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THE CENTRIFUGAL CONTACTOR AS A CONCENTRATOR IN SOLVENT EXTRACTION PROCESSES

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ABSTRACT

The possibility was explored of using solvent extraction in centrifugal contactors to concentrate metal ions from a waste stream when their distribution ratio values are favorable. The theoretical basis for such a concentrator was developed and is presented here, along with experimental results which show that a centrifugal contactor is capable of acting as such a concentrator.

INTRODUCTION

An impressive feature of centrifugal contactors, when compared with other solvent-extraction equipment, is their ability to operate at very high and very low organic-to-aqueous (O/A) flow ratios. In this work we build on this feature by testing to determine if, at such O/A flow ratios, the normally high extraction efficiency of centrifugal contactors is still high. If this is the case, then the contactors can be used to concentrate (by factors of 10 to 1000 or more) those metal ions that have a high distribution ratio (D value) during extraction and/or a low D value during stripping. For process streams containing such metal ions, one should be able to reduce, and in some cases eliminate, the need for downstream processing of one or more effluent streams.

There are three general areas where the centrifugal contactor could be very useful as a concentrator. The first area is the concentration of dilute feed streams so that the final process feed has a much smaller volume and process costs are reduced accordingly. The second area is the concentration of process effluents so that the need for further processing (for example, concentration by water evaporation) is greatly reduced or eliminated. The third area is the concentration and recovery of contaminants from groundwater. In addition, a contactor concentrator could be used to recover and concentrate any extractant or modifier that is dissolved or entrained in the aqueous effluent (raffinate) if pure diluent is the organic feed. In this way, any impact of residual extractant in the treated waste can be minimized.

To concentrate a component using solvent extraction, the D values (the concentration of the component in the organic phase divided by its concentration in the aqueous phase after the two phases have been equilibrated) must be favorable. For extraction processes, this means having a high D value so that the component is concentrated in the organic phase even though the O/A flow ratio (the R value) is low. For stripping processes, this means having a low D value so that the component is concentrated in the aqueous phase even though the R value is high. The ideal situation is to have a high D value as the component is extracted into the organic phase and a low D value as the component is stripped (back extracted) into the aqueous phase. How one finds such appropriate extracting or stripping agents is not discussed in this paper.

For component concentration using solvent extraction processing, the equipment that could be considered is reviewed first, and the reasons for choosing the centrifugal contactor are identified. Second, a theory for the design of concentrators is developed. Third, experimental results are given on the use of the centrifugal contactor to concentrate $Nd(NO_3)_3$.

EQUIPMENT

While several kinds of equipment can be used to concentrate a component using the very high and very low D values that solvent extraction can provide, a centrifugal contactor of the Argonne design is seen as particularly favorable (1-3). Other possibilities include (1) supported liquid membranes, (2) mixer settlers, (3) spray columns, and (4) pulsed columns.

Supported liquid membranes (SLMs) have the advantage that the organic phase is not normally lost to the aqueous phase, except by dissolution. Their drawback is that the D value for the extraction side must be very high (>1000), while that for the strip side must be very low (<0.001) to effectively remove and concentrate a species.

Mixer settlers, pulsed columns, and, especially, spray columns hold up much larger volumes of liquid for a given throughput than is the case with the centrifugal contactor. Thus, they would require more solvent in inventory and would take much longer to reach steady state. In addition, for the mixer settlers and pulsed columns, the range of O/A flow ratios is limited, from about 0.25 to 4, so that concentrating effects are limited to about a factor of 16. For typical pulsed columns, the continuous phase would be the aqueous phase in the extraction column and the organic phase in the stripping column.

Because the centrifugal contactor (1) provides easy access to the solvent, (2) has low liquid holdup for a given throughput, and (3) allows operation at any O/A flow ratio, it is the equipment of choice when using a solvent extraction process to concentrate a component. However, while the contactor can be operated easily at any O/A flow ratio, no data are available on whether or not the contactor maintains its high extraction efficiency at these very high or low O/A flow ratios. The experimental work reported here was carried out to answer this question.

A centrifugal contactor of the Argonne design works as shown in Fig. 1. In this design, two immiscible liquids flow into the annular mixing zone formed by the spinning rotor and the stationary housing wall. They are quickly dispersed in the turbulent two-phase flow created by the spinning rotor wall. The dispersion flows down the mixing zone and enters the centrifugal separating zone of the rotor through an opening in the bottom. Here the dispersion breaks rapidly under the high centrifugal forces. The separated phases flow over their respective weirs and are thrown from the rotor into their respective collector rings in the housing. Each liquid leaves its collector ring through a tangential exit port. A slinger ring minimizes the amount of the more-dense phase that leaks down into the collector ring for the less-dense phase. Phase separation is generally considered satisfactory if each effluent from a contactor stage contains <1% of the other phase.

A key feature of contactor operation with respect to very high or very low O/A flow ratios is the energy being dissipated in the highly turbulent flow of the mixing zone. This energy ensures that intimate mixing of the two phases is attained no matter what the O/A flow ratio. As a result, the extraction efficiency is

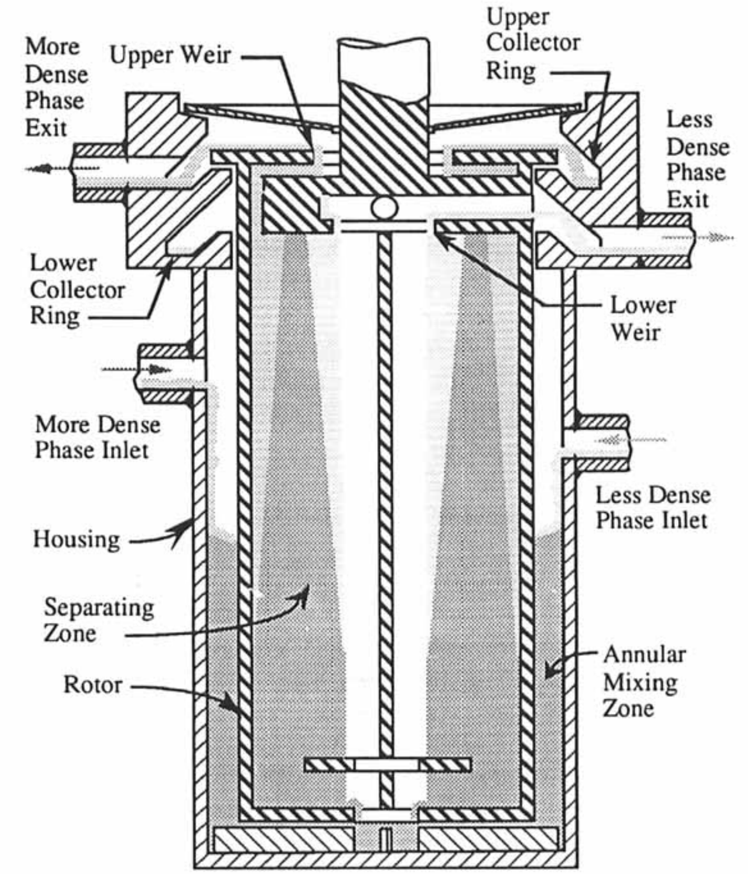

FIGURE 1. Schematic of Operating Centrigufal Contactor

high, typically greater than 90% for small (2-cm) contactors, where the O/A flow ratios range from 0.9 to 2.5 in single-stage operation (2). For larger (9- and 25-cm) contactors, extraction efficiencies of essentially 100% were obtained for an O/A flow ratio of 1.0 in single-stage operation (1,2). Based on this work on the extraction efficiency of centrifugal contactors at flow ratios close to 1.0, it was expected that extraction efficiency would remain high at O/A flow ratios far from 1.0. This assumption was tested in the neodymium extraction and stripping tests reported here. Additional information on design and operation of centrifugal contactors is given by Leonard (3).

CONCENTRATOR THEORY

Basic Ideas

In solvent extraction processes, the distribution coefficient (D) of each component is required for process analysis. A second quantity, the O/A flow ratio (R) for the process or section of the process, is also important. These two quantities are combined to form the extraction factor (E) for the component, which is given by

$$E = RD \tag{1}$$

For a given process stage, the extraction factor gives the moles of a component leaving in the organic phase divided by the moles of this same component leaving in the aqueous phase. If E is greater than 1.0, the component is being concentrated in the organic phase; if less than 1.0, in the aqueous phase. A stripping factor (S) can be defined as 1/E. When E is high, conditions are favorable for extraction. When S is high, conditions are favorable for stripping.

When a component is being extracted, its extraction factor should be in the range of 2 to 10 or higher. Since, for a given system, the D value is fixed, the extraction factor is set by the choice of R value. On the one hand, a high R value gives a high E value, so that extraction is easy and only a few process stages are required for a given decontamination factor (D.F.). As a first approximation, the D.F. for an extraction section with n stages is given by

$$\text{D.F.} = E^n \tag{2}$$

Thus, a process with an E of 10 will typically need quite a few less stages than a process with an E of 2 for a given D.F. On the other hand, a low R value gives good component concentration in the organic phase. However, the E value will also be lower, so that extraction is harder and more process stages will be required for a given D.F. In design of the extraction section of a concentrator, the R value chosen is a compromise between a high value for good component extraction with only a few contactor stages and a low value for good component concentration in the organic phase but with more contactor stages.

When a component is being stripped, its extraction factor should be in the range of 0.5 to 0.1 or lower. As a first approximation, the stripping factor (S.F.) for a stripping section with n stages is given by

$$S.F. = E^{-n} \tag{3}$$

Thus, a process with an E of 0.1 will typically need quite a few less stages than a process with an E of 0.5 for a given S.F. By converse reasoning to that given for the extraction section, the R value chosen in designing the stripping section is a compromise between a low value for good component stripping with only a few contactor stages and a high value for good component concentration in the aqueous phase but with more contactor stages.

Limits

Two factors, other-phase carryover and stage efficiency, could limit the effectiveness of the centrifugal contactor as a concentrator.

Other-Phase Carryover

One limit on the basic theory comes from the effect of other-phase carryover. Because of other-phase carryover, the actual D value in Eq. 1 must be replaced with an effective D value (D_{eff}). Typically, D_{eff} changes in such a way that the concentrating effect is diminished. When other-phase carryover is low, D_{eff} is approximated by

$$D_{eff} = \frac{D + f_0}{1 + f_a D} \tag{4}$$

where f_a is the fraction of organic phase in the effluent from the aqueous-phase exit, and f_0 is the fraction of aqueous phase in the effluent from the organic-phase exit (4). This equation shows that, no matter how high D is in the extraction section, D_{eff} will always be less than $1/f_a$ but will be essentially unaffected by f_0. Since f_a will be low (<0.01), with the aqueous phase being the predominant phase in the extraction section of a concentrator, the D value will have to be fairly high before D_{eff} will become important. Since D_{eff} is essentially unaffected by f_0, low flow of the organic phase resulting in high other-phase carryover should be only a minor problem in operating a concentrator.

Conversely, Eq. 4 shows that, no matter how low D is in the stripping section, D_{eff} will always be greater than f_0, but will be essentially unaffected by f_a. Since f_0 will be low (<0.01), with the organic phase being the predominant phase in the stripping section of a concentrator, the D value will have to be fairly low before D_{eff} will become important. Since D_{eff} is essentially unaffected by f_a, low flow of the aqueous phase resulting in high other-phase carryover should be only a minor problem in operating a concentrator.

As other-phase carryover increases, Eq. 4 becomes less and less accurate. It should not be used if other-phase carryover is much greater than 1%. Instead, the stage-to-stage concentration profiles for the various components during concentrator operation should be calculated using the more general equations presented in (4). As explained there, these equations have been incorporated into a Microsoft Excel worksheet named SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) so that these stage-to-stage calculations are easy to carry out.

Extraction Efficiency

In design of a contactor for which the rotor diameter and speed are fixed, the annular gap between the spinning rotor and the stationary housing wall must be small enough that extraction efficiency is high. However, the gap should not be so small that the two-phase dispersion backs up in the mixing zone and overflows into the lower collector ring for the exiting less-dense phase. By optimization of the annular gap, the contactor can be made to operate at extraction efficiencies that are greater than 95%, typically, 98 to 99%, while reasonable liquid levels are maintained in the annular mixing zone at O/A flow ratios close to 1.0 (1,2). In the tests reported below, the range of O/A flow ratios over which extraction efficiencies were measured was extended to 0.01 - 32. These tests were made to determine if, when one phase is present in the annular mixing zone with only a small amount of the other phase, the extraction efficiency is still high.

One mechanism for lowered extraction efficiency in a stage comes from the liquid flow. If the flow of one phase is so small that it flows in spurts, the extraction efficiency will be degraded. This intermittent flow is seen to be a possible problem with smaller contactors, for example, the 2-cm contactor, which has a nominal throughput of 40 mL/min (1). In such cases, surface tension forces have a large effect on the liquid flow in the interstage lines. As contactors are made larger and thus have increased throughput capacity, the low-flow stream flow rate becomes larger for the same O/A flow ratio. Eventually, the interstage flow becomes continuous. When this happens, any degradation of the extraction efficiency in the contactor stage due to intermittent flow at low-flow conditions should disappear.

CONCENTRATOR DESIGN

The basic configuration for concentrator design using centrifugal contactors is given here. Then the basic design variables (the distribution

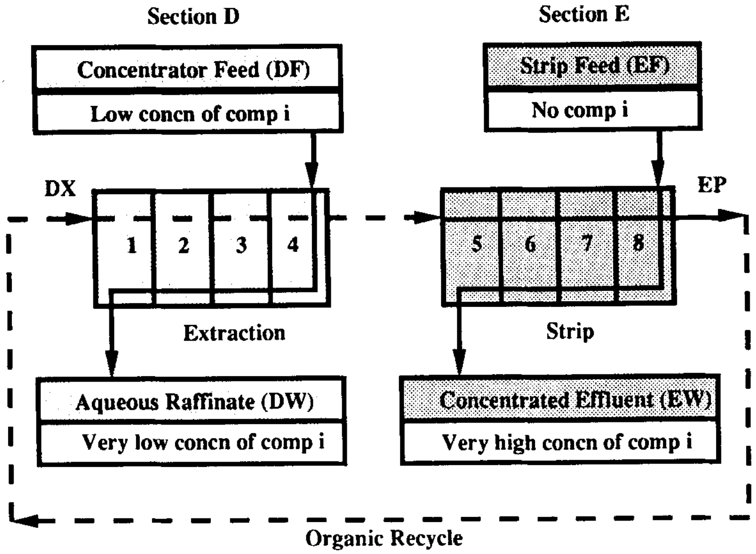

FIGURE 2. Schematic of Concentrator with Eight Contactor Stages

coefficients, the O/A flow ratios, and number of stages), are evaluated for their effect on concentrator design, and a rule of thumb is presented for estimating an overall concentration factor. Finally, the SASSE worksheet is used to determine the effect of various operational parameters on an eight-stage concentrator. These parameters are extraction efficiency, other-phase carryover, and solvent recycle.

Basic Configuration

A schematic of a typical concentrator design is shown in Fig. 2. Each section will have one or more stages. In the schematic, four stages are shown for each of the two sections. With a high extraction factor (≥10) in the extraction section, 90% of the concentrating effect in the organic phase will be realized with only one stage. The use of additional extraction stages lowers the component concentration in the aqueous raffinate and pushes the concentrating effect even closer to 100%. With lower extraction factors, typically ≥2, several stages will be required to realize a concentrating effect of 90% or higher in the organic phase.

Conversely, with a low extraction factor (≤0.1) in the strip section, 90% of the concentrating effect in the aqueous phase will be realized with only one stage. The use of additional stripping stages increases the component concentration in the concentrated aqueous effluent and pushes the concentrating effect even closer to 100%. With higher extraction factors, typically ≤0.5, several stages will be required to realize a concentrating effect of 90% or higher in the aqueous phase.

In addition to the extraction and strip sections shown in Fig. 2, some processes may have one or more components entrained in or partially extracted into the organic phase coming from the extraction section. If these components are harmful or unwanted in the concentrated effluent, a scrub section of one or more stages can be inserted between the extraction and strip sections. Typically, the aqueous effluent from the scrub section joins with the aqueous feed to form a combined feed for the extraction section and comes out as part of the aqueous raffinate.

Another of the concentrator design shown in Fig. 2 is the complete recycle of the organic phase. This requires that the extraction and strip sections be balanced. To do this, enough of the concentrated component must be removed from the organic phase (EP) leaving the strip section so that one achieves the low component concentration desired in the aqueous raffinate (DW) from the extraction section. In some cases, a solvent cleanup section must be inserted after the strip section.

If the O/A flow ratio is very high in the extraction section, then the centrifugal contactors for the stripping section should be smaller than those for the extraction section to reduce startup time. To have the concentrator working from the outset, the low-flow phases should be introduced at a high flow on startup so that they fill properly all the concentrator stages. If this is done, the concentrator will be fully functional even though it is still in a startup mode. One could then put each of the stages in the stripping section on full aqueous phase recycle until the desired concentrating effect is reached. This would speed up the approach to steady state and ensure that, when the initial aqueous concentrate exits the contactor, it is close to its steady state concentration.

When a component (metal ion) has a high D value for extraction, stripping can be difficult. For this reason, a complexant will typically be included in the strip feed to bring the component back into the aqueous phase. When using a complexant, one has to evaluate (1) its contribution to the final aqueous composition, (2) its solubility in the organic phase, and (3) the possibility that the complexant might form a solid precipitate with the component being stripped. Such

TABLE 1. Effect of O/A Flow Ratio on Total Stages Required

Rel. Amt. of Comp. Concn.	O/A Flow Ratio		Extr. Factor		Overall Concn. Factor	Extr. Stages for D.F. of 1.0E+6	Strip Stages for S.F. of 1.0E+6	Total Stages Req'd
	Extr.	Strip	Extr. (D=100)	Strip (D=0.01)				
Low	0.5	2	50	0.02	4	4	4	8
Med	0.1	10	10	0.1	100	6	6	12
High	0.02	50	2	0.2	2500	20	20	40

a precipitate may not be bad if it can be recovered (for example, by filtration) in such a way that a further volume reduction (concentration) of the component is achieved. When a significant amount of the complexant would be carried out of the strip section in the organic phase, the complexant strip section should be designed to minimize this loss by feeding most of the complexant to the first strip stage.

Design Variables

For a given system where the D values are fixed by the chemistry of the components and the solvent, the main design variables are the O/A flow ratio and the number of stages. Equations 1-3 with $D_{extr} = 100$ and $D_{strip} = 0.01$ were used to calculate the effect of the O/A flow ratio on the total number of stages required. The results are shown in Table 1 for three levels of concentrating effect. The low level of concentrating effect uses O/A flow ratios close to 1.0, so that both the extraction and stripping factors are high and the total number of stages required is low. The tradeoff is that the overall concentrating factor is low, only 4 for the example shown in Table 1. The medium level of concentrating effect uses O/A flow ratios somewhat further from 1.0, so that both the extraction and stripping factors are lower and the total number of stages required is higher. However, the overall concentrating factor is also higher, 100 for the example shown in Table 1. The high level of concentrating effect uses O/A flow ratios even further from 1.0 so that both the extraction and stripping factors are only 2.0 and the total number of stages required is much higher. The tradeoff is that the overall concentrating factor is also very high, 2500 for the example shown in Table 1.

Note that the overall concentrating factor (O.C.F.) in Table 1 is the concentration of a component in the aqueous effluent from the strip section, x_{strip}

(EW in Fig. 2), divided by the concentration of the same component in the aqueous feed to the extraction section, x_{extr} (DF in Fig. 2), that is,

$$\text{O.C.F.} = \frac{x_{strip}}{x_{extr}} \tag{5}$$

In Table 1, O.C.F. is obtained indirectly by assuming that (1) other-phase carryover is zero, (2) extraction efficiency is 100%, and (3) there are a sufficient number of extraction and strip stages that D.F. and S.F. are high, for example, 10^6. With these assumptions, which lead to the highest possible level of component recovery, the resulting overall concentration factor (O.C.F.--high recovery) can be written in terms of the R values for the stripping section (R_{strip}) and the extraction section (R_{extr}) as

$$\text{O.C.F.--high recovery} = \frac{R_{strip}}{R_{extr}} \tag{6}$$

To set a medium level for the concentrating effect shown in Table 1, one must balance the number of stages required with the desired concentrating effect. Our choice was to relate the O/A flow ratio for a flowsheet section to the D value for the key component to be concentrated in that section using

$$R = \frac{1}{\sqrt{D}} \tag{7}$$

Equations 1 and 7 combine to give

$$E = \sqrt{D} \tag{8}$$

With this choice for a balanced design, the overall concentrating factor (O.C.F.--balanced) is given by

$$\text{O.C.F.--balanced} = \sqrt{\frac{D_{extr}}{D_{strip}}} \tag{9}$$

Model Analysis

A SASSE worksheet outlined in Leonard et al. (4) includes (1) the more general equations presented there to handle high amounts of other-phase carryover and (2) the effect of extraction efficiency on the D value for each component at each stage as presented in Leonard (5). Using this worksheet, the neodymium concentration in the aqueous effluent (EW) from the strip section was explored as a function of extraction efficiency, other-phase carryover (both f_a and f_o), and organic phase recycle.

The system modeled was a feed with a high salt content and a neodymium concentrator with eight stages, as shown in Fig. 2. The aqueous DF feed had a composition of $7\text{x}10^{-7}\underline{M}$ Nd with $2.0\underline{M}$ $NaNO_3$ and $0.02\underline{M}$ HNO_3 so that D_{Nd} in the extraction section would be about 500 when the organic DX feed is the TRUEX-NPH solvent, that is, $0.20\underline{M}$ CMPO [octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide] and $1.4\underline{M}$ TBP (tributyl phosphate) in NPH (normal paraffin hydrocarbon, mainly normal dodecane). The R value in the extraction section was 0.01 so that each stage had an extraction factor of 5 with respect to neodymium. The loaded solvent entered the stripping section where the neodymium was removed by countercurrent contact with an aqueous solution of $0.1\underline{M}$ HNO_3 containing $0.05\underline{M}$ of the complexant HEDPA (1-hydroxyethane-1,1-diphosphonic acid) so that D_{Nd} in the stripping section was about 0.002. The concentration of HEDPA in the strip (EF) feed was chosen so that there was 10 times more HEDPA than neodymium in the concentrated (EW) effluent. The R value in the stripping section was 100 so that each stage had a stripping factor of 5 with respect to neodymium. For this analysis, the base case was an extraction efficiency of 100%, f_a and f_o of 0.005 (0.5%), and no organic recycle.

Results of the model evaluation are listed in Table 2. For this model, Eq. 6 gives an overall concentrating factor of 10,000 when there is no other-phase carryover. Since the base case (case 1) has 0.5% other-phase carryover, the O.C.F. was found to be lower, 6470. Thus, as shown in Table 2, the concentrated aqueous effluent (EW) for case 1 is $4.53\text{x}10^{-3}\underline{M}$ Nd. When the organic phase is recycled (case 2), the neodymium concentration in EW increases about 1%, and the neodymium concentration in the aqueous raffinate (DW) increases about 12%. The stage-to-stage concentration profiles for the organic and aqueous phases of these two cases, given in Fig. 3, show that the effect of organic recycle is negligible for this design. The one other case with organic phase recycle (case 8) again showed very little effect of this solvent recycle. Organic recycle would become important if there were insufficient stages in the stripping section to adequately remove the concentrated species.

When other-phase carryover is lowered from its base-case fractional value of 0.005 (0.5%, case 1 in Table 2) to 0.001 (case 3), the overall concentrating factor

TABLE 2. Summary of SASSE Model Evaluation. Case 1 is the base case.

Case	Fract. Extr. Eff.	Other-Phase Carryover Fraction O in A	A in O	Section	Org. Recycle	Nd Concn in Effluents, M DW	EW	EP
1	1.0	0.005	0.005	Both	no	1.15E-8	4.53E-3	7.58E-7
2	1.0	0.005	0.005	Both	yes	1.30E-8	4.57E-3	7.64E-7
3	1.0	0.001	0.001	Both	no	2.30E-9	6.31E-3	2.04E-7
4	1.0	0.010	0.010	Both	no	2.47E-8	3.30E-3	1.21E-6
5	0.9	0.005	0.005	Both	no	2.62E-8	4.41E-3	1.16E-6
6	0.8	0.005	0.005	Both	no	4.76E-8	4.22E-3	1.84E-6
7	0.7	0.005	0.005	Both	no	7.68E-8	3.95E-3	2.98E-6
8	0.7	0.005	0.005	Both	yes	8.23E-8	4.11E-3	3.10E-6
9	1.0	0.005	0.350	Extr.	no	1.16E-8	4.53E-3	7.66E-7
		0.350	0.005	Strip				

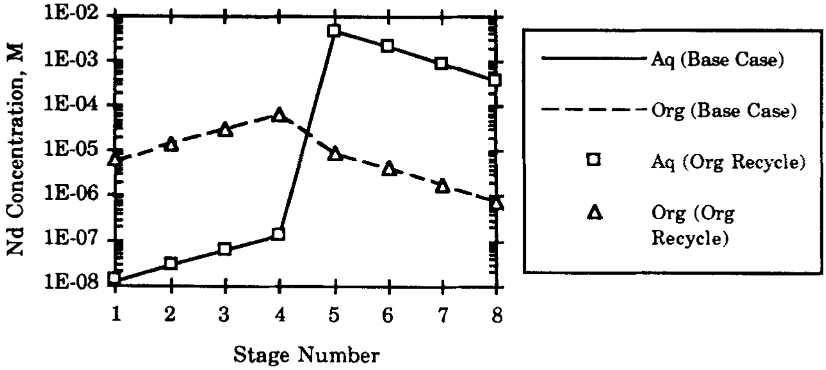

FIGURE 3. Effect of Organic Recycle on Neodymium Concentration Profiles in the 8-Stage Concentrator

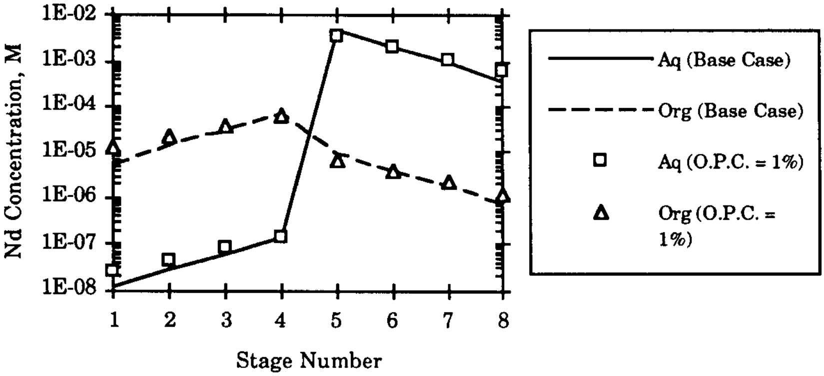

FIGURE 4. Effect of 1% Other-Phase Carryover (O.P.C.) on Neodymium Concentration Profiles in the 8-Stage Concentrator

was found to increase from 6470 to 9010, very close to the value of 10,000 for the case of no other-phase carryover and many stages in each section (so that D.F. and S.F. are very high). Conversely, when other-phase carryover is increased from its base-case value to 0.010 (case 4), the overall concentrating factor decreases from 6470 to 4710. These results show that concentrator operation is sensitive to small changes in the other-phase carryover that are within the range of normal contactor operation. The stage-to-stage concentration profiles for the organic and aqueous phases of cases 1 and 4, given in Fig. 4, show how increasing other-phase carryover (O.P.C.) affects the neodymium concentration in the various concentrator stages.

As the extraction efficiency drops (cases 5, 6, and 7 in Table 2), the overall concentrating factor is reduced, as indicated by the decrease in the EW values for neodymium. However, even for the worst-case modeled, case 7, which has an extraction efficiency of 70%, the overall concentrating factor is still quite high, 5640. These results show that, while concentrator operation is sensitive to changes in the extraction efficiency, it will still work. The stage-to-stage concentration profiles for the organic and aqueous phases of cases 1 and 7, given in Fig. 5, show how decreasing extraction efficiency (E.E.) affects the neodymium concentration in the various concentrator stages.

Finally, when there is 35% other-phase carryover in the low-flow phase (case 9 in Table 2), the overall concentrating factor is unaffected, although the

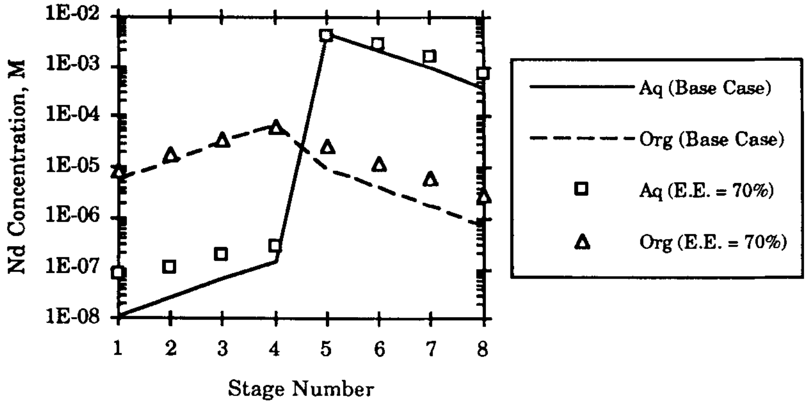

FIGURE 5. Effect of 70% Extraction Efficiency (E.E.) on Neodymium Concentration Profiles in the 8-Stage Concentrator

neodymium concentration in DW increases by 1%. This result was expected based on the D_{eff} analysis given above. The stage-to-stage concentration profiles for the organic and aqueous phases of cases 1 and 9, given in Fig. 6, also show that the neodymium concentration in the various concentrator stages is not affected by this change.

Overall, this more-detailed analysis of concentrator operation shows that, over the range of variables expected for contactor operation, concentrator operation should be reasonably effective.

EXPERIMENTAL WORK

The purpose of the experimental work was to determine if contactor efficiency remains high at extremely high and extremely low O/A flow ratios. In the first phase of the work, one-stage contactor tests were run at very low O/A flow ratios, contacting aqueous and organic phases with a very high D value for neodymium. As a result, most of the neodymium was concentrated into the organic effluent. The focus here was to find the efficiency of the contactor as it was extracting at these very low O/A flow ratios. In the second phase of the work, a two-

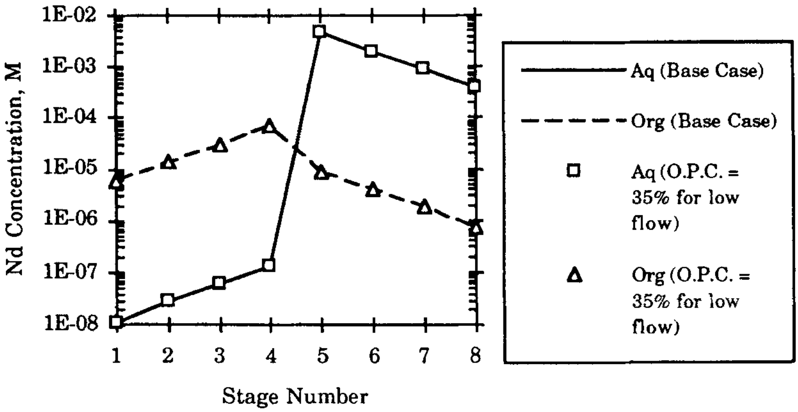

FIGURE 6. Effect of High (35%) Other-Phase Carryover (O.P.C.) in the Low Flow Streams on Neodymium Concentration Profiles in the 8-Stage Concentrator

stage contactor test was run with the first stage as an extraction stage and the second as a stripping stage. In the stripping stage, a high O/A flow ratio was used with a process having a low D value for neodymium so that neodymium was effectively concentrated into the aqueous effluent. The focus of this test was on the efficiency of the second contactor stage as it stripped neodymium at a very high O/A flow ratio. Taken together, the experimental work allows one to evaluate the efficiency of the contactor when it is used as a concentrator at extremes in the O/A flow ratio.

The organic phase in these tests contains 0.2M CMPO and 1.4M TBP with either NPH or nDD (normal dodecane) as the diluent. These solutions are referred to here as TRUEX-NPH or TRUEX-nDD, respectively. More details on the TRUEX process, which is used to remove long-lived transuranic elements from nuclear wastes, are available elsewhere (6-9). The contactor tests were carried out in the remote-handled 4-cm contactor described by Leonard (3).

Test Method

In two series of tests, neodymium was extracted from an aqueous phase into an organic phase at very low O/A ratios, about 0.01, in a process with a D_{Nd} value of about 500. Thus, since the overall extraction factor was about 5, the neodymium was

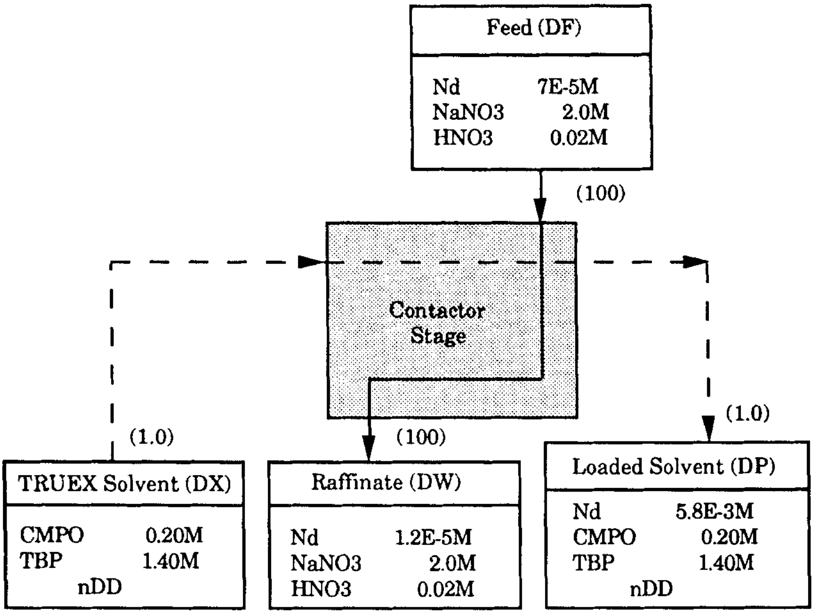

FIGURE 7. Flowsheet for Single-Stage Concentrator Tests at O/A of 0.01. Effluent concentrations are shown for the case where the extraction efficiency is 100% and D_{Nd} is assumed to be 500. Relative flow rates are shown in parentheses.

concentrated in the organic phase. The flowsheet used for the extraction tests, shown in Fig. 7, was run at DF flow rates of 200, 300, and 400 mL/min for each test series. The Nd concentration in the DF feed was chosen low enough that Nd loading of the solvent would never exceed 10% ($<6.7\times10^{-3}\underline{M}$ Nd in the organic phase). This prevents the formation of a second organic phase. With an extraction factor of 5, the Nd concentration in the DW raffinate is still high enough ($>5\times10^{-6}\underline{M}$) to be detected by inductively coupled plasma/atomic emission spectrometry (ICP/AES) with ±10% accuracy. The effluent concentrations in Fig. 7 show that, even if the extraction efficiency is 100% and D_{Nd} twice that expected, the Nd concentration in each effluent will be within its desired range.

Two-stage contactor tests were conducted to measure the extraction (stripping) efficiency when neodymium is stripped from the organic phase at very

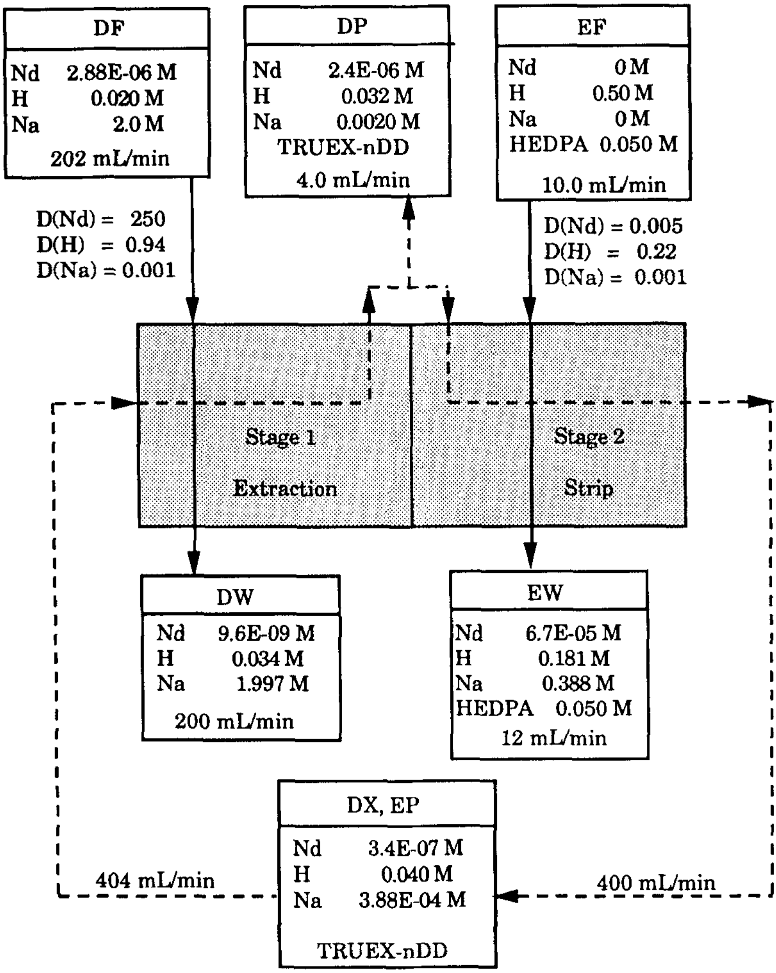

FIGURE 8. Flowsheet for Two-Stage Contactor Test. Effluent concentrations are for the case where the extraction efficiency is 100%, the D values for stages 1 and 2 are as shown, and the aqueous-phase carryover from stage 1 to stage 2 is 0.5%.

high O/A flow ratios. The flowsheet for this test is shown in Fig. 8. In the first stage, neodymium was loaded into the organic phase from an aqueous phase at normal O/A flow ratios (close to 1.0). In the second stage, the concentrating stage, the neodymium was stripped from the organic phase into another aqueous phase at a high O/A flow ratio. The D value for neodymium in the second stage was low because of the HEDPA complexant in the aqueous feed to stage 2. As a result, the neodymium was concentrated in the aqueous effluent from the second stage.

Since the O/A flow ratio in the second stage (stage 2) of this test is high, a small fraction of other-phase carryover in the organic effluent from stage 1, which is the organic influent to stage 2, will make a large difference in the O/A flow ratio for stage 2. For example, the flowsheet in Fig. 8 assumes 0.5% aqueous phase in the organic phase flowing from stage 1 to stage 2. This decreases the O/A flow ratio from 40 to 33. In addition, the sodium concentration in the EW effluent is fixed by this other-phase carryover and was used to determine the amount of other-phase carryover during the tests.

To avoid the precipitation of the neodymium salt of HEDPA in stage 2, a batch test of the flowsheet shown in Fig. 8 was made prior to running the flowsheet in the 4-cm contactor. The solubility of the neodymium salt of HEDPA was found to be about $5.8\text{x}10^{-5}\underline{M}$. Based on this solubility and the need to get neodymium concentrations high enough to be analyzed, the neodymium concentration in the aqueous feed to stage 1 was set at $2.88\text{x}10^{-6}\underline{M}$. Given the O/A flow ratios stated above along with the D_{Nd} values shown in Fig. 8 for stages 1 and 2, this feed concentration gives a neodymium concentration in the HEDPA stripping solution that is saturated with the neodymium salt of HEDPA.

In both the stripping and extraction tests (two each), the appropriate D_{Nd} value for a stage was determined by equilibrating portions of the organic and aqueous effluents from the stage at the temperature measured during the test. All tests were done between 22 and 25°C. For organic phase analyses, the neodymium concentration was measured after the neodymium was stripped back into the aqueous phase using a $0.05\underline{M}$ HEDPA solution in $0.5\underline{M}$ HNO_3. As noted above, all neodymium analyses were done by ICP/AES, which has a neodymium detection limit of $3.6\text{x}10^{-8}\underline{M}$ when Na salts are $0.4\underline{M}$ or less. The one exception was the DW samples for the flowsheet shown in Fig. 8. Because the predicted neodymium concentrations were so low for these samples, they were analyzed using isotope dilution mass spectrometry (IDMS), which has a lower neodymium detection limit, $7\text{x}10^{-9}\underline{M}$.

TABLE 3. Summary of Extraction Efficiency Results at Various O/A Flow Ratios

Element	O/A Flow Ratio	Fractional Extraction Efficiency	Notes
Nd	0.0096 ± 0.0004	0.796 ± 0.076	a
Nd	0.0101 ± 0.0013	0.877 ± 0.099	b
U	0.5 to 2.5	$0.986^{+0.01}_{-0.03}$	c
Nd	2.67 ± 0.03	0.961 ± 0.024	d
Nd	32.8 ± 1.7	0.851 ± 0.130	e

[a] Composite of the three tests in the second test series at O/A = 0.01.

[b] Composite of the three tests in the first test series at O/A = 0.01.

[c] Extraction efficiency and error range were estimated from earlier measurements as discussed in the text. Most of these extraction efficiency measurements were made at an O/A of 1.0.

[d] Composite of two tests carried out while loading the solvent with neodymium for the high O/A flow ratio tests.

[e] Composite of two stripping tests.

Results

The fractional extraction (stripping) efficiency (F_e) is the amount of a component in the aqueous phase entering a stage that is extracted into (stripped from) the organic phase relative to the amount that would be extracted (stripped) if the two phases were equilibrated in the stage. Thus, F_e based on the aqueous phase is written as

$$F_e = \frac{x_{i+1} - x_i}{x_{i+1} - x_i^*} \tag{10}$$

where x_{i+1} is the component concentration in the aqueous phase entering stage i, x_i is its concentration in the aqueous phase leaving stage i, and x_i^* is the x_i value if the two exiting phases are equilibrated at the same O/A volume ratio as exists in stage i (5). Using Eq. 10 to calculate F_e for the extraction and stripping tests described above, the F_e values shown in Table 3 were obtained. When these results are plotted in Fig. 9, it appears that contactor operation at these extreme O/A flow ratios is

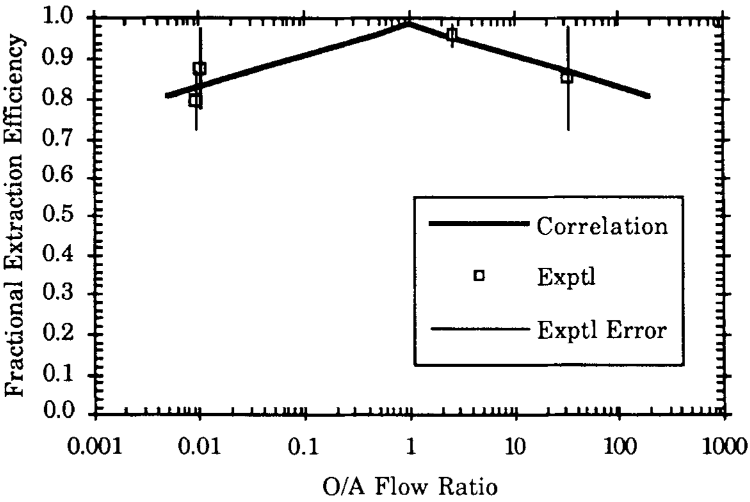

FIGURE 9. Overall Correlation of O/A Flow Ratio with Extraction Efficiency

accompanied by some loss in extraction efficiency. This efficiency, which is >95% for O/A ratios close to 1.0, drops down to about 80% for these extreme ratios. The value of F_e when R is 1.0 was estimated to be 98.6% from earlier measurements using uranium where the O/A flow ratios ranged from 0.5 to 2.5, see (1, 2, and 10). The drop in the fractional extraction efficiency is represented by

$$F_e = 0.986\left(1 - 0.08\left|\log_{10} R\right|\right) \tag{11}$$

This equation is the correlation shown in Fig. 9.

The results of our tests with the 4-cm contactor show that extraction efficiency is only slightly affected when the O/A flow ratio is very high or very low. As shown by the calculated results in Table 2 and Fig. 5, the contactor concentrator would be quite effective even when F_e is only 70%. Typically, for this case, additional contactor stages would be required to meet a specific process goal. In some cases, an O/A flow ratio with a slightly less favorable concentrating effect might also be required.

The error on the extraction efficiency measurements was highest for the stripping tests. There were two reasons for this. First, D_{Nd} was found to be about 0.12 rather than the 0.005 expected. This lowered the stripping factor and so magnified the error in calculating extraction efficiency. Second, some white precipitate was observed in the EW effluent after the test. This was not entirely unexpected since the test was run very close to the solubility of the neodymium salt of HEDPA.

Using the 4-cm contactor to evaluate the contactor as a concentrator represents a balance between the various factors that become important as contactor size changes. Because the contactor is relatively small, it has the drawback that its flow rates are low. For example, at an O/A flow ratio of 0.01, when the total flow was a maximum of 404 mL/min, the flow of the organic phase was a maximum of 4 mL/min. Thus, the organic phase entered the contactor in droplets controlled by the surface tension of the liquid in the feed line. This periodic and somewhat erratic flow rate could degrade the extraction efficiency. However, the small size of the contactor also has two benefits. First, the volumes of liquid required are reasonable for a laboratory-scale test. Second, the contactor gives a worst-case value for F_e that might be observed in an actual process plant. For the larger contactors in a plant, the low-flow phase would have a higher absolute flow, and thus, its flow should be continuous. When this is the case, contactor operation could show an extraction efficiency higher than that given by Eq. 11. Thus, the use of Eq. 11 to determine the effect of the O/A flow ratio on extraction efficiency should result in a conservative process design.

A way to improve extraction efficiency in a contactor stage would be to recycle the low-flow phase at each stage so that the actual O/A flow ratio in the stage is close to 1.0. If the low-flow phase is then pumped to the next stage at the appropriate low-flow rate, the overall O/A flow ratio can be maintained at the desired very high or very low flow ratio. For this type of operation, the F_e value for the stage should be close to 1.0 (100%).

CONCLUSION

The ability of the Argonne centrifugal contactor to act as a concentrating device for solvent extraction processes was demonstrated over a wide range of O/A flow ratios, from 0.01 to 33. Over this range, we found that extraction efficiency in the contactor stays high enough that good concentrator operation can be realized. A correlation was developed for the effect of the O/A flow ratio on the extraction efficiency.

In addition, a theory was developed to facilitate the design of contactors operating as concentrators. It shows that such a concentrating process can tolerate significant other-phase carryover in the low-flow phase. As a rule of thumb, the overall concentrating factor for a balanced design is given by $(D_{extr}/D_{strip})^{1/2}$ for a given feed component.

This concentrator has several possible applications: concentration of dilute feed streams so that the final process feed has a much smaller volume and process costs are reduced accordingly, concentration of process effluents so that the need for further processing (for example, concentration by water evaporation) is greatly reduced or eliminated, concentration and recovery of contaminants from groundwater, and recovery of extractants and other organics from aqueous effluents.

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