Proceedings of Global 2007, Boise, Idaho, USA
4. **Jubin, R. T., Collins, E. D., Felker, L. K., Spencer, B. B., Walker, E. A., Vedder, R. J., Taylor, R. D., Binder, J. L.** (2009) *CETE R&D at the Oak Ridge National Laboratory Supporting Management of Nuclear Waste*, Proceedings of Waste Management '09, Phoenix, AZ, USA
5. **Weaver, B., Kappelmann, F.A.** (1968) *Preferential extraction of lanthanides over trivalent actinides by monoacidic organophosphates from carboxylic acids and by mixtures of carboxylic and aminopolyacetic acids*, J. Inorg. Nucl. Chem., 30, pp. 263-272
6. **Hill, C., Guillaneux, D., Berthon, L.** (2002) *SANEX-BTP process development studies. Proceedings of the International Solvent Extraction Conference, ISEC 2002*, pp. 1205-1209

7. **Mincher, B. J., Martin, L. R., Schmitt, N. C.** (2008) *Tributylphosphate Extraction Behavior of Bismuthate-oxidized Americium*, *Journal of Inorganic Chemistry*, 47, 6984-6989
8. **Martin, L. R., Mezyk, S. P., Mincher, B. J.** (2009), *Determination of Arrhenius and Thermodynamic Parameters for the Aqueous Reaction of the Hydroxyl Radical with Lactic Acid*, *Journal of Physical Chemistry A*, 113, pp. 141-145
9. **Law, J. D., Herbst, R. S., Peterman, D. R., Tillotson, R. D., Todd, T. A.** (2004) *Development of a Cobalt Dicarbolide/Polyethylene Glycol Solvent Extraction Process for Separation of Cesium and Strontium to Support Advanced Aqueous Reprocessing*, *Nuclear Technology*, 147(2), pp. 284-290
10. **Law, J. D., Herbst, R. S., Peterman, D. R., Todd, T. A., Romanovskiy, V. N., Babain, V. A., Smirnov, I. V.** (2005) *Development of a Regenerable Strip Reagent for Treatment of Acidic, Radioactive Waste with Cobalt Dicarbolide-based Solvent Extraction Processes*, *Solvent Extraction and Ion Exchange*, 23(1), pp. 59-84
11. **Horwitz, E. P., Dietz, M. L., Fisher, D. E.** (1991) *SREX, A New Process for the Extraction and Recovery of Strontium from Acidic Nuclear Waste Streams*, *Solvent Extraction and Ion Exchange*, 9(1), pp. 1-25
12. **Bonnesen, P. V., Delmau, L. H., Moyer, B. A., Leonard, R. A.** (2000) *Robust Alkaline-side CSEX Solvent Suitable for Removing Cesium from Savannah River High Level Waste*, *Solvent Extraction and Ion Exchange*, 18 (6), pp. 1079–1108
13. **Riddle, C. L., Baker, J. D., Law, J. D., McGrath, C. A., Meikrantz, D. H., Mincher, B. J., Peterman, D. R., Todd, T. A.** (2005) *Fission Product Extraction (FPEx): Development of a Novel Solvent for the Simultaneous Separation of Strontium and Cesium from Acidic Solutions*, *Solvent Extraction and Ion Exchange*, 23(3), pp. 449-461