Loading and flow-rate dependence of the transfer rates in a centrifugal contactor using organic ligand $CyMe_4$-BTBP

Daniel Magnusson[1], Andreas Geist[1], Rikard Malmbeck[2], Udo Müllich[1]
[1]Karlsruher Institut für Technologie, Institut für Nukleare Entsorgung, Karlsruhe, Germany, [2]European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe, Germany

Abstract

Centrifugal contactors are efficient and compact devices for running hydrometallurgical separation processes. Due to the short residence time in the centrifugal contactors the equilibrium distribution ratios are usually not reached. This can result in huge errors in the flowsheet calculations, which lead to badly designed processes. An estimation of the apparent distribution ratios can, however, be done using stage efficiencies. The stage efficiencies depend on many different parameters including loading and flow-rates.

CyMe4-BTBP is the current European reference extracting agent for the development of trivalent actinide separation processes such as r-SANEX [1] [2] and 1c-SANEX [3]. The CyMe4-BTBP ligand is known to have slow transfer kinetics, which is why this system's kinetics has been investigated further. Experiments were run in a single stage centrifugal contactor to see the influence of different metal loadings of the ligand, different flow-rates and different flow-rate ratios. As expected, stage efficiency was reduced with higher loading, higher flow-rates and lower organic to aqueous ratio. The transfer rate was constant for the different flow-rates but decreased with the higher loading and lower organic to aqueous phase ratio. A first order dependence of the free ligand concentration was observed for the transfer rate. Using the information from the experimental data, the apparent distribution ratios for a single stage centrifugal contactor can be calculated for varied loadings and flow-rates.

Introduction

In the partitioning and transmutation concept (P&T) the aim is to recover valuable metals from the spent nuclear fuel for further use in the nuclear fuel cycle and/or to reduce waste radiotoxicity and volumes [1]. For the reduction of the long term radiotoxicity of the spent fuel an efficient separation of the minor actinides (MA) is crucial. For this purpose many hydrometallurgical processes have been designed [2-6] and constantly new processes are under development.

To demonstrate the separation efficiency of a promising new system laboratory scale processes are carried out. These processes can be run with either simulate or genuine spent fuel solutions. The demonstration processes are, however, time-consuming and very costly due to the waste that is produced. In addition, there is often a limited amount of both the spent fuel solution and the organic ligands, which means only one try is possible. This makes it very important to have a well designed process that has been optimised to meet the requirements for a successful demonstration. Important parameters for the optimisation are the total number and distribution of stages between extraction, scrubbing and stripping sections, concentrations (ligand, metal, acidity, complexing agents, etc.) and flow-rates. In a multi stage process the optimisation often becomes complicated and therefore computer codes have been developed for this type of calculation [7-9].

Commonly used equipment for the small scale demonstration processes is the centrifugal contactor. The benefit with this equipment is that it can be made small and has an efficient phase separation which reduces the space and volumes needed for the test. A drawback is however that the contact time is very short due to the small mixing chamber. This means that the stage efficiency can become very low if the system has slow kinetics. It is therefore important to have a good model for the overall transfer kinetics.

The stage efficiency and the transfer kinetics can be studied in a single stage set-up. The efficiency is dependent on several factors such as the contact time (flow-rates), surface area (mixing efficiency, phase ratio), reagent concentrations, temperature, etc. In this paper, stage efficiencies and transfer rates were studied under varied conditions in a single stage centrifugal contactor. The influence of changed flow-rates, flow-rate ratios and metal loading is reported. The organic phase used in the study was based on the $CyMe_4$-BTBP molecule [10]. $CyMe_4$-BTBP is the current European reference extracting agent for the development of trivalent actinide separation processes such as r-SANEX [6] [11] and 1c-SANEX [12] [13]. This molecule is known to have slow kinetics [10] [14] which is beneficial for this type of study. In addition, a lot of extraction data are already available [10].

Single stage experiments

Figure 1 shows that for the experiments a single stage centrifugal contactor installed in a glovebox was used.

The centrifugal contactor is a BXP012 type, produced by Rousselet-Robatel, and has a rotor diameter of 12 mm. A syringe pump was connected to accurately pump the organic and aqueous solutions into the contactor. One pump with two syringes was used, which means that the organic to aqueous flow-ratio (O/A) could only be set using syringes with different diameters for the two solutions. The organic phase for all the experiments comprised 0.015 M CyMe4-BTBP and 0.25 M DMDOHEMA in TPH. Since only a limited amount of organic phase was available, it had to be washed between some of the experiments. This was done by contacting the solution with a 0.5 M glycolate solution

(set to pH 4) in a separation funnel (repeated twice). Prior to all the tests the organic phase was contacted with an aqueous phase containing 1 M HNO_3.

Figure 1: Single stage centrifugal contactor installed in a glovebox

Experiments changing the flow-rates, O/A and metal loading were carried out. The list of experiments and conditions can be seen in Table 1. The nitric acid concentration in the aqueous phase was 1.35 M in all the tests.

Table 1: List of different single stage experiments

	Flow-rates [mL/h]		O/A	Am Conc.
Test	Aq	Org		[mM]
1	100	100	1	0.03
2	75	75	1	0.03
3	50	50	1	0.03
4	30	30	1	0.03
5	20	20	1	0.03
6	10	10	1	0.03
7	8	20	2.5	0.03
8	50	20	0.4	0.03
9	100	20	0.2	0.03
10	40	20	0.5	0.03
11	20	20	1	1.0
12	20	20	1	1.9
13	20	20	1	3.0

The experiments were carried out by first starting up the centrifugal contactor (4 000 rpm) and then starting the pump with both syringes connected. The system was run until steady state was achieved, after which samples were collected from both the outlets. Tests 1-3 were run without interruption and only the flow-rate was changed. The syringes were then refilled, after which tests 4-6 were carried out. The remaining tests were run in the same way but with a stop between each to refill and either change the syringes (tests 7-10) or the aqueous feed solution (11-13). Between tests 11-13 the contactor was also emptied since the concentration of Am was varied (otherwise the time to reach steady state would be longer). Batch extraction tests were also carried out for the different conditions.

Results and discussion

The results from the single stage experiments can be seen in Table 2.

Table 2: Results from the single stage and batch tests

	Single Stage	Batch	Stage Efficiency	Transfer Rate
Test	D	D	E [%]	B [s^{-1}]
1	0.93	34	50	0.017
2	1.12	34	54	0.016
3	1.58	34	63	0.015
4	2.80	34	76	0.017
5	3.77	34	81	0.015
6	5.39	34	87	0.012
7	10.8	39	97	0.087
8	1.91	54	45	0.005
9	1.23	52	22	0.003
10	2.44	52	57	0.007
11	13.0	34*	96	0.072
12	9.17	26*	94	0.050
13	2.56	18*	75	0.011

* In the batch tests for 11-13 a precipitation was formed and therefore calculated equilibrium D had to be used. The calculations were based on the other samples plus some unpublished batch experiments.

The stage efficiency (E) is calculated using Equation 1.

$$E = \frac{C_{Feed} - C_{Out}}{C_{Feed} - C_{Eq}} \qquad \text{Eq. 1}$$

- C_{Feed} = the metal concentration in the aqueous feed;
- C_{Out} = the metal concentration in the aqueous product;

- C_{Eq} = the metal concentration in the aqueous product at equilibrium.

The transfer rate (B) is achieved by simulating a single stage experiment and varying the transfer rate until the calculated distribution ratio matches the experimental. The method is further described in [9].

In experiments 1-6 it can be seen that the apparent distribution ratios and the stage efficiencies increase with reduced flow-rates, as expected. The transfer rates agree well between the tests (except for number 6), which indicates that the transfer rate model works well for predicting apparent distribution ratios at different flow-rates. In the set of experiments with different O/A it can be noted that test number 7 has much higher stage efficiency than the other samples. This is partly explained by the fact that the washed organic phase still contained some Am. The amount was, however, small and only interfered in test 7 due to the large amount of organic phase compared to aqueous. The transfer rate is also very high and the most reasonable explanation for this is that when the organic phase is continuous, the surface area becomes much larger and hence a faster transfer is observed. In samples 8-10 the aqueous phase is expected to be continuous and with reduced organic phase volume (lower O/A) the surface area is decreased as well as the transfer rate. In the loading experiments (11-13) the apparent distribution ratios for tests 11 and 12 appear to be much higher than expected while for test 13 the value is in agreement with the expectations. A reasonable explanation for this is that in tests 11 and 12 the organic phase was continuous instead of the aqueous phase. This was unexpected since the O/A was one as in tests 1-6. The critical O/A where the continuous phase switches has, however, not been investigated for this system. From the data presented here it seems like at O/A equal one either of the two phases can be continuous and it is probably decided by the way the contactor is filled. If the organic phase enters first, it becomes continuous and remains so. More experiments have to be carried out to investigate this phenomenon.

The transfer rate has a first order dependence on the free BTBP concentration in the organic phase [15] [16]. By using this, the transfer rate for test 13 can be recalculated for 15 mM free BTBP (one Am occupies two BTBP [10]). The result is a B of 0.015 s^{-1} which is in good agreement with the average from test 1-5 (0.016 s^{-1}). Using B equal to 0.016 s^{-1} in combination with correction for the loading on both the transfer rates and the equilibrium distribution ratios the apparent distribution ratios for tests 1-5 and 13 can be calculated with good agreement towards the experimental values (Table 3). A different B has to be used for the experiments with continuous organic phase (not enough data to estimate here) and a model has to be developed to be able to predict the changes in the transfer rate due to the O/A.

Table 3: Experimental and calculated apparent distribution ratios

	Single Stage	Calculated
Test	D	D
1	0.93	0.88
2	1.12	1.17
3	1.58	1.73
4	2.80	2.83
5	3.77	4.15
13	2.56	2.80

Conclusions

The stage efficiencies and transfer rates were determined for different conditions in a single stage centrifugal contactor. With higher flow-rates the stage efficiency decreased while the transfer rate remained constant. When the O/A is lowered the transfer rate is reduced due to a smaller surface area, which also drastically decreases stage efficiency. It was observed that in the case of organic continuous phase the transfer rate increased significantly. At high loading the transfer rate decreased linearly with the free ligand concentration. With this information both the transfer rate and the equilibrium distribution ratio can be estimated for different loadings of the organic phase. Using these data apparent distribution ratios can be predicted for varied flow-rates and loadings by computer code calculations.

Further studies on the O/A ratio dependence and continuous phase behaviour need to be carried out in order to be included in the model. Also, the influence of the nitric acid on the transfer rate needs to be investigated.

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