Process development studies and demonstration of an r-SANEX process using C5-BPP – selective separation of trivalent actinides from lanthanides

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Abstract
In this study, an optimised solvent comprising 0.01 mol/L C5-BPP + 0.5 mol/L 2-bromo-hexanoic acid in a diluent mixture of TPH and 10% 1-octanol was developed and tested for the selective extraction of trivalent actinides from lanthanides. In batch experiments and single centrifugal contactor tests the equilibrium extraction data and kinetics of the system in extraction, scrubbing and stripping modes were evaluated and a 16-stage flow-sheet was developed.

The flow-sheet was successfully tested in a spiked continuous counter-current centrifugal contactor demonstration test. It turned out that 16 stages were insufficient for a complete recovery of An(III), although a fairly clean An(III) product fraction was obtained with only low contaminations of Ln(III). The high selectivity of the C5-BPP extractant for An(III) over Ln(III) was shown.

The results of the spiked test are presented and discussed.

Introduction
The separation of Am(III) and Cm(III) from lanthanides (Ln(III)) plays a crucial role in the partitioning & transmutation strategy investigated in Europe and worldwide.[1-2] Much effort has been conducted to develop liquid-liquid counter-current separation processes based on soft-donor extractants, leading to the successful demonstration of several processes.[3-4] However, for a better understanding of the underlying fundamental principles of selectivity of these extractants, we stepped back and investigated similar extractants with structural modifications.

Besides the well-known BTP[4] and BTBP[5] class of An(III) selective extractants, alkylated bis-pyrazolylpyridines[6] (BPPs) also show a high selectivity for An(III) over Ln(III). A particular member of this class, C5-BPP (2,6-Bis(5-(2,2-dimethylpropyl)-1*H*-pyrazol-3-yl)pyridine, Figure 1), was studied in more detail and it was found that it may be suitable for use in an r-SANEX process for separating An(III) from Ln(III).[7] However, the addition of a lipophilic anion (e.g. 2-bromohexanoic acid, Figure 1) is required, as the ligand does not extract the metal nitrates directly (in contrast to BTP and BTBP extractants). The extraction mechanism was found to follow an ion exchange mechanism (Equation 1). As shown by TRLFS,[8-9] the extracted complexes consist of An(III) coordinated by three BPP molecules; the lipophilic anions required for charge compensation are not directly coordinated to the metal ion. Due to the ion exchange mechanism, An(III) extraction by C5-BPP is only possible from low concentrated nitric acid (~0.1 mol/L), while back-

extraction can be performed at higher nitric acid concentrations. However, the extractant is protonated at nitric acid concentrations >1 mol/L and precipitates, which limits the use of highly concentrated HNO_3. As the distribution ratios of An(III) at 1 mol/L HNO_3 were still too high for an efficient back-extraction, the addition of 10 vol.-% 1-octanol into the solvent was used to reduce the An(III) distribution ratios.[7]

Equation 1 $\qquad M_{aq}^{3+} + 3\ HA_{org} + 3\ L_{org} \rightleftharpoons [MA_3L_3]_{org} + 3\ H_{aq}^{+}$

M = Am, Cm
HA = 2-bromohexanoic acid
L = C5-BPP

C5-BPP
2,6-Bis-[5-(2,2-dimethyl-propyl)-
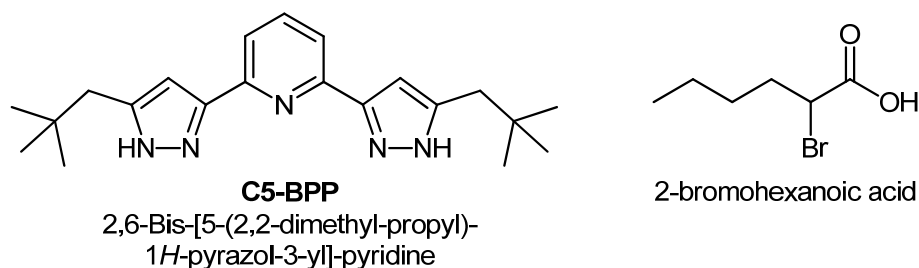1*H*-pyrazol-3-yl]-pyridine

2-bromohexanoic acid

Figure 1. Chemical structures of C5-BPP and 2-bromohexanoic acid.

Single stage centrifugal contactor tests

We chose C5-BPP as a possible candidate for a new r-SANEX process to separate the trivalent actinides Am(III) and Cm(III) from the trivalent lanthanides. An optimised solvent comprising 0.01 mol/L C5-BPP + 0.5 mol/L 2-bromohexanoic acid in a diluent mixture of TPH and 10% 1-octanol was used. The batch experiments were very promising and batch shaking tests showed the equilibrium distribution ratios to be reached within a very short time compared to other nitrogen donor ligands.[7] Therefore, a preliminary flow-sheet consisting of three sections (extraction, scrubbing, An(III) stripping) was elaborated and tested in single stage centrifugal contactor tests to evaluate the stage efficiencies of the system.

Figure 2 shows the results of a single centrifugal contactor test in the extraction of An(III) and Ln(III) from 0.16 mol/L HNO_3 as a function of the total flow-rate (A/O=1). The selectivity of the C5-BPP extractant is clearly resembled in the observed trend over the whole lanthanide series and the extraction of Am(III) and Cm(III). Am(III) is best extracted with equilibrium distribution ratios of 4.5, followed by Cm(III) with equilibrium distribution ratios of 2.1. The distribution ratios decreased with increasing total flow-rate in the counter-current experiment, as expected due to the extraction kinetics: A higher flow-rate leads to lower contacting time in the mixing chamber. The results show that for Cm(III) to be extracted the flow-rates should not exceed values of 20/20 mL/h (A/O). Therefore, even lower flow-rates were used in the full test.

The scrubbing and stripping sections were tested in similar single centrifugal contactor experiments, leading to similar observations. These data were used for the computer-code optimisation of the full test flow-sheet, described in the next section.
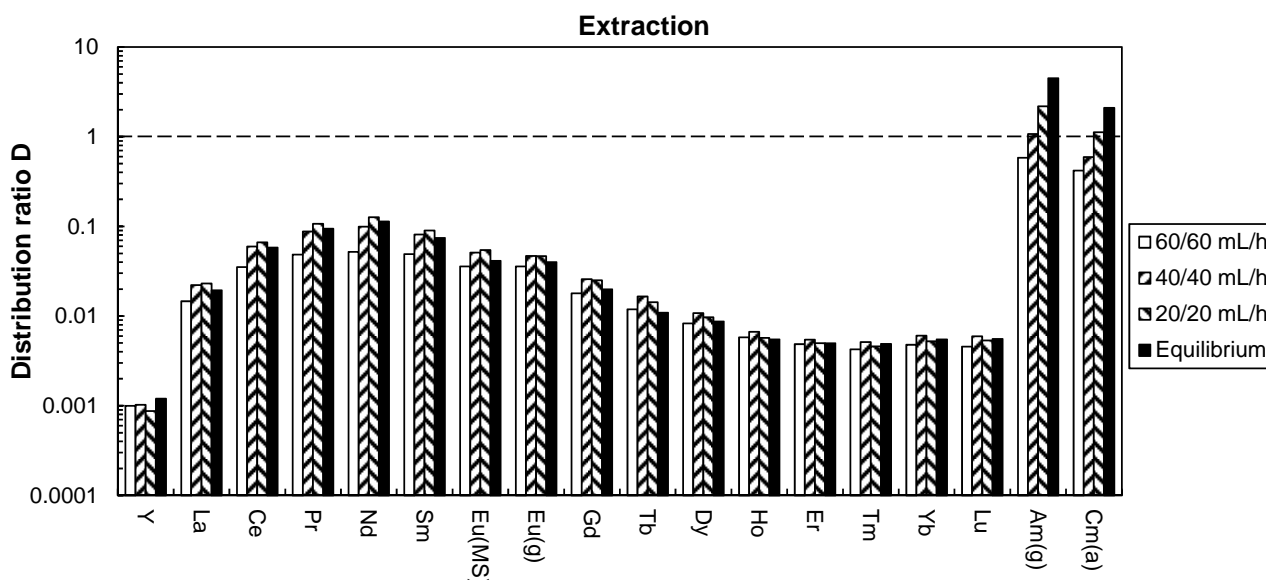
Figure 2. Results of a single centrifugal contactor test: extraction of An(III) and Ln(III) from 0.16 mol/L HNO$_3$ as a function of the total flow-rate (A/O=1).

Flow-sheet design

The flow-sheet was designed based on equilibrium data obtained from batch shaking experiments as well as single centrifugal contactor tests using different flow-rates. Computer-code optimisation calculations were performed to optimise the number and distribution of the different process stages (extraction, scrubbing, and stripping) , as described in ref.[10]. The total number of stages was limited to 16, due to the experimental setup of the centrifugal contactor battery, and the test was planned to be finished within one day. Therefore, 10 stages for extraction, 2 stages for scrubbing, and only 4 stages for An(III) stripping were planned, although the calculations already showed that this may not be enough to achieve sufficiently good separation and recovery of An(III). A schematic representation of the flow-sheet is given in Figure 3.
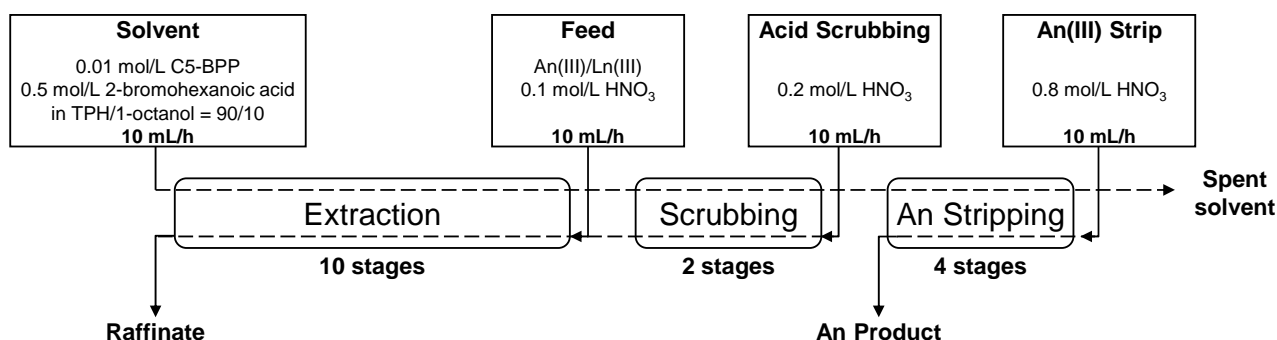

Figure 3. Flow-sheet of the C5-BPP demonstration process.

Results and Discussion

The r-SANEX process is foreseen to follow a preceding DIAMEX process, as known in the literature as the DIAMEX + SANEX strategy.[11] Therefore, the DIAMEX product will be the feed for the consecutive r-SANEX process, consisting of the trivalent lanthanides and actinides. In light water reactor fuel only the light lanthanides are present. However, we added also low amounts of the heavier lanthanides to our feed, for scientific curiosity reasons, while the concentrations of the light lanthanides resemble those found in DIAMEX product solutions. The composition of the feed solution used for our process demonstration test is given in Table 1.

Table 1. Composition of the feed solution for the demonstration of the r-SANEX process.

Element	Concentration [mg/L or as shown]	Element	Concentration [mg/L]	Element	Concentration [mg/L]
^{241}Am	5 MBq/L	Pr	265	Dy	22
^{244}Cm	5 MBq/L	Nd	980	Ho	19
^{152}Eu	9 MBq/L	Sm	193	Er	19
Y	93	Eu	59	Tm	19
La	297	Gd	74	Yb	16
Ce	564	Tb	18	Lu	13
HNO_3	0.1 mol/L				

The process demonstration test was run in a 16-stage annular centrifugal contactor setup[12] installed in a fume-hood, following the flow-sheet shown in Figure 3. The test was run for 7 h, 15 min with regular sampling of the outlets of the contactor battery. After 7 h, 15 min the steady-state was reached and the test was stopped. The content of the contactors' mixing chambers was sampled and analysed. Figures 4 and 5 show the ^{241}Am and ^{152}Eu (gamma) as well as the ^{241}Am and ^{244}Cm (alpha) profiles, respectively. Table 2 shows the mass balances, recoveries and process decontamination factors obtained during the C5-BPP test.

Am was well extracted with a distribution ratio of 2.7 in the feed-stage. In the whole extraction section Am distribution ratios were quite low with values from 1.7 to 2.7, explaining the relatively flat profile. Surprisingly, the Am distribution ratios increased in the scrubbing section, with a maximum distribution ratio of 9.7. In this section, lower distribution ratios would have been expected, as the nitric acid concentration should have been slightly higher than in the extraction section. However, the aqueous/organic ratio and the total flow-rate in the scrubbing section changed and probably lead to higher extraction efficiency. In the stripping section, the Am profile was steeper and the distribution ratios decreased to 0.5. Obviously, the total number of stages was insufficient for sufficient decontamination and recovery of Am, so more stages in the extraction and stripping sections would be required.

Curium distribution ratios were even lower compared to Am with distribution ratios in the extraction section between 1.0 and 2.5. The lower extraction of Cm was expected from earlier experiments. This lead to a loss of Cm to the raffinate up to 24%. Of course, this value is far too high. However, with slight adjustments of the process, especially a higher number of stages, the loss could be reduced. With further adjustments, especially a precise nitric acid concentration control, also an Am/Cm separation might be possible. In

the scrubbing and stripping sections the Cm distribution ratios were also lower compared to Am.

The Eu profile very well resembles the profile of all lanthanides (including the heavier lanthanides). For Eu, maximum distribution ratios of 0.05 were observed. The best extracted lanthanides Pr and Nd showed maximum distribution ratios of 0.16. The lanthanide profiles were flat in the extraction section and the lanthanides were routed to the raffinate. In the scrubbing section the profiles show a steep decrease in the concentrations, leading to a good separation from An(III).
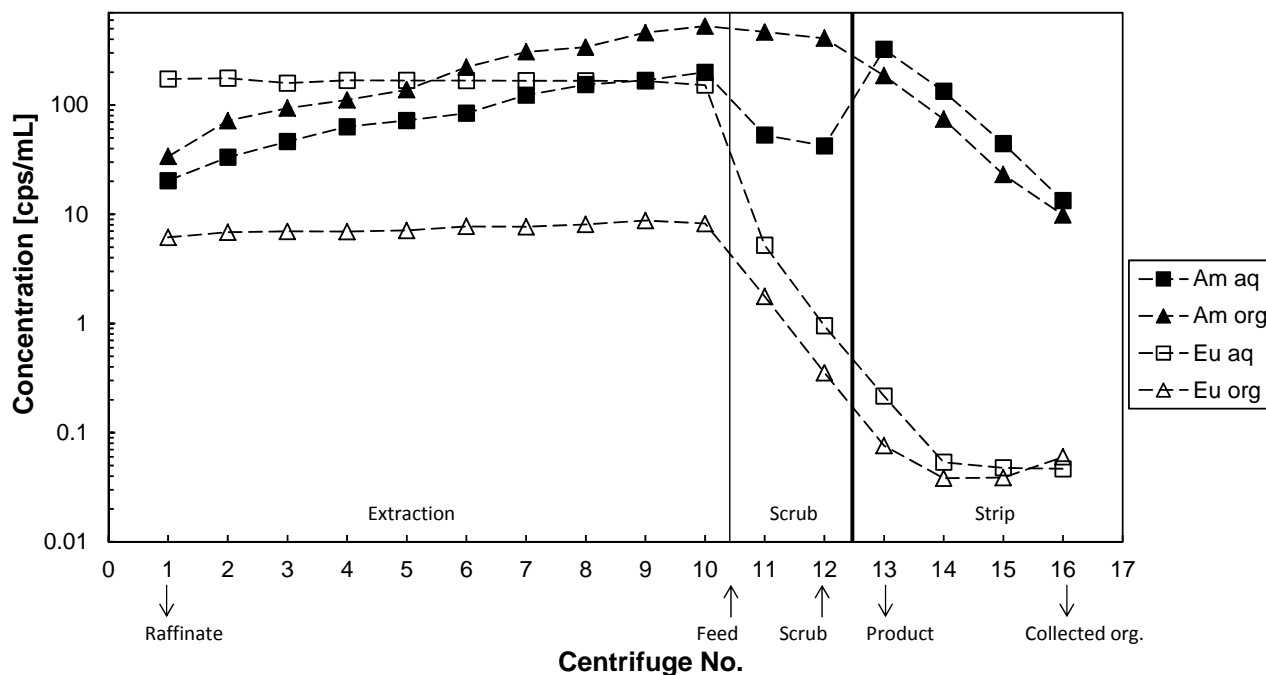

Figure 4. Experimental aqueous and organic concentration profiles of [241]Am and [152]Eu, determined by gamma-spectroscopy.
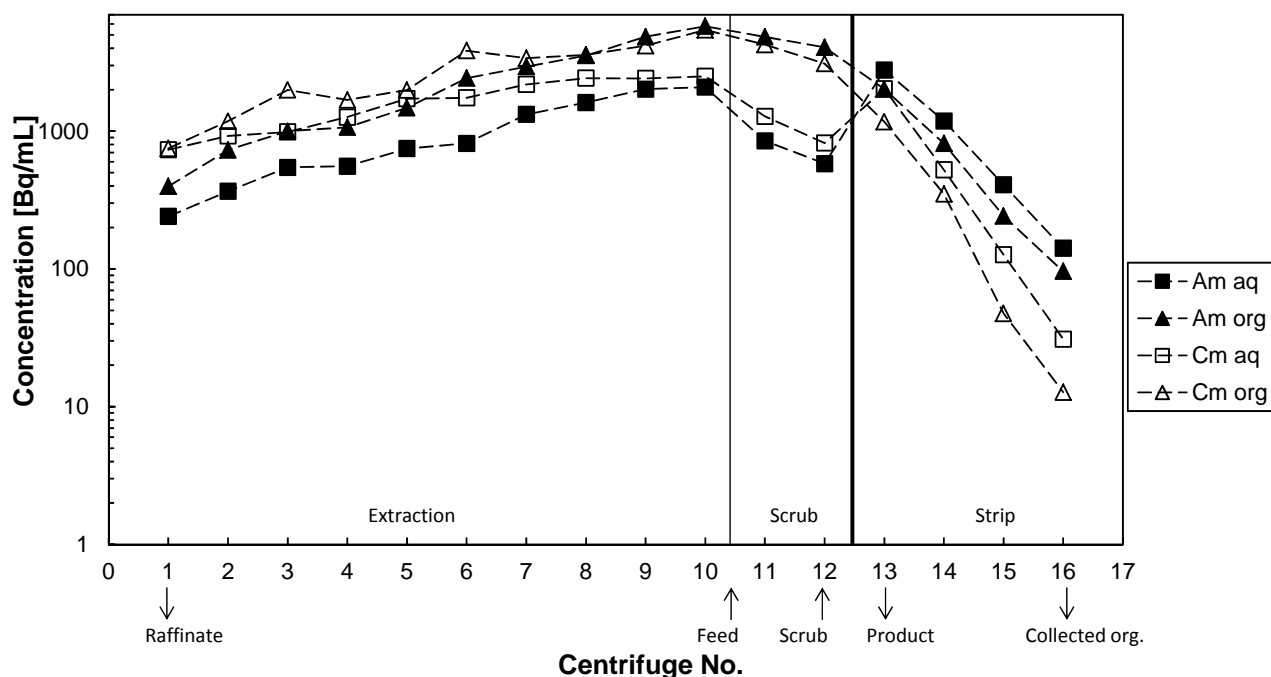
Figure 5. Experimental aqueous and organic concentration profiles of [241]Am and [244]Cm, determined by alpha-spectroscopy.

The feed/raffinate process decontamination factors in Table 2 underline the observations made from the profiles. The lanthanides were mostly routed to the raffinate with only low amounts of the best extracted lanthanides found in the An product. The highest contamination was caused by Nd(III) with 1.2% found in the product. The distribution of the lanthanides followed the trend described in ref.[7] and shown in Figure 2. The feed/raffinate decontamination factors of Am (12.0) and Cm (4.2) were quite low and have to be increased. This could either be done by increasing the total number of stages or by decreasing the nitric acid concentration in the extraction section. Decreasing the nitric acid concentration would increase the An(III) distribution ratios, see the extraction mechanism shown in Equation 1.

The spent solvent was only contaminated with 1.7% Am(III). Here, also two options are available to decrease the spent solvent contamination: increasing the number of stripping stages or increasing the nitric acid concentration of the stripping solution. The use of a higher nitric acid concentration however is limited, as the extractant C5-BPP may be protonated and precipitated.

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Table 2. Mass balance, recovery and process decontamination factors obtained during the C5-BPP test.

Element	% in raffinate	% in spent solvent	% in An(III) product	DF$_{feed/raffinate}$
^{241}Am	8.6	1.7	89.7	12.0
^{244}Cm	24.0	0.0	76.0	4.2
Y	100.0	D.L.	0.0	1.0
La	100.0	D.L.	0.0	1.0
Ce	99.6	D.L.	0.4	1.0
Pr	99.1	D.L.	0.9	1.0
Nd	98.8	D.L.	1.2	1.0
Sm	99.7	D.L.	0.3	1.0
Eu	99.9	0.0	0.1	1.0
Gd	99.7	D.L.	0.3	1.0
Tb	100.0	D.L.	0.0	1.0
Dy	100.0	D.L.	0.0	1.0
Ho	100.0	D.L.	0.0	1.0
Er	100.0	D.L.	0.0	1.0
Tm	100.0	D.L.	0.0	1.0
Yb	100.0	D.L.	0.0	1.0
Lu	100.0	D.L.	0.0	1.0

D.L. = below detection limit

Conclusions

The presented r-SANEX process based on C5-BPP showed a good selectivity for An(III) over Ln(III). A 16-stage spiked demonstration test showed the principal feasibility of the desired An/Ln separation with this solvent. A high purity of the An(III) product was obtained with only low contaminations of Ln(III). However, the total number of stages would have to be increased to increase the An(III) recovery and to minimise losses to the raffinate and spent solvent.

Acknowledgements

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