A N, N′-di-n-OKTYL-TODGA-dicarbollide extractant for actinide (III) separation from acidic waste solutions

Mária Bubeníková¹, Pavel Selucky², Jiří Rais³, Bohumír Grüner⁴, Petr Švec⁴
¹Nuclear Research Institute Rež plc, Czech Republic,
²Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Czech Republic

Abstract

Spent nuclear fuel reprocessing produces high level liquid waste (HLLW), which contains dangerous nuclides, especially minor actinides (²⁴¹Am, ²⁴³Cm, ²³⁷Np) responsible for the long-term radiotoxicity of the waste. Therefore, partitioning of minor actinides from other fission products, in particular from lanthanide elements because of their almost identical chemical and physical properties, is a many-faceted challenge of current nuclear treatments.

In recent years, several HLLW partitioning processes utilising variety of extractants such as octyl(phenyl)-N,N-di-iso-butyl-carbamoylmethylphosphine oxide (CMPO) – TRUEX process [1], trialkylphosphine oxide – TRPO process [2], diisooctylphosphoric acid – DIDPA process [3], substituted malonamides – DIAMEX process [4], and N,N,N′,N′-tetraacyl diglycolamide (TODGA) within the ARTIST or TODGA/TBP process [5] have been developed for actinides separation. However, none of the processes provided any substantial actinides (III)/lanthanides (III) selectivity. Several processes such as SANEX (Selective ActiNides EXtraction) [6] or ALINA (Actinide - Lanthanide INtergroup separation in Acidic medium) [7] have been proposed for subsequent selective separation of actinides (III) from lanthanides (III).

Recently, the extractants based on two cobalt bis(dicarbollide) (1-) ions (COSAN) by amicid bonds covalently bound (directly or via diethyleneglycol connectors) to organic, diglycolyl acid platform (with different alkyl/aryl substituents on the amide nitrogen), have been developed for usage in nuclear treatment. The extractant N,N′-di-n-oktyl-TODGA-COSAN with the formula \( [(N,N′)-(8-(OCH₂CH₂)₂-1,2-C₆H₄)₂(1′,2′-C₆H₄H₂)]-3,3′-Co(N,N′-n-C₆H₄)NCOCH₂]ONa \) has been evaluated for separation of actinides from acidic waste solutions issuing from PUREX reprocessing [8] [9]. The extractant enabled effective extraction of trivalent actinides and lanthanides from acidic nitric acid solutions. The extraction efficiency of N,N′-di-n-oktyl-TODGA-COSAN was significantly higher (2-5 orders in magnitude) in comparison with organic TODGA (without cobalt bis(dicarbollide) ions) or synergetic mixtures of organic TODGA and chloroprotected cobalt bis(dicarbollide). The extractant provided sufficient solubility in an ecological low polar solvent mixture of hexyl methyl ketone (2-octanone) and n-dodecane (1:1 vol.). The stable organic phases with extractant concentration of 0.1 M could be easily prepared. The extractant exhibited good hydrolytical stability towards 3 M HNO₃, pertinent for acidic HLLW.

The extractant N,N′-di-n-oktyl-TODGA-COSAN enabled good separation of actinides(III) and lanthanides(III) from bulk of fission products present in the model PUREX feed. The co-extraction of some undesirable elements as Zr, Mo, Pd, which are present in relatively high concentration in PUREX raffinate solution, was suppressed by using oxalic acid and hydroxyethylhexamethylenetriacetic acid (HEDTA) in the feed solution. However,
undesired co-extraction of Ag has not been solved yet. The N,N'-di-octyl-TODGA-
COSAN similarly as other TODGA-like compounds did not show any substantial
actinide(III)/lanthanide(III) selectivity.

For selective separation of actinides (III) from lanthanides (III) the hydrophilic complexing
agent of diethylene-triamine-N,N',N',N''-pentaacetic acid (DTPA) with sodium nitrate
alone or in combination with different carboxylic buffers (citric acid, glycine, glycolic acid,
lactic acid, malic acid) has been tested. As found, a practical and effective Am(III)
separation from loaded organic phase could be achieved by using a stripping agent
composed of 0.05 M DTPA and 1 M citric acid as a buffer and 1 M NaNO₃ at pH 3.0
(SF₂Eu/Am = 13). For efficient removal of americium from the organic phase containing major
fraction of lanthanides, repeated stripping with stripping agent or higher number of
counter-current units would be necessary. Lanthanides (III) remaining in the organic phase
could be consecutively effectively stripped by using solution of ammonium citrate or
ammonium DTPA at pH ~7 (the D₂Eu obtained were lower than
0.01). The organic phase can be regenerated by moderately concentrated nitric acid of
about 3 M. As a partial drawback of the system a high sensitivity of trivalent metal
extraction to pH changes at the stripping step may be noted.
Acknowledgements

Special thanks are due to the Grant Agency of the Czech Republic (Project No. 104/09/0668 and Project No. 106/11/2319) and the Radioactive Waste Repository Authority (Project 2009/002/Su) for partial support.

References


