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# Flow-sheet design for an innovative SANEX process using TODGA and $SO_3$-Ph-BTP

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**Abstract**

An innovative SANEX process was designed using an organic phase comprising TODGA in TPH + 5% 1-octanol and an aqueous phase containing $SO_3$-Ph-BTP for the selective strip. The flow-sheet was optimized using batch data, single stage data and data from previously run TODGA processes. Recoveries for some key elements were calculated for selective strip section of the process using the SX Process program. According to the calculations, the An(III) are recovered from the PUREX raffinate with insignificant amounts of impurities. The presented flow-sheet will be used for a centrifugal contactor demonstration process which is expected to be successful.

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*Keywords*: innovative-SANEX; $SO_3$-Ph-BTP; Centrifugal Contactor; Flow-sheet; TODGA; SX Process.

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## 1. Introduction

The partitioning and transmutation concept (P&T) [1] aims at separation of the actinides from the PUREX raffinate and returning them to a reactor for further transmutation. The benefits of this concept are, reduced long term radiotoxicity and lower heat production in the final repositories. This means that a smaller and more efficient repository can be built [2].

Efficient separation of the actinides from the PUREX raffinate is very important for a successful P&T cycle. Np can be recovered by modifying the PUREX process [3] but the Am and Cm have to be recovered in additional separation processes. In Europe, during the NEWPART, PARTNEW and EUROPART projects, the DIAMEX+SANEX concept was developed for the separation of the Am + Cm [4-6]. Here Am + Cm and the lanthanides (Ln) were first co-separated by the DIAMEX (DIAMide EXtraction) process [7-11] directly from the HAR. Am + Cm were then separated from the Ln in a following SANEX (Selective ActiNide EXtraction) process [12, 13]. In the present European ACSEPT project, which follows EUROPART, a new type of process has been developed, the so called 1-cycle SANEX [14, 15]. The 1-cycle SANEX is dedicated to recover the minor actinides directly from a PUREX raffinate by selective extraction. The benefit with this process is the reduction of process steps from two to one compared with the DIAMEX+SANEX concept.

A different way for a one step separation is the innovative SANEX [16]. Here the An(III) and Ln(III) are first co-extracted, leaving the remaining fission and corrosion products in the raffinate, followed by a selective stripping of the An(III). Processes using this method have been tested earlier [17, 18] but they all have in common that a complicated pH control is necessary for the selective stripping. Recently a new molecule for the selective stripping was designed, the so called $SO_3$-Ph-BTP [19]. The $SO_3$-Ph-BTP is a water soluble molecule with high separation factor between Ln(III) and An(III), even at high acidity (>2 M $HNO_3$).This means that the acidity in the separation section can be chosen in a way that small changes can be neglected, without using a buffer solution.

An innovative SANEX process was designed using the $SO_3$-Ph-BTP. The co-extraction of the An(III) and Ln(III) can be carried out by using the extraction and scrub section from previously run TODGA processes [10, 11]. The TBP can be replaced by 1-octanol (5% vol) [20] which reduces the acid extraction. The selective strip was designed by using the SX Process program [21] to calculate the recoveries. The model was based on batch data and single stage experiments in a centrifugal contactor.

## 2. Flow-sheet

The first part of the flow-sheet, extraction and scrubbing, has been tested in a spiked demonstrations process in Forschungszentrum Jülich (FZJ) [10] and in a hot demonstrations process at the Institute for Transuranium Elements (ITU) [11]. Both the tests were successfully carried out in a centrifugal contactor set-up. The flow-sheet for the extraction and scrubbing is shown in figure 1a. The recoveries come from the demonstration process run at the ITU. The replacement of TBP with 1-octanol will slightly reduce the acid extraction but the An/Ln recoveries are expected to be more or less the same. Since the organic formulation using 1-octanol gives a bit higher distribution ratios the co-extraction of fission products like Zr, Sr and Pd could be a problem. Unpublished results show however that these elements can be efficiently scrubbed using the same masking agents/acidity concentrations as with the TBP.

Figure 1b shows the layout of the selective An/Ln strip. The selective strip section has to be split into two parts, An strip and Ln re-extraction. By adding a clean solvent flow the Ln that have been lost to the aqueous phase in the An strip will be re-extracted instead of ending up in the An product. The Ln stripping can be done at low acidity (~0.01 M $HNO_3$) or more efficiently (less stages) by a glycolic acid solution set to pH 4. In this case 4 stages for Ln stripping should be sufficient. The buffered solution also makes the stripping less sensitive to the acid carried over from the previous section.

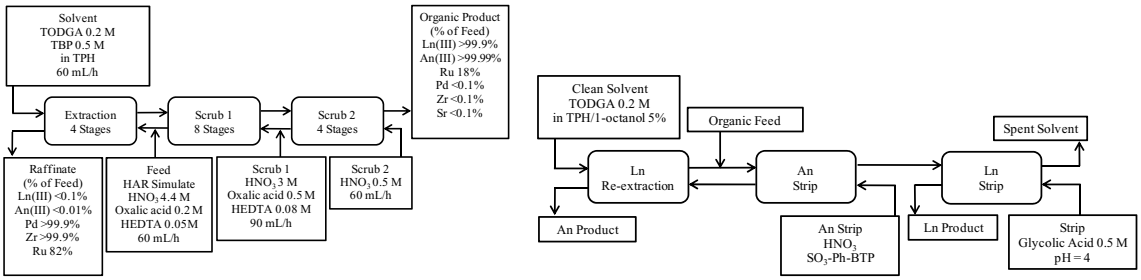


Fig. 1. (a) Flow-sheet for the extraction and scrubbing with measured recoveries. (b) Layout of the selective An/Ln strip.

## 3. Model

Calculations were carried out for the selective strip using the SX Process program [21]. In the preliminary calculations equilibrium distribution ratios as a function of the acidity were used. The equilibrium batch data are presented in [19]. The calculations were carried out for Am, Eu and La. La is the worst case for the Ln since it has the lowest distribution ratio while Eu was used as radio-tracer in the single stage kinetics experiments. The functions used for the calculations with equilibrium distribution ratios are shown in table 1. Polynomial fits to the batch data was used which means that the functions can not be extrapolated ($HNO_3$ range 0.14-0.93 M, in the aqueous phase at equilibrium).

Table 1. Functions for calculations using equilibrium distribution ratios. $C_{HNO3}$ is the aqueous nitric acid concentration at equilibrium. The concentration of $SO_3$-Ph-BTP is fixed to 18 mM.

| Solute | Function |
|---|---|
| $HNO_3$ | $8.81E\text{-}04*(C_{HNO3})^3 - 1.22E\text{-}02*(C_{HNO3})^2 + 5.47E\text{-}02*(C_{HNO3}) + 4.52E\text{-}03$ |
| Am | $4.58*(C_{HNO3})^3 - 2.72*(C_{HNO3})^2 + 7.61E\text{-}01*(C_{HNO3}) - 5.80E\text{-}02$ |
| La | $-1.53E+01*(C_{HNO3})^3 + 7.56E+01*(C_{HNO3})^2 - 1.95E+01*(C_{HNO3}) + 2.00$ |
| Eu | $2.93E+03*(C_{HNO3})^3 - 1.03E+03*(C_{HNO3})^2 + 1.94E+02*(C_{HNO3}) - 4.04$ |

By using single stage data, correction can be done for the kinetics. The method is further described in [21] but the main feature is that an over all transfer rate is used in the calculations to estimate the apparent distribution ratios. Single stage data for Am and Eu was used while the transfer rate for La was set to the same value as Eu.

## 4. Single stage experiments

A BXP012 type centrifugal contactor from Rousselet-Robatel was used for the single stage experiments. The mixing part of the contactor is small compared to the estimated flow-rates, and therefore the transfer kinetics might limit the apparent distribution ratios. The transfer kinetics are however expected to be fast [19] compared to regular extraction with molecules such as $CyMe_4$-BTBP [22]. A syringe pump was used to accurately deliver the wanted flow-rates (one pump with two syringes, flow-rate ratios where set by the syringes diameters). The whole set-up is installed in a glovebox.

The transfer kinetics had to be tested for both the An strip and the Ln re-extraction. Three different flow-rates were tested for each section, see table 2. Am tracer was used to represent the actinides while Eu tracer was used for the lanthanides. Both the An stripping and Ln re-extraction were carried out with an aqueous phase comprising 18 mM $SO_3$-Ph-BTP and 0.35 M $HNO_3$ and an organic phase comprising 0.2 M TODGA in TPH with

5% 1-octanol. In the An stripping the tracers were included in the organic phase while in the Ln re-extraction the tracers were added in the aqueous phase.

Table 2. Flow-rates used in the single stage experiments.

| Ln re-extraction | | An strip | |
|---|---|---|---|
| Flow-rate aq [mL/h] | Flow-rate org [mL/h] | Flow-rate aq [mL/h] | Flow-rate org [mL/h] |
| 20 | 20 | 20 | 40 |
| 40 | 40 | 40 | 80 |
| 60 | 60 | 60 | 120 |

## 5. Results and discussion

Table 3 shows the calculated recoveries for the selective strip using equilibrium distribution ratios. The calculations were done using a strip solution comprising 18 mM $SO_3$-Ph-BTP and 0.35 M $HNO_3$. The strip consisted of 12 stages, 6 for An strip and 6 for Ln re-extraction. As expected from the batch data, excellent separation was achieved. The high separation gives good safety margins towards changes in the distribution rations due to for example slow kinetics.

Table 3. Recoveries for the selective strip [% of organic feed].

| | Am | La | Eu |
|---|---|---|---|
| An product | >99.99 | 3.02E-03 | 1.03E-11 |
| Loaded organic phase | 7.83E-04 | >99.99 | >99.99 |

The results from the single stage experiments are shown in table 4. The stage efficiency is the percentage of the maximum substance transferred while the transfer rate is found by simulating a single stage contactor and changing the transfer rate until the apparent distribution ratio matches the experimental value. The transfer rate calculations are further described in [21].

Table 4. Results from the single stage experiments.

| | Flow-rate | Distribution Ratio | | Stage Efficiency E [%] | | Transfer Rate B [$s^{-1}$] | |
|---|---|---|---|---|---|---|---|
| | Org/Aq [mL/h] | Am | Eu | Am | Eu | Am | Eu |
| Ln Re-extraction | 60/60 | 0.074 | 3.6 | 473 | 86 | - | 0.060 |
| | 40/40 | 0.051 | 4.6 | 333 | 90 | - | 0.061 |
| | 20/20 | 0.040 | 4.7 | 264 | 90 | - | 0.032 |
| | Equilibrium | 0.015 | 10.4 | | | | |
| An Strip | 120/60 | 0.67 | 31.1 | 44 | 42 | 0.012 | 0.012 |
| | 80/40 | 0.070 | 19.6 | 90 | 67 | 0.091 | 0.021 |
| | 40/20 | 0.036 | 13.5 | 96 | 96 | 0.11 | 0.11 |
| | Equilibrium | 0.014 | 12.9 | | | | |

In the Ln re-extraction experiment the distribution ratio for Am is higher than the equilibrium value. This leads to stage efficiencies higher than 100%, which is not possible, but can be explained by contamination inside the centrifugal contactor. These values must be discarded but for the process development, the equilibrium distribution ratio can be used since it will represent the worst case scenario. For Eu the transfer rates at 60 and 40 mL/h agree well while at 20 mL/h the value is a bit low and has to be measured again. In the An strip the aqueous phase of the first sample (120/60) was less clear than the other samples. No organic phase could however be

observed in the sample and the mass balance was around 100%. The distribution ratio for Am is much higher than expected though, which suggests that the mixing was inefficient at this flow-rate. Due to the problems with the 120/60 sample the 80/40 sample didn't completely reach steady state, which was observed in the mass balance. The organic phase had however reached steady state since it had the double flow-rate (steady state is reached fast in the mixing part but some liquid has to pass through to have the mixer concentrations at the outlets). If the aqueous phase concentration is corrected to fit the mass balance, the 80/40 sample gets the same transfer rate as the 40/20 sample, i.e. 0.11 for Am. The same correction could not be done for Eu since the concentration in the aqueous phase was too low and a small error would give large impact on the transfer rate. For the process calculations the transfer rate for Eu (and La) was therefore set to the value at 40/20.

Table 5 shows the recoveries for the selective stripping with correction for the kinetics. In the calculations the flow-rates were set to 40 mL/h (clean organic phase, organic feed and An strip).

Table 5. Recoveries for the selective strip [% of organic feed] with kinetics corrections.

| | Am | La | Eu |
|---|---|---|---|
| An product | >99.99 | 1.92E-02 | 2.02E-04 |
| Loaded organic phase | 1.55E-04 | >99.98 | >99.99 |

As can be seen there is no big difference in the recoveries between the equilibrium calculations and the calculations with the kinetics, except for Eu in the An product. The amount of Eu in the An product is however still very small. A larger difference will appear if the flow-rates are increased but due to the low stage efficiency in the An strip at 120/60 mL/h, lower flow-rates should be used. If needed, the high separation gives the possibility to reduce the number of stages in the selective strip.

## 6. Conclusions

A flow-sheet for an innovative SANEX process was designed by combining the TODGA and $SO_3$-Ph-BTP molecules. Single stage experiments were carried out to test the transfer kinetics of the selective strip. The experiments showed that the kinetics of the $SO_3$-Ph-BTP system is fast, which is in agreement with earlier performed batch studies. Bad mixing efficiency was however observed when high flow-rates was used which limits the flow-rates to 40 mL/h. By using the SX process program the recoveries for the selective strip were calculated. The calculations shows that >99.99% of the An can be recovered with <0.02% Ln contamination.

A flow-sheet with the total amount of 32 stages, 16 for extraction and scrubbing, 12 for selective An stripping and 4 for Ln stripping is proposed for a demonstration process. The process is expected to recover >99.9% of the An from a PUREX raffinate with only small amounts of impurities.

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## References

[1] Magill, J., Berthou, V., Haas, D., Galy, J., Schenkel, R., Wiese, H.-W., et al. Impact Limits of Partitioning and Transmutation Scenarios on Radiotoxicity of Actinides in Radioactive Waste. *Nuclear Energy* 2003; **42**:263-277.

[2] *Potential Benefits and Impacts of Advanced Nuclear Fuel Cycles with Actinide Partitioning and Transmutation*, in *Nuclear Science*2011, OECD/NEA: Paris.

[3] Madic, C., Lecomte, M., Baron, P., and Boullis, B. Separation of long-lived radionuclides from high active nuclear waste. *Comptes Rendus Physique* 2002; **3**:797-811.

[4] Madic, C., Hudson, M.J., Liljenzin, J.-O., Nannicini, R., Facchini, A., Kolarik, Z., et al., *New partitioning techniques for minor actinides*, 2000: European Report.

[5] Madic, C., Testard, F., Hudson, M.J., Liljenzin, J.O., Christansen, B., Ferrando, M., et al., *PARTNEW - New Solvent Extraction Processes for Minor Actinides - Final Report*, 2004.

[6] Madic, C., Hudson, M.J., Baron, P., Ouvrier, N., Hill, C., Arnaud, F., et al. EUROPART. European Research Programme for Partitioning of Minor Actinides within High Active Wastes Issuing from the Reprocessing of Spent Nuclear Fuels. *FISA Conference* 2006;

[7] Baron, P., Berthon, L., Charbonnel, M.-C., and Nicol, C. State of Progress of DIAMEX Process. *GLOBAL 97* 1997; 366-370.

[8] Serrano-Purroy, D., Baron, P., Christiansen, B., Malmbeck, R., Sorel, C., and Glatz, J.P. Recovery of minor actinides from HLLW using the DIAMEX process. *Radiochimica Acta* 2005; **93**:351-355.

[9] Sasaki, Y., Sugo, Y., Suzuki, S., and Tachimori, S. The Novel Extractants, Diglycolamides, for the Extraction of Lanthanides and Actinides in $HNO_3$-n-Dodecane System. *Solvent Extraction and Ion Exchange* 2001; **19**:91-103.

[10] Modolo, G., Asp, H., Vijgen, H., Malmbeck, R., Magnusson, D., and Sorel, C. Demonstration of a TODGA-Based Continuous Counter-Current Extraction Process for the Partitioning of Actinides from Simulated PUREX Raffinate, Part II : Centrifugal Contactor Runs. *Solvent Extraction and Ion Exchange* 2008; **26**:62 - 76.

[11] Magnusson, D., Christiansen, B., Glatz, J.-P., Malmbeck, R., Modolo, G., Serrano-Purroy, D., et al. Demonstration of a TODGA based Extraction Process for the Partitioning of Minor Actinides from a PUREX Raffinate -- Part III: Centrifugal Contactor Run using Genuine Fuel Solution. *Solvent Extraction and Ion Exchange* 2009; **27**:26 - 35.

[12] Modolo, G., Sypula, M., Geist, A., Hill, C., Sorel, C., Malmbeck, R., et al. Development and demonstration of a new SANEX process for actinide(III)/lanthanide(III) separation using a mixture of CyMe4-BTBP and TODGA as selective extractant. *Tenth International International Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation (10-IEMPT)* 2008; 235-241,

[13] Magnusson, D., Christiansen, B., Foreman, M.R.S., Geist, A., Glatz, J.-P., Malmbeck, R., 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* 2009; **27**:97 - 106.

[14] Wilden, A., Schreinemachers, C., Sypula, M., and Modolo, G. Direct Selective Extraction of Actinides (III) from PUREX Raffinate using a Mixture of CyMe4-BTBP and TODGA as 1-cycle SANEX Solvent. *Solvent Extraction and Ion Exchange* 2011; **29**:190 - 212.

[15] Magnusson, D., Geist, A., Wilden, A., and Modolo, G. Direct Selective Extraction of Actinides(III) from PUREX Raffinate using a Mixture of CyMe4-BTBP and TODGA as 1-cycle SANEX Solvent. Part II: Flow-sheet Design for a Counter-Current Centrifugal Contactor Demonstration Process. *Solvent Extraction and Ion Exchange* 2013; **accepted**.

[16] Bourg, S., Hill, C., Caravaca, C., Rhodes, C., Ekberg, C., Taylor, R., et al. ACSEPT—Partitioning technologies and actinide science: Towards pilot facilities in Europe. *Nuclear Engineering and Design* 2011; **241**:3427-3435.

[17] Hérès, X., Sorel, C., Miguirditchian, M., Camès, B., Hill, C., Bisel, I., et al. Results of recent counter-current tests on An(III)/Ln(III) separation using TODGA extractant. *GLOBAL* 2009;

[18] Persson, G., Svantesson, I., Wingefors, S., and Liljenzin, J.O. Hot test of a TALSPEAK procedure for the separation of actinides and lanthanides using recirculating DTPA-lactic acid solution. *Solvent Extraction and Ion Exchange* 1984; **2**:89-113.

[19] Geist, A., Müllich, U., Magnusson, D., Kaden, P., Modolo, G., Wilden, A., et al. Actinide(III)/lanthanide(III) Separation Via Selective Aqueous Complexation of Actinides(III) Using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-Yl)-Pyridine in Nitric Acid. *Solvent Extraction and Ion Exchange* 2012; **accepted**.

[20] Geist, A. and Modolo, G. TODGA Process Development: an Improved Solvent Formulation. *GLOBAL* 2009;

[21] Magnusson, D. and Malmbeck, R. Development of a Solvent Extraction Model for Process Tests in Short Residence Time Centrifugal Contactors. *Solvent Extraction and Ion Exchange* 2012; **30**:115-126.

[22] Magnusson, D., Christiansen, B., Glatz, J.P., Malmbeck, R., Modolo, G., Serrano-Purroy, D., et al. Towards an optimized flow-sheet for a SANEX demonstration process using centrifugal contactors. *Radiochimica Acta* 2009; **97**:155-159.