

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

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### Abstract

Spent nuclear fuel reprocessing produces high level liquid waste (HLLW), which contains dangerous nuclides, especially minor actinides (<sup>241,243</sup>Am, <sup>245</sup>Cm, <sup>237</sup>Np) 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], diisodecylphosphoric acid – DIDPA process [3], substituted malonamides – DIAMEX process [4], and N,N,N',N'-tetraoctyl 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 amidic 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  $\{[(N,N'-(8-(OCH_2CH_2)_2-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})-3,3'-Co)(N,N'-n-C_8H_{17})NCOCH_2]_2O\}Na_2$  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 synergic 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 HNO<sub>3</sub>, 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 hydroxyethylethylenediaminetriacetic acid (HEDTA) in the feed solution. However,

undesired co-extraction of Ag has not been solved yet. The N,N'-di-n-oktyl-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'',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 NaNO<sub>3</sub> at pH 3.0 ( $SF_{Eu/Am} = 13$ ). 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 citrate with ammonium DTPA at pH ~7 (the  $D_{Eu}$  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.

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