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ANNULAR CENTRIFUGAL CONTACTORS FOR SOLVENT EXTRACTION

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ABSTRACT

Annular centrifugal contactors suitable for laboratory use in solvent extraction work have been designed and tested for both hydraulic performance and mass-transfer efficiency. The 2-cm contactors have nominal flow rates of 80 mL/min and mass-transfer efficiencies of at least 85% as measured by the extraction of uranium. These contactors work well for organic-to-aqueous (O/A) flow ratios greater than 0.8. Multistage units allow proposed flow sheets to be tested on a continuous basis in the laboratory. Scale-up to larger plant-size units is straightforward.

INTRODUCTION

Solvent extraction is based on the transfer of a solute between two immiscible phases. The amount of solute exchanged for any such system is limited by the ratio of the solute concentration in each phase at equilibrium. Multiple extractions

are used to improve separation factors to levels of commercial importance. Equipment to carry out these multistage extractions is reviewed by Treybal (1). The various designs can be divided into two major categories: continuous (differential) contact equipment and mixer-settlers. The new type of equipment discussed here, the annular centrifugal contactor for laboratory use, belongs to this latter category.

Centrifugal contactors of the general type described in this paper were first developed at the Savannah River Laboratory (SRL). Two basic designs were used. In a plant-scale design (2), a separating rotor and a mixing paddle were suspended from a common drive shaft. The organic and aqueous phases were mixed by the paddle in a mixing chamber which also served as a pump to discharge the mixture up into the rotor. Here the phases were separated under centrifugal force and discharged as separate streams. In a design of a multistage miniature laboratory contactor (3), the rotor and the mixing paddle were mounted on separate shafts.

More recently, the SRL designs were modified at Argonne National Laboratory (ANL) to a simpler design which has lower fabrication costs and easier remote maintenance (4). The ANL design is referred to as the annular centrifugal contactor because of its annular mixing zone which distinguishes the ANL contactor from the SRL contactor. The ANL contactor retains the desirable operating characteristics of the SRL units such as high stage efficiency, high throughput, and short residence time. These characteristics are particularly desirable in processing reactor fuels since they lead to reduced radiolytic damage to the solvent and permit practical plant-scale operations in units that are sized for criticality safety.

The ANL annular centrifugal contactor has been built in plant-scale and laboratory-scale units. Single-stage laboratory contactors provide a means of evaluating immiscible liquid pairs as practical extraction systems. Multistage laboratory contactors allow evaluation of proposed flow sheets on a continuous counter-

current basis. This paper is an account of the work done at ANL on these miniature centrifugal contactors.

In this paper, annular centrifugal contactor operation is described qualitatively. Then, information is given on the hydraulic performance of single-stage and multistage units. Next, the result of mass-transfer efficiency and flowsheet tests are presented. Finally, scale-up considations are reviewed. Further details are available elsewhere (5).

QUALITATIVE DESCRIPTION OF CONTACTOR OPERATION

Contactor operation may be qualitatively followed using the schematic shown in Fig. 1. Two immiscible liquids flow into the Couette mixing zone which is the annular region between the spinning rotor and the stationary housing. The more dense phase is typically an aqueous phase and the less dense phase is typically an organic phase so that the terms aqueous and organic used throughout this paper mean, in a more general sense, the more dense phase and the less dense phase, respectively. The liquid-liquid dispersion formed in the Couette mixing zone flows by gravity to the rotor inlet in the bottom of the rotor and thus into the centrifugal separating zone within the rotor. Here, the dispersion breaks rapidly under the high centrifugal force. The separated phases flow over their respective weirs and are thrown by centrifugal force 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 prevents the aqueous exit stream from leaking down into the organic collector ring.

To achieve good contactor operation, five additional design features are needed. First, to allow the dispersion to flow by gravity into the rotor, stationary radial vanes under the rotor are required to break up the rotational velocity of the dispersion. Second, the rotor inlet must be made small enough with respect to the organic-phase weir to pump the liquids through

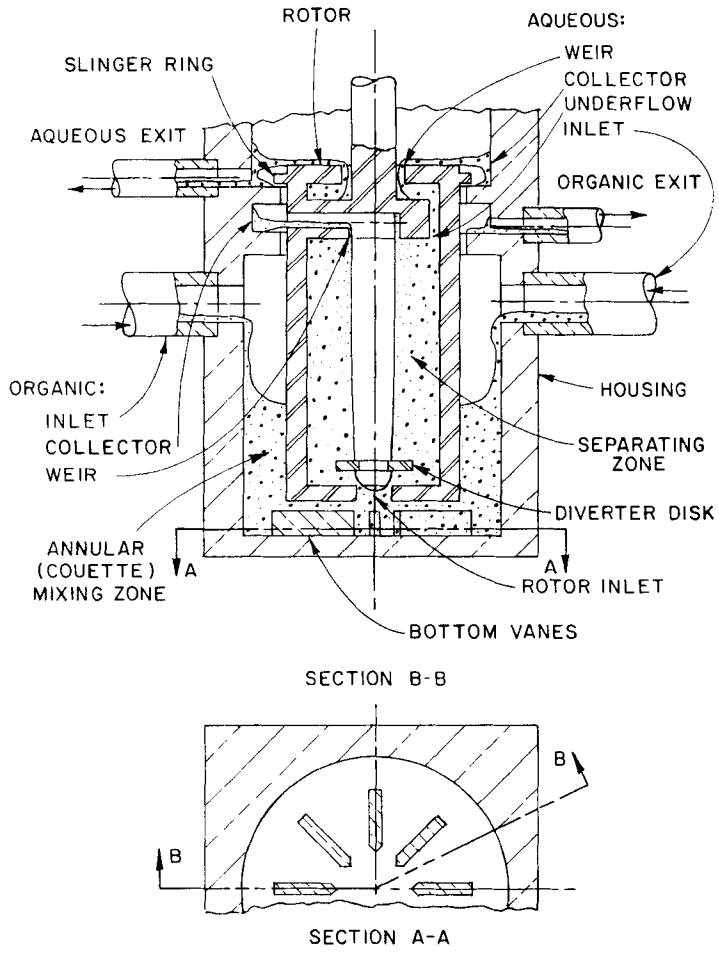

FIG. 1. Schematic of the annular centrifugal contactor.

the rotor. Third, axial vanes within the rotor are required to cause the liquids in the rotor to spin at the same rate as the rotor. Fourth, a diverter disk, located inside the rotor above the inlet, forces the entering dispersion into the middle region of the separating zone. Fifth, the organic and aqueous weirs must have appropriate dimensions so that the dispersion

band is located in the separating zone, that is, between the organic weir and the aqueous underflow.

For multistage operation, a series of units like that shown in Fig. 1 are connected together. The exiting streams of each stage flow by gravity in countercurrent fashion to adjacent stages. Thus, each rotor acts as a mixer, a centrifugal settler, and a pump.

The normal limit to contactor throughput is determined by the thickness of the dispersion band. This band is actually a hollow dispersion cylinder. At a given rotor speed, dispersion-band thickness increases as throughput increases until, at maximum throughput, the dispersion band reaches either the organic weir (with subsequent appearance of aqueous phase in the organic exit stream) or the aqueous underflow (with subsequent appearance of organic phase in the aqueous exit stream).

The O/A flow ratio has an important effect on contactor throughput. As the O/A ratio increases, the liquid height over the organic weir increases while the liquid height over the aqueous weir decreases. This shifts the dispersion band outward from the organic weir to the aqueous underflow. Thus, at low O/A ratios, phase contamination (when maximum throughput is exceeded) will be due to aqueous phase in the organic exit stream. At high O/A ratios, phase contamination (when maximum throughput is exceeded) will be due to organic phase in the aqueous exit stream. At some intermediate O/A ratio, the full volume of the separating zone will be used and both exiting phases will experience other-phase contamination at the same time if maximum throughput is exceeded. At this O/A ratio, the contactor capacity is the greatest.

An additional limitation may be imposed upon contactor capacity by the level of the dispersion in the mixing zone. If this level rises above the level of the organic-phase collector ring, the effluent organic phase will be contaminated.

HYDRAULIC PERFORMANCE

Hydraulic performance results are given here for both single-stage and multistage operation. Hydraulic performance is considered acceptable only if both exiting streams have less than 1% phase contamination (6). In addition, for single-stage units, the inlet line pressures in terms of liquid height must be less than the height of the organic collector ring.

Each rotor has a diameter of 20 mm and a separating zone length of 33 mm. Except as noted, the radial gap between the rotor and the housing in the Couette mixing zone is 5.0 mm. All hydraulic performance tests were made with an aqueous phase of 3.0 M HNO_3 and an organic phase of 30 vol % tributyl phosphate (TBP) in n-dodecane (nDD). The rotor speed for all tests was 6000 rpm unless noted otherwise.

Liquid-liquid dispersion in the Couette mixing zone is shown in Fig. 2. For the acrylic housing used in these photographs, the Couette gap is only 3.4 mm. This housing also has a larger inside diameter at the top of the Couette mixing zone. The flow and no-flow conditions shown here allow the crazing on the surface of the housing to be distinguished from the dispersion and allow it to be located relative to the bottom of the rotor. The highly turbulent Couette flow has a very efficient dispersing action as can be seen by the formation of the dispersion even before the aqueous phase (coming in from the right) is completely out of its tangential inlet line.

Single-Stage Operation

Single-stage capacities are given as a function of O/A ratio in Figs. 3 and 4. The results are seen to vary significantly in the O/A range from 0.1 to 1.0 depending on whether the Couette mixing zone is initially aqueous- or organic-continuous. This is due to a resistance to phase inversion from organic-continuous to aqueous-continuous in the Couette mixing zone. Instead of inverting, the dispersion becomes very

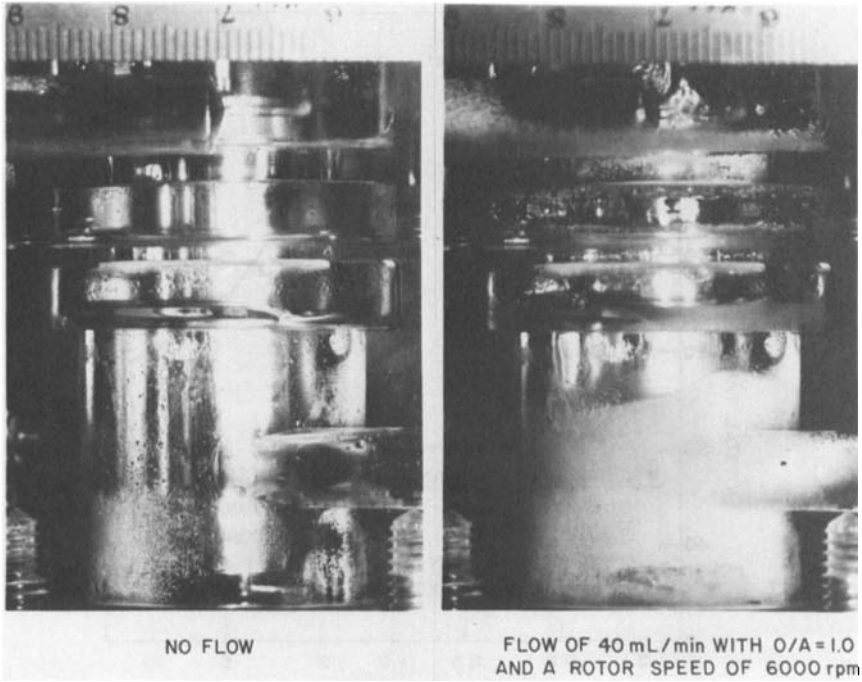

FIG. 2. Liquid-liquid dispersion in the Couette mixing zone of a single-stage contactor.

viscous as the low volume fraction of the continuous organic phase gives the dispersion a high structural viscosity when the aqueous droplets are forced to move past each other. This high structural viscosity inhibits flow into the rotor inlet orifice and causes the dispersion to back up in the annular mixing zone until some of the dispersion comes out the organic exit stream. If the O/A ratio does become low enough, the phase inversion to aqueous-continuous can take place. By contrast, the aqueous- to organic-continuous phase inversion occurs easily.

Outside this region of organic- to aqueous-continuous phase inversion, single-stage hydraulic performance is excellent. The phase-contamination data indicate that the dispersion band inside the rotor shifts from the organic weir to the aqueous

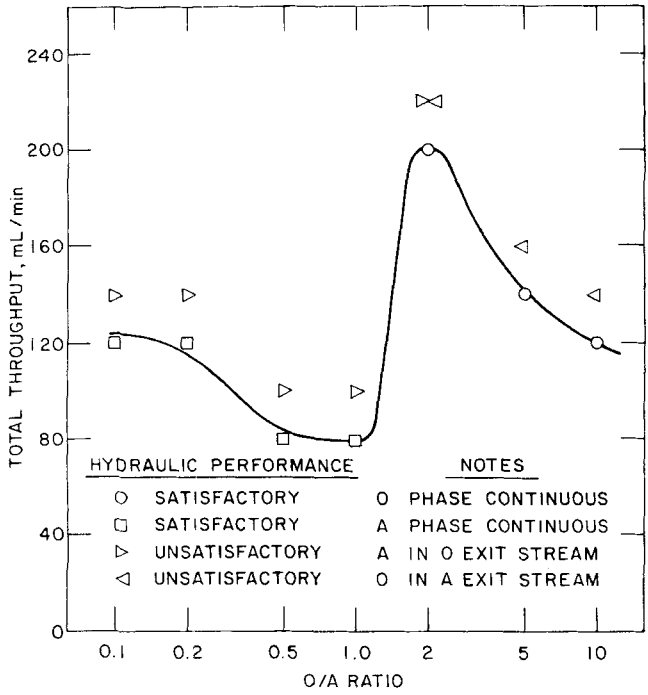

FIG. 3. Effect of O/A ratio on single-stage contactor capacity with the Couette mixing zone initially aqueous-continuous.

underflow as the O/A ratio increases. The dispersion band appears to fill the separating zone at an O/A value of 2, which corresponds to the greatest capacity of the contactor. Although this 200-mL/min capacity is impressive, a more conservative value of 80 mL/min is recommended to allow for reduced performance at other O/A ratios.

Further testing indicates that the resistance to organic- to aqueous-continuous phase inversion can be reduced by increasing the Couette gap, by increasing the bottom vane height, and by increasing the vane-to-rotor gap. Increasing the rotor length would also help by allowing the dispersion level in the mixing zone to rise to a greater height without reaching the organic collector ring.

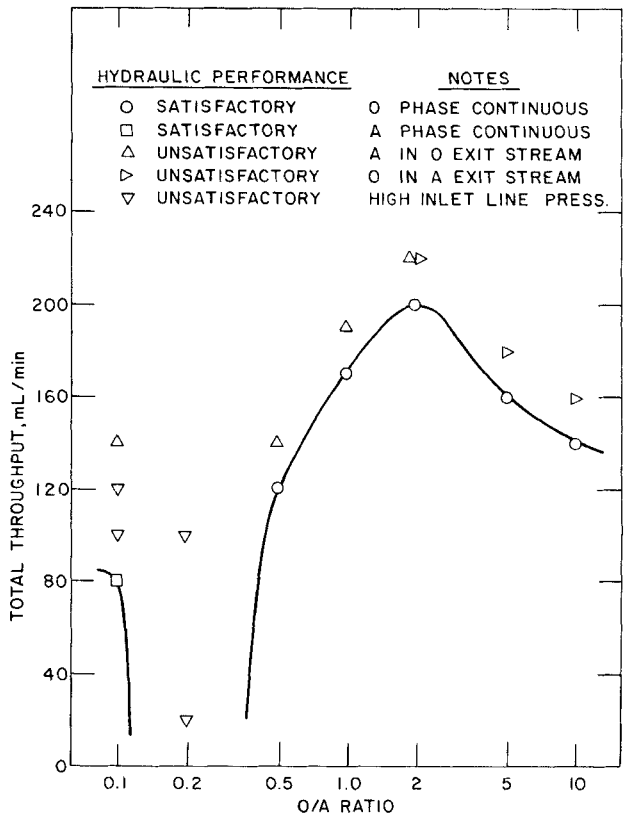

FIG. 4. Effect of O/A ratio on single-stage contactor capacity with the Couette mixing zone initially organic-continuous.

Identification of the continuous phase was done in two ways. First, the appearance of the exit streams was noted. Normally, the phase which had been the continuous phase in the mixing zone is cloudy after separation and the phase which had been the dispersed phase in the mixing zone is clear after separation. However, if there is a small amount of continuous phase exiting with the clear dispersed phase, this continuous phase can be dispersed into the previously clear dispersed phase and make it cloudy. Here again, the dispersion of aqueous phase

in the organic phase occurs more easily than the reverse case of the dispersion of organic phase in the aqueous phase. Secondly, the coalescence behavior of dispersion drained from the Couette mixing zone was observed. The breaking front of the coalescing dispersion band is next to the bulk liquid of the previously dispersed phase. The breaking front of the dispersion band has the largest droplets and the most distinct interface. The volume fraction of the dispersed phase in the dispersion band is greater than 0.5.

Eight-Stage Operation

Eight-stage hydraulic performance tests were made on the unit shown in Fig. 5. One motor drives all eight stages through a common drive belt. Except for external feed pumps, the hydraulic lift of each rotor supplies the gravity head needed for countercurrent interstage liquid flow. The spindles above each rotor, not being stainless steel, are protected from acid fumes by a purge of dry air flowing downward below the spindle and exiting just above the aqueous exit port.

Contactor capacity is given as a function of O/A ratio in Fig. 6. The range of acceptable operation is essentially that region of the single-stage operation which is satisfactory for both aqueous- and organic-continuous startups. The multistage capacity at any O/A ratio is 80% of that for single-stage operation. In addition, at low flow rates, the 0.12 to 0.35 range of inoperable O/A ratios is increased to 0.0 to 0.7.

The reason for the reduced operating region of the multistage contactor appears to be the variation of flow rate with time. For a single-stage unit, the FMI (Fluid Metering, Inc., Oyster Bay, NY) pumps supply a very constant feed rate for both phases. For a multistage unit, the interstage flow can fluctuate significantly. The major source of these fluctuations appears to be

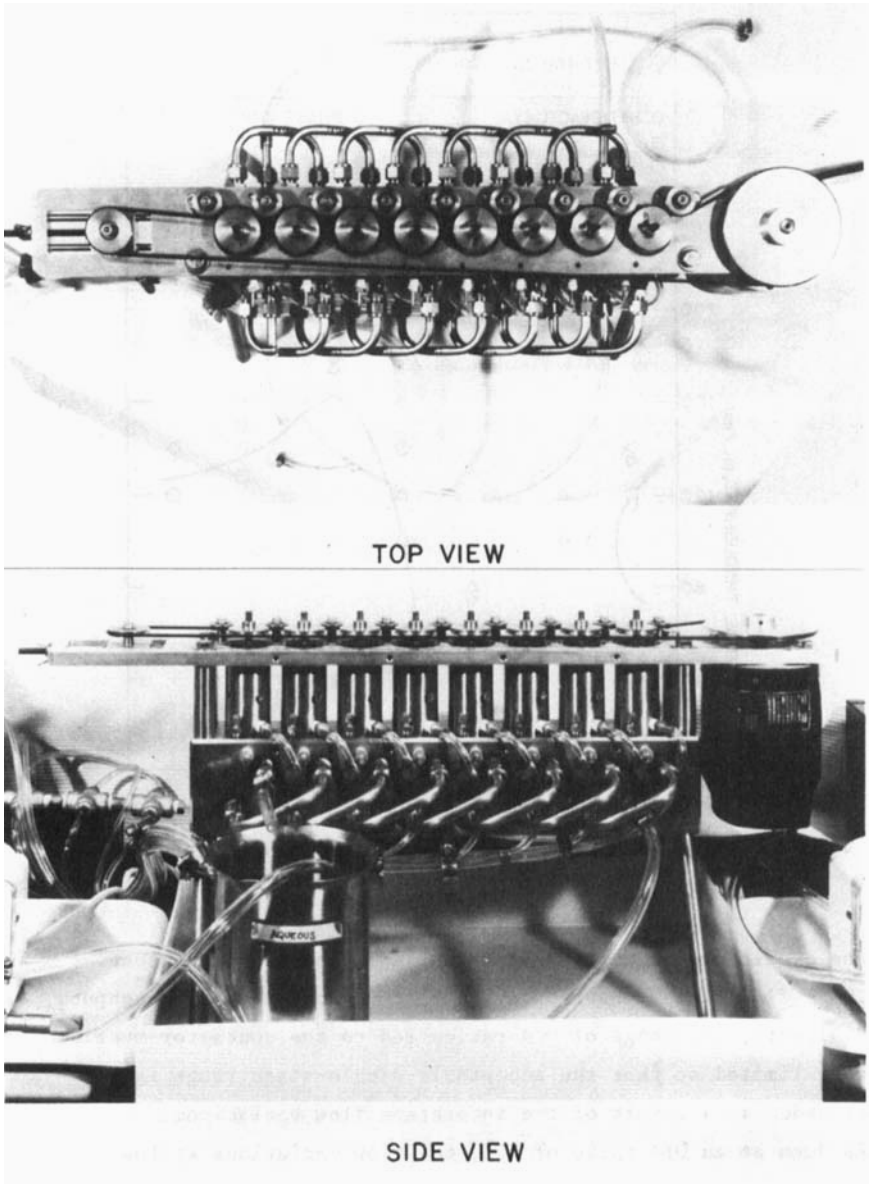

FIG. 5. Eight-stage miniature contactor.

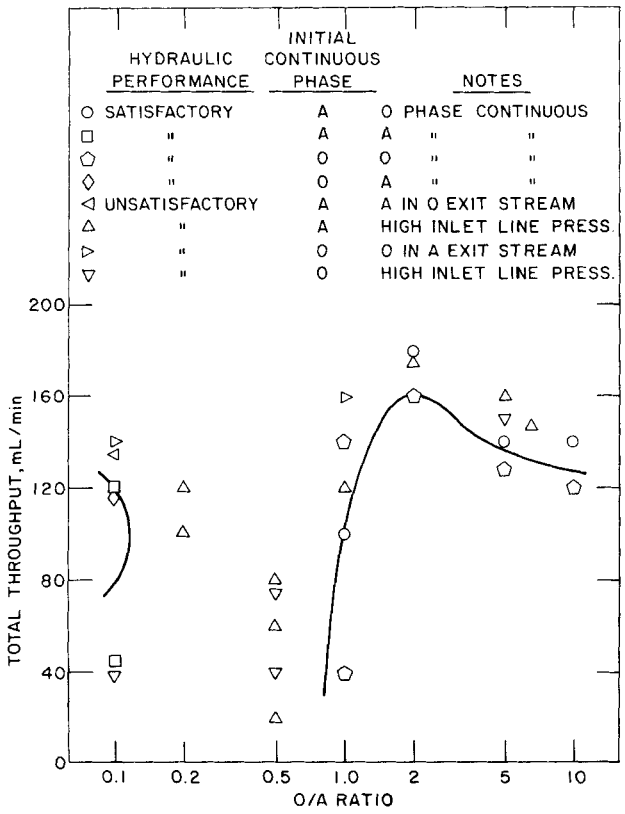

FIG. 6. Effect of O/A ratio on eight-stage contactor capacity.

the cyclic variation of dispersion level in the mixing zone. These flow variations reduce the maximum acceptable throughput. Similarly, the range of O/A ratios fed to the contactor must be more limited so that the acceptable single-stage range is not exceeded as a result of the interstage flow variations. As seen at an O/A ratio of 0.1, the flow variations at low throughputs are more significant than at higher throughputs so that the contactor runs better if the flow rate is not too low. Away from the region of troublesome organic- to aqueous-continuous phase inversion, low flow rates are no problem.

In a multistage contactor, operating at an unfavorable O/A ratio, the resistance to phase inversion from organic- to aqueous-continuous is seen as the backup of liquid in the interstage feed lines to a stage. Just before a phase inversion occurs, the interstage back-pressure may become so high that liquid is forced out the stage purge-air exit port just above the aqueous exit port. As the resistance to phase inversion is being overcome in this fashion, the resistance to phase inversion can be initiated in the adjacent stages, especially that stage which is fed by the aqueous exit stream. Thus, this resistance to phase inversion can give rise to a flow regime where flow performance is erratic and the contactor is essentially inoperable.

Tests have been made with other rotor speeds and other liquid pairs. Contactor capacity increases as rotor speed increases from 3600 to 6000 rpm. However, between 6000 and 9000 rpm, contactor capacity is unchanged. Besides the pairs mentioned below during the mass-transfer tests, the following two immiscible liquid pairs show good hydraulic performance relative to the performance of 3 M HNO_3 with 30 vol % TBP in nDD: (1) 4 M HNO_3 with 15 vol % tricaprylmethyl ammonium nitrate ($TCMA \cdot NO_3$) in diethylbenzene (DEB) and (2) 3 M HNO_3 with 0.5 M dihexoxyethyl phosphoric acid (HDHoEP) in DEB.

MASS-TRANSFER EFFICIENCY

Single-stage extraction efficiency tests were made with the same pair of immiscible liquids used in the hydraulic performance tests described above. To the 3 M HNO_3 aqueous phase was added 0.050 M uranyl nitrate (12.9 g U/L). Extraction efficiency is defined as the amount of uranium actually extracted divided by the amount of uranium that would be extracted if the two phases were in equilibrium. The extraction efficiency for the uranium tests was typically 94%, with the range being from 90 to 97%. All tests were made with the organic phase continuous.

The throughput was varied between 40 and 100 mL/min; the O/A ratio, from 0.9 to 2.5; and the rotor speed, from 4000 to 7500 rpm. The small changes in extraction efficiency that were seen corresponded to changes in the liquid level in the Couette mixing zone. As the mixing-zone liquid level rose as a result of higher throughput, lower O/A ratio, or higher rotor speed, the extraction efficiency increased.

In addition, several uranium stripping tests were made with 30 vol % TBP in nDD which contained 0.020 M uranyl nitrate and 0.56 M HNO_3. The aqueous phase was distilled water. All stripping efficiencies were greater than 95%.

Extraction efficiency tests were also made with a modified single-stage contactor in which the radial vanes were replaced with a disk to increase hydraulic capacity by lowering the liquid level in the mixing zone. However, at the highest O/A ratio of 2.5, where the mixing-zone liquid level is the lowest, the extraction efficiency dropped to 78%. This is attributed to a cyclic momentary loss of contact of the dispersion with the rotor when the dispersion level in the mixing zone is low. During this fraction of a second, the dispersion settles into a pool below the rotor, and the inlet streams flow unmixed into the pool. Such hydraulic behavior has been observed visually in other, similar test conditions. The radial vanes cause phase mixing even at very low flow rates and are considered more suitable than the disk for low flow-rate operation.

Multistage mass transfer efficiencies were measured using flow sheets based on the Purex flow sheet for nuclear fuel reprocessing (7). The actual flow sheets used and the overall results are shown in Fig. 7. For the extraction section, stage-to-stage aqueous uranium exit concentrations are listed in Table 1 along with the calculated stage efficiencies. These results show that the uranium extraction efficiency is 85 $\pm$ 2% over a fourfold range of uranium concentrations. For the stripping test, the uranium concentration for the aqueous

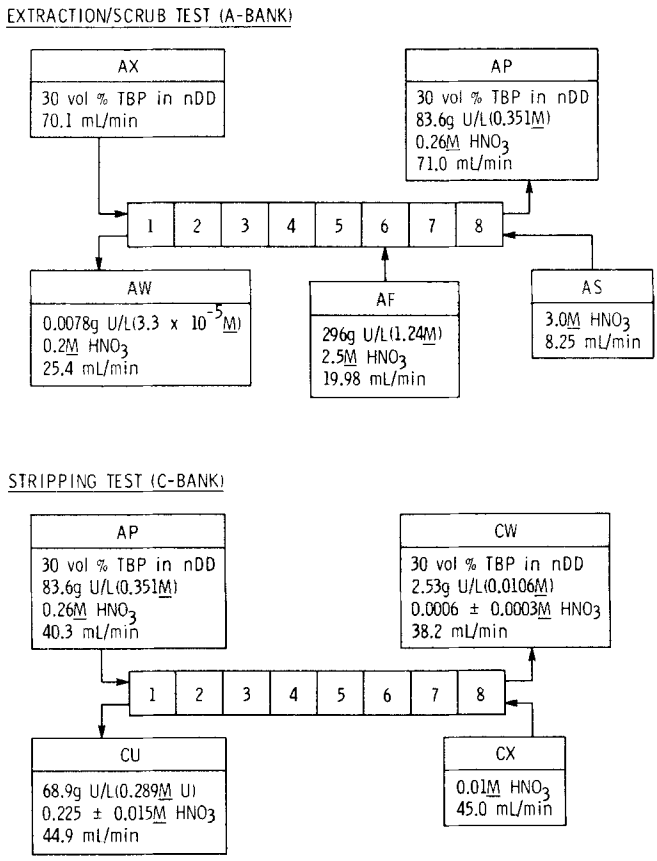

FIG. 7. Purex flow sheets for eight-stage mass transfer efficiency tests.

exit stream at each stage is shown in Fig. 8. The equivalent results for 100% stage efficiency, calculated with the SEPHIS code (8), are shown in the same figure for comparison. Hand calculation of stripping efficiency gives 85 ± 15% which reflects the larger variations in this test. These variations include (1) the possibility that the unit was not quite at steady state when stage sampling was started, (2) uneven withdrawal of the interstage samples, and (3) the greater sensitivity of the stripping efficiency measurement to the uranium analysis.

TABLE 1
Stage-to-Stage Results for Uranium Extraction Test

Stage	Uranium Concentration, M, in Aqueous Exit Stream	Stage Efficiency, %
1	3.3×10^{-5}	86
2	2.2×10^{-4}	87
3	1.6×10^{-3}	83
4	8.8×10^{-3}	86
5	5.55×10^{-2}	83
6	2.5×10^{-1}	87
Average stage efficiency		85 ± 2

A third, less detailed, multistage mass-transfer efficiency test was made using Aralex (Argonne Alcohol Extraction) flow sheets proposed for the recovery of actinides from sodium carbonate waste streams produced in nuclear fuel reprocessing (9). The extractant, a water-immiscible aliphatic alcohol, is 2-ethyl-1-hexanol (2-EHOH). The overall uranium decontamination factor for the extraction/scrub portion of the flow sheet indicates an 85% stage efficiency for uranium back-extraction. In the stripping test, a precipitate was formed in the sodium carbonate stripping section. This interfacial precipitate filled 80% of one separating zone without upsetting hydraulic performance at a 20-mL/min flow rate. Based on this stripping test, the flow sheet was modified so that the precipitate is not formed (9).

While the reason for the slightly lower mass-transfer efficiency in multistage tests relative to single-stage tests is not clear, this lower value of 85% is recommended as a conservative basis for any process design using centrifugal contactors.

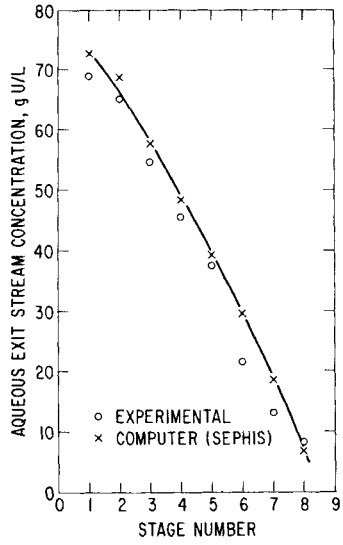

FIG. 8. Results of eight-stage stripping test.

SCALE-UP CONSIDERATIONS

Scale-up of laboratory (2-cm) contactor performance to larger sizes required for plant production is straightforward based on tests on 9-cm and 25-cm contactors, which have nominal capacities of 8 and 120 L/min, respectively. First, the larger units have higher mass-transfer efficiencies, greater than 95% and typically 98 $\pm$ 2%. Secondly, in the larger units, the resistance to the organic- to aqueous-continuous phase inversion is insignificant so that they show good performance at all O/A ratios. Thirdly, the volume fluctuations in the Couette mixing zone of these larger units are much smaller relative to the total liquid volume than in the 2-cm contactors. Thus, the loss of capacity in multistage operation relative to single-stage operation should be much less as contactor size increases. Fourthly, particulates have less effect as the size of the flow

channels increase. Finally, an air-controlled aqueous weir is used in the larger units and allows the dispersion band to be positioned in the separating zone of the rotor. Thus, the full volume of the rotor separating zone can be used at all O/A ratios.

A further aid to contactor scale-up is the development of a dimensionless dispersion number (10). This number, N_{Di}, is defined as

$$N_{Di} = \frac{1}{t_R} \sqrt{\frac{\Delta Z}{a}} \qquad (1)$$

where a = average acceleration on the dispersion, m/s^2

t_R = nominal residence time in the separating zone, s

ΔZ = thickness of the dispersion band, m

This dispersion number allows the degree of mixing in the Couette zone to be related to the capacity of the separating zone. For the work reported here, the organic-continuous dispersion number is 8.4×10^{-4} based on a residence time of 1.631 s at a maximum throughput of 200 mL/min and a separating zone volume of 5.43 cm^3, an average acceleration of 2.40×10^3 m/s^2 (245 g's) at a rotor speed of 6000 rpm, and a dispersion band thickness of 4.52×10^{-3} m. In practice, N_{Di} appears to be almost independent of the mixing intensity.

ACKNOWLEDGMENT

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6. The maximum acceptable phase contamination is arbitrarily set at 1% to provide a measurable basis for comparing maximum throughputs under various operating conditions. In plant operations with this type of contactor, throughput would be set below the maximum throughput as defined above in order to hold phase cross-contamination well below 1%.

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