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EFFICIENCY OF CONTACTORS

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A paper proposed for presentation at the
International Solvent Extraction Conference 1986
Munich, Germany
September 11-16, 1986

and for publication in the Proceedings

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EFFICIENCY OF CONTACTORS*

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INTRODUCTION

The efficiency of any type of solvent extraction equipment, in terms of losses, purity of products, and throughput, depends on the effectiveness of contact and disengagement of the two phases, and on kinetic exchange rates. Many studies on mixer-settlers, including a large number reported at ISEC's, have considered the relations of mixer configuration and other mixing parameters to droplet size, phase coalescence, and transfer of solute between phases. The droplet sizes determine interfacial area, which is a paramount factor in determining the transfer of solute between phases and the efficiency of the contact. The droplet size also determines the coalescence characteristics and the degree of entrainment from a given settling system. Kinetic factors for equilibration of extractable species both between and within the aqueous and organic phases can cause substantial differences between the performance of rapid contactors and other types.

Information on these factors and their application is the expected result from current studies on Savannah River Plant (SRP) contactors. The Savannah River Plant has reported on the operation of mixer-settlers and a centrifugal contactor for the Purex process and several other tributylphosphate-based processes.[1,2,3] The mixer-settlers were developed in the 1950's at SRP and have been operated with no modifications since that time. Because of time constraints during the initial development, the units were not fully optimized for maximum efficiency or flexibility. After an acceptable design was established to meet the requirements, further development was curtailed.

In 1966, short-residence centrifugal contactors replaced the Purex 1A mixer-settler bank. The desirability of improved decontamination of product streams and increased capacity has led to the present studies on impeller effects in mixer-settlers, and kinetic effects in the centrifugal contactors.

SUMMARY

The Savannah River Plant has two separations plants that began Purex operations in 1954 and 1955 with pump-mix mixer-settlers as contactors to process nuclear fuels. The only changes to the extraction equipment were replacement of most of the mixer-settlers in one plant with larger units in 1959, and the further replacement of the large 1A bank with a bank of rapid-contact centrifugal contactors in 1966. Improved performance of the old units has become highly desirable, and an experimental program is underway.

Good contact between the phases, and adequate settling without entrainment of the opposite phase are required for high efficiency operation of the mixer-settlers. Factors that determine efficiency are mixer design, drop size generated, and phase coalescence properties. The original development work and accumulated plant data confirm that the tip speed of a given impeller design determines the throughput capacity and extraction performance. An experimental unit with three full-scale stages has been constructed and is being utilized to test different impeller designs; reduced pumping and better mixing with lower speeds appear to be the key factors for improvement.

Decontamination performance of the rapid-contact centrifugal contactors is limited by the number of scrub contacts and the time of contact because of slowly equilibrating fission product species. Where solvent degradation is not a factor, the longer scrub contact of mixer-settlers gives better decontamination than the centrifugals. This kinetic effect can be overcome with long scrub contacts that follow the initial short extraction and short scrub contacts in the centrifugal contactors. A hybrid experimental unit with both rapid contact sections and longer contact scrub sections is under development to establish the degree of improvement that might be attained.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. D[illegible]

DISCUSSION

Mixing Relationships

The relations between mixing conditions, approach to equilibrium, and entrainment have received extensive study. The two most significant correlations proposed are N^3D^2 and tip speed, π ND, where N is rotation rate and D is impeller diameter. Constant N^3D^2 is considered to give constant power per unit mass of solution and to be the proper relation to use in scaling similar configurations for equivalent mixing intensity. Tip speed has been suggested as a primary determinant of drop size, through the effect on turbulence around the impeller. Drop size in turn affects the settling time and degree of entrainment in a given system.

ISEC '71 has several related studies on mixing conditions, drop size, emulsion properties, and settling characteristics, with a variety of correlations between these variables and impeller rotation rate and diameter.[4,5,6,7] A few of the many other studies also can be cited.[8,9,10] The differences really are small, with drop size or settling rate correlations with N and D in the range of $N^{1.0}$ to $N^{1.5}$ and $D^{0.8}$ to $D^{1.0}$, with some other relations also proposed. Additionally, coalescence rate in some correlations is cited as dependent only on the flow rate of the dispersed phase per unit area of coalescing surface. However, drainage of the continuous phase from the emulsion band also is cited as a flow counter to the settling path of the dispersed phase droplets that also must affect emulsion band characteristics.

A more recent, very pertinent study, which includes a review of much other work, is on the interfacial area generated under different mixing conditions with water and several organic materials.[11] Experimental variables included the volume fraction of dispersed phase, tank size, impeller size, impeller speed, and fluid properties of the phases. The simple results of the tests were that the interfacial area was primarily dependent upon the tip speed among the mechanical mixing variables, with little separate influence of power per unit volume. The dependence is nearly linear. The Sauter mean diameter of drops in a distribution is equivalent to a drop that has the same surface to volume ratio as the dispersed phase as a whole and is inversely proportional to the interfacial area. Hence, the mean drop size also is nearly linearly (inversely) dependent on the tip speed.

The relation to mixer-settler operation is straightforward. The interfacial area will determine the approach to equilibrium in an extraction operation, and the interfacial area depends on the tip speed. Further, drop size will determine the settling time and the degree of entrainment with a given settler design, and drop size again depends on tip speed.

SRP Mixer-Settlers and Mixing Variables

Three sizes of mixer-settlers were involved in the original SRP development work. The banks for the original Purex installations that started operating in 1954 and 1955 were pump-mix units with impeller diameters of 12.7 and 17.8 cm.[12,13] The impellers act as centrifugal pumps to move the aqueous phase. In 1959, so-called "Jumbo" banks with 22.9 cm impellers replaced the original banks in one of the Purex plants.[13] The other Purex plant was converted to processing enriched uranium normally and also was utilized for processing thorium, uranium-233, irradiated plutonium, and other special feed materials.

The development work confirmed by plant operation was that the pump-mix design gave good operation for losses and entrainment over a limited range of solution throughput rates. Higher impeller speeds necessary to pump the heavy aqueous phase at higher rates generate finer drops that do not settle in the reduced time, and that result in increased entrainment and lower efficiency. Substantially lower than normal impeller speeds give inadequate phase contact, hence low efficiency again. At high throughput rates, the upper and lower limits on impeller speed converge. Near the throughput limit, the operable impeller speed range is relatively few revolutions per minute.

Plant data showed early that decontamination and losses are affected differently by impeller speed. In the scrub section of a bank, for example, impurities in the bulk organic phase are to be back-extracted into a small volume of dispersed droplets of aqueous phase, an unfavorable geometric arrangement for transfer. The dispersion conditions in the scrub section that give adequate contact without excessive mixing, with the consequent, entrainment of the scrub solution, are likely to be different from the conditions in the extraction section that give good efficiency and low losses of product. Analogous conditions may exist where the organic phase is the scrubbing section. The result is that the same impeller speed and impeller design generally are not good where different flow ratios exist in the same bank.

The total flow of both phases appears to be a significant measure of coalescence rate per unit area for the SRP units. The original development work showed that the defined cutoff of 3% entrainment of aqueous in organic was reached at the same impeller speed for the same total flow for a wide range of flow ratios.[12,13] This would give a constant total disengaging rate per unit area at a given impeller speed, but a large variation in disengaging rate if based on the dispersed phase only. Additionally, the experimental data discussed in the next paragraph also presents a reasonable grouping based on total flow of the mixed phase, but a wider spread when considered on the bases of the separate phases. Logically the continuous phase must have some effect on the settling rate of the dispersed phase since it must drain from the emulsion counter to the movement of the dispersed drops, as noted previously.

Experience in entrainment and efficiency with three different sized banks and impellers in Purex, enriched uranium processing, Thorex, and other programs can be examined in terms of disengaging rate per unit settling area and impeller speed. Limits on performance can be based on both excess entrainment or on serious loss of efficiency, as measured by losses or contamination of end streams. Given in Table 1 are the specific areal flows of the combined phases, the tip speeds of the different sized impellers, and the observed result. A graph (Figure 1) of the data compares the different limiting flows and the tip speeds. These data cover wide variations in solution properties that influence mixing and settling in the different processing systems. These varying properties include densities and viscosities as well as substantial differences in observed interfacial tensions between the aqueous and organic phases as a result of solvent degradation products and different tributylphosphate (TBP) strengths. The data spread is large, but much smaller than when based on dispersed phase settling only.

The general relations provide some guidance for the experimental work. Flow capacity, as set by entrainment or efficiency with the present centrifugal impellers, increases as the impeller speed decreases. The obvious approach is to modify the impellers so that they mix better at slower speeds and still pump adequately. Some of the early development work, after startup and too late for implementation, showed that appreciable improvement might be made with relatively simple modifications.[14] To explore impeller effects, a three-stage plant-scale experimental unit has been constructed with transparent walls and top to allow observation of the mixing and settling zones. The results of the test work in progress will be presented at the conference.

Kinetic Effects on Performance

The rate of exchange of solutes between phases is influential in losses of valuable products and in purity of the products. In Purex and related tributylphosphate processes, the extraction rates of uranium, plutonium, and other actinide products are quite rapid. Hence, short contact times with reasonable contacting efficiency can attain low losses in the extraction banks at times as short as 10 to 15 seconds per stage, as in the SRP centrifugal contactors.

The fission products that limit decontamination are ruthenium and zirconium. Ruthenium specifically has many different ionic species in both aqueous and organic phase, including a whole family of nitrato-nitrosyl ruthenium compounds, with slow equilibration between these species, as attested to by many studies. Zirconium also appears to have slower extraction rates than plutonium and uranium. It is proposed that slow conversion of hydrolyzed and polymeric zirconium species are responsible for the rates.[15]

TABLE 1. Limiting Settling Conditions

Mixer-Settler Service	Observation	Emulsion Disengaging Rate ml/min/cm^2	Impeller Tip Speed, cm/sec
1. 1A, Large Purex, Extraction	Emulsions, 1AW losses	14.7	383
2. 1B, Large Purex, Partition	Pu loss to organic U stream.	13.9-12.7	419-407
3. 1C, Large Purex, U Strip	Gross entrainment, both aqueous and organic end streams.	28.2 21.2 22.2 19.5	287 263 293 287
4. 1E, Large Purex, U Strip	Aqueous entrainment in 1EW organic.	17.2	275
5. 2A Small Purex, 2nd Pu Extraction	High losses, low decontamination.	27.1	226
	Entrainment, scrub section only.	14.0	249
6. 2B, Small Purex, 2nd Pu Strip	Aqueous entrainment in 2BW organic.	9.1	139
7. 1E, Small Purex, 2nd U Strip	Aqueous entrainment in 1EW organic.	6.9 8.6	363 353
8. 1A, Small Enriched U, Extraction	1AW losses increased, decontamination decreased.	9.4	422
9. 2A, Small Np, Extraction	2AW losses	11.3	226
10. 1A, Small Thorex, Extraction	Emulsions	17.8	266
11. 1B, Small Thorex, Partition	Aqueous entrainment in organic.	17.2 19.3	283 266
12. 2B, Small Thorex, Th Strip	End stream entrainment.	19.8	233

Note: Impeller diameters are 22.9 cm on large banks, 17.8 cm on small 1E bank, and 12.7 cm on all other small banks.

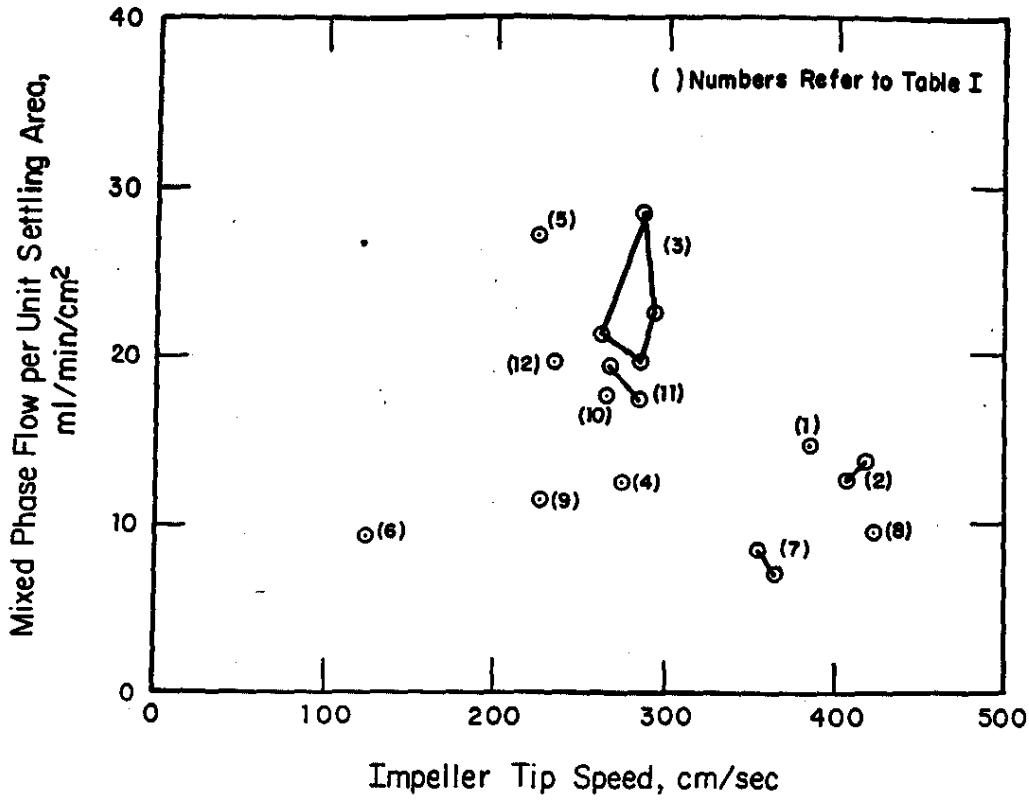

FIGURE 1. Limiting Settling Rates

Short-residence centrifugal contactors replaced the large Purex mixer-settlers in 1966 as part of a program to reduce solvent degradation effects. The units solved the degradation problem, but brought a new fission product extraction pattern that was assigned to kinetic effects.[3] It was proposed that decontamination performance might be improved by combining rapid extraction and scrubbing, followed by slow scrubbing. The rapid contact would recover the uranium and plutonium produced and separate the bulk of the fission products; the slow scrubbing would allow equilibration and back extraction of the small amount of ruthenium and zirconium carried through the centrifugal scrub stages. The results of an experimental program are expected to be equally applicable to high TBP Purex flowsheets and low TBP flowsheets for recovery of enriched uranium.

Separate tests with laboratory-scale centrifugal contactors and mixer-settlers were made as a preliminary step to the testing of hybrid extraction equipment. Decontamination factors for zirconium were determined in center-fed 16-stage centrifugal contactors and mixer-settler units with an enriched uranium recovery flowsheet utilizing 7.5% TBP. The feed solution was chemically the same as plant feed, with a one-thousandth aliquot of plant feed to provide zirconium tracer. In one pair of runs, a portion of the regular plant solvent with its accompanying degradation products was added to the laboratory solvent. The results are shown in Table 2. The longer scrubbing time of the mixer-settlers gave distinctly better decontamination in series 1 and 2. Increased temperatures gave better decontamination with both mixer-settlers and centrifugals; the benefits of increased temperature have long been noted. Decontamination decreased markedly when plant solvent was added; more in the mixer-settler run than in the centrifugal run, but the mixer-settler still was the better of the two.

More experimental facilities have been constructed with both short and long contact stages. The system should resolve the combined effect of short contact during extraction and initial scrubbing, which should reduce the formation of solvent-bound zirconium species, and long contact in additional scrub stages. The equipment has a

mini-centrifugal bank of 16 extraction stages that can be divided between extraction and scrub stages as desired and 12 mini-mixer-settler scrub stages. The residence times are 5-30 seconds per stage in the centrifugal bank and 3-5 minutes per stage in the mixer-settlers. The results of the test work in progress will be reported at the conference.

TABLE 2. Scrubbing Time and Decontamination

Feed Solution: 5 g/L U, 1.4 M HNO_3, 1.5 M $Al(NO_3)_3$

Radioactive Spike: 1/1000 volume addition of plant feed solution;

Temperature	Zr-95 Decontamination Factor	
	Centrifugal Contactor	Mixer-Settler
33^0C	70	370
50^0C	130	820
50^0C (With Plant Solvent spike)	110-140	180

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