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UNIVERSITÉ D'OTTAWA
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ABSTRACT

The liquid-liquid extraction and stripping of uranium were studied in a one stage mixer-settler. The organic phase consisted of adogen 384 (a tertiary amine extractant) and isodecanol (as a phase modifier) in a kerosene diluent. A synthetic leach solution resembling industrial sulphuric acid leach solutions at Rabbit Lake in Canada was used in the extraction runs. An ammonium sulphate solution with NH_4OH addition for pH control was used in the stripping runs. Of particular interest in this study were the rates of mass transfer, drop sizes in the mixer, and coalescence and crud formation in the settler. The principal variables in the experiments were the impellor speed, feed rates, and the amount of solids present in the feed.

Uranium transfer between the organic and aqueous phases was rapid for both extraction and stripping. Stage efficiencies within the mixer were generally greater than 95% for all runs except extraction runs at the lowest impellor speeds. Mass transfer was therefore substantially complete by the time the phases were separated in the settler. Measurements of drop sizes were not sufficiently accurate to allow the testing of specific functional relationships between the drop size and the impellor speed.

The settler dispersion band was especially sensitive to solids introduced either in the feed or by precipitation. Although increased solids content lead to crud formation, it also enhanced coalescence in the settler.

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NOMENCLATURE

Symbol

A	cm ²	horizontal cross sectional area of the settler
A _s	cm ²	surface area of a drop
A(h)		force of adhesion between two drops at a distance h (equation 6-12)
c	-	constants
D	cm	impellor diameter
D _v	cm ² /s	diffusivity
d	cm	drop diameter
d ₃₂	cm	Sauter mean diameter (equation 6-13)
E	-	extraction coefficient concentration of a component in one phase divided by its concentration in a second phase
E _{MS}	-	Murphree stage efficiency for mass transfer (equation 7-1)
f _N (d')		number frequency distribution with respect to the log of the drop diameter (equation 6-17)
g	cm/s ²	gravitational acceleration (equation 8-7)
H	cm	dispersion band height
H _r	cm	reduced dispersion band height (equation 8-11)
H ₀	cm	dispersion band height at the end of a run
H _N	cm	normalized dispersion band height (equation 8-10)
K		equilibrium constant
k	mol/cm ² /s	mass transfer coefficient (equation 3 section A.7.4)
L	cm	length scale of the main flow
M	g/gmole	molecular weight

Symbol

N	rev/s	impellor speed
N_p	-	power number (equation 5-2)
O/A	-	organic to aqueous phase volume ratio
P	cm^5/s^3	total impellor power (equation 5-1)
Q	cm^3/s	total flowrate in the settler
Q_c	cm^3/s	pumping rate in a mixing vessel
r	cm	length
S	cm^{-1}	total surface area per unit volume of dispersion (equation 8 section A.7.4)
s		step length (appendix A.3.1)
T	cm	mixing vessel diameter
t_c	s	coalescence time of a drop (equation 8-2)
u	cm/s	$= \sqrt{u^2(d)}$ defined below
$u^2(d)$	cm^2/s^2	time averaged mean square velocity fluctuation in turbulent flow
x	mol/cm^3	aqueous phase concentration
y	mol/cm^3	organic phase concentration

GREEK OR LATIN SYMBOLS

Symbol

ϵ	cm ² /s ³	power dissipation per unit mass of dispersion
$\overline{\epsilon}_v$		power dissipation per unit volume of dispersion
η	cm	length scale of maximum energy dissipating eddies - Kolmogoroff length (equation 5-12)
μ	g/cms	viscosity
τ	s	average residence time in the mixer
$\bar{q}(t)$	-	residence time distribution (equation 7-2)
ρ	g/cm ³	density
σ	g/s ²	interfacial tension
ϕ	-	volume fraction of the continuous phase in a dispersion

SUPERSCRIPITS

y exponent in equation 8-9 for the dispersion band height

', ", and '" single, double, and triple primes
signify the first, second, and third
derivatives (appendix A.3.1)

SUBSCRIPTS

Symbol

- c refers to the continuous phase
- d refers to the dispersed phase
- m mean value of a property in a dispersion
- x refers to the aqueous phase in mass transfer calculations
- y refers to the organic phase

DIMENSIONLESS NUMBERS

- $N_p = P/N^3 D^5$ power number
- $N_{vi} = \mu_d u / \sigma$ viscosity number
- $Re = \rho_m u d / \mu$ Reynold's number- microscale
- $Re_{imp} = \rho_m N D^2 / \mu_m$ Reynold's number- main flow (impellor)
- $Sh = k d / D_v$ Sherwood number
- $We = \rho_m u^2 (d) d / \sigma$ Weber number- microscale

1. INTRODUCTION

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1. INTRODUCTION

1.1 LIQUID-LIQUID EXTRACTION AND INDUSTRIAL URANIUM

MILLING OPERATIONS

This project is concerned with the concentration and purification of uranium in industrial milling operations. A brief description of the overall milling operations follows as an aid to putting the liquid-liquid extraction unit operation into perspective. More complete descriptions of the processes are given by Merritt (44), Ritcey and Ashbrook (59), and Carino (14).

Uranium recovery from ores is accomplished by the dissolution of the uranium into an aqueous phase. This can be done by in situ leaching for low grade ore bodies, or more commonly by mining the ore and transporting it to a mill where it is crushed, ground, leached, and filtered. Either sulfuric acid or alkaline (sodium carbonate) leaches may be used, the latter being preferred where the ore type leads to excessive acid consumption. Uranium in the ore may be present in the $U(+4)$ or $U(+6)$ states. The $U(+4)$ state must be oxidized to $U(+6)$ to ensure dissolution in the sulfuric acid leach phase. Sodium chlorate is therefore added to the leach in order to oxidize ferrous ions to ferric ions, which in turn oxidize $U(+4)$ to $U(+6)$. Leach

solutions typically have a low concentration of uranium (ranging from 0.1 to 10 g/L), and contain many impurities.

With some ores, such as the former Madawaska Mines in Canada, the uranium can be directly precipitated from the leach liquor to be further refined and processed elsewhere. Normally this is not possible due to the high levels of impurities in the ore. Two processes are used to concentrate and purify the uranium from a dilute leach solution. The oldest method is the use of solid ion exchange resins. The second method is the use of highly selective tertiary amines in a liquid-liquid extraction process. The amines readily extract aqueous uranium at low pH's (pH 1-2), and release it when contacted with a second aqueous phase at a pH of 4 to 4.5. These two steps are called extraction and stripping respectively. The commonly used amine extractants also pick up arsenic (weakly) and molybdenum (strongly), which may have to be removed in scrub or regeneration stages. This project is concerned with this liquid-liquid extraction process.

Liquid-liquid extraction is used by Gulf Minerals and Uranerz in Saskatchewan. (Uranerz commenced production in July 1982. Gulf Mineral's uranium milling operations at Rabbit Lake were recently taken over by Eldorado Nuclear Limited.) Mixer settlers are used to contact then separate the organic and aqueous phases in a multistage,

countercurrent operation. Extraction of uranium from the ore leach and stripping the organic uranium complexes back into another aqueous phase each require from three to five stages. A solvent regeneration stage is used at Gulf Minerals to clean an organic bleed stream in an alkaline (soda ash) solution. Two or three scrub stages were planned for Uranerz to remove arsenic. The most common operating problem at the Gulf Minerals extraction circuit is the formation of crud. Crud is a heterogeneous phase that collects at the interface between the organic and aqueous phases in a settler. Its effects on the circuit are described in more detail in Chapter 9. After the uranium has been stripped, it is precipitated by the addition of bases, filtered, and calcined to a product containing 60-70% uranium.

1.2 THE OBJECTIVES AND SCOPE OF THIS PROJECT

The overall objective of this project was to study the physical and chemical aspects of the solvent extraction of uranium by a tertiary amine in a one stage mixer-settler. This overall objective was subdivided into the following minor objectives:

1. To determine the equilibrium distribution of uranium between the aqueous and organic phases under the conditions of interest to this project. Procedures were to be developed for the preparation of the phases for the mixer-settler runs. The information obtained at this stage of the project was of fundamental importance to the mass transfer studies that were later undertaken.

2. To measure the density, viscosity, and interfacial tension of the phases over a range of equilibrium concentrations of uranium. This would provide information about the physical properties of the system as commonly required when analyzing physical processes such as turbulence, drop breakup, and phase separation in a mixer-settler. This information would also reveal the changes in the physical properties that occur during extraction and stripping.

3. To design and build a mixer-settler unit that

would allow the study of drop sizes and mass transfer in the mixer and phase separation in the settler. The unit was to be geometrically similar to equipment used by other researchers, such that estimates of power dissipation, drop sizes, and mass transfer in the mixer could be made based on correlations in the literature.

4. To develop photographic techniques for the determination of drop size distributions in the mixer. The resulting data could then be compared to correlations in the literature, making use of the measured physical properties and estimates of turbulence.

5. To develop phase sampling techniques for the determination of mass transfer efficiencies in the mixer. The resulting data would then be studied in the light of information of chemical equilibrium, physical properties, turbulence, and drop size distributions.

6. To observe the behaviour of the dispersion band height and phase entrainment in the settler.

7. To determine if crud or stable emulsions would form during the runs. A hypothesis of interest was whether one may reduce the formation of crud by reducing the impellor speed in the mixer while still maintaining acceptable rates of mass transfer.

Parts of this project are similar to original work that was done in the 1950's at Oak Ridge National Laboratories, which is summarized in a report by Ryon and Lowrie (65).

2. PROJECT SUMMARY

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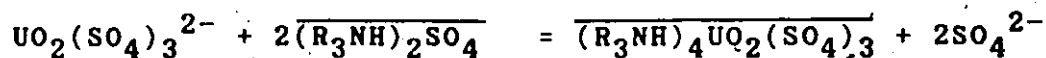
2. SUMMARY

2.1 INTRODUCTION

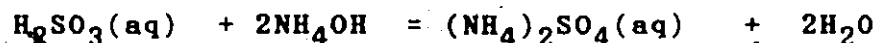
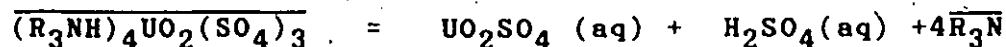
This section summarizes the procedures, major results, and discussions of the project. Detailed discussions of each subject area of the project are given in sections 3 through 9. Tables and figures in this section are copies of tables and figures of later sections.

Adogen 364, a tertiary amine extractant similar to tri-capryl amine, was used in this study. The chemistry of the extraction and stripping processes are discussed in more detail in section 3, but they may be summarized by the equations below (overlines denote organic phase complexes);

Extraction (@ pH 1.6)



Stripping (@ pH 4.0)



Note that the uranium will have a preference for the organic phase at a pH of 1.6, while its phase preference reverses at higher pH's. This provides the motivation for using the solvent extraction process for the concentration and purification of uranium, in addition to the fact that the organic extractant is highly selective for uranyl complexes (as opposed to impurities such as iron).

2.2 THE MIXER/SETTLER RUNS

2.2.1 Equipment

The one stage mixer/settler used in this investigation is shown schematically in Figure 2.1. The equipment was constructed of acrylic plastic. The mixing cell was fully baffled (4 baffles of width one tenth of mixer diameter) and fully enclosed. A side window was added to the mixer for taking photographs of a dispersion that was drawn from the mixer and pumped back to the feed inlet. A sampler for each phase was installed flush with the inner wall in the upper half of the mixer. These consisted of phase preferentially wetted filter paper supported on a porous teflon disc, and were connected to a vacuum pump. A stainless steel 6 flat-bladed disc impellor was used to agitate the mixer. A microscope\35mm camera combination was used for photomicrography of the droplets passing through

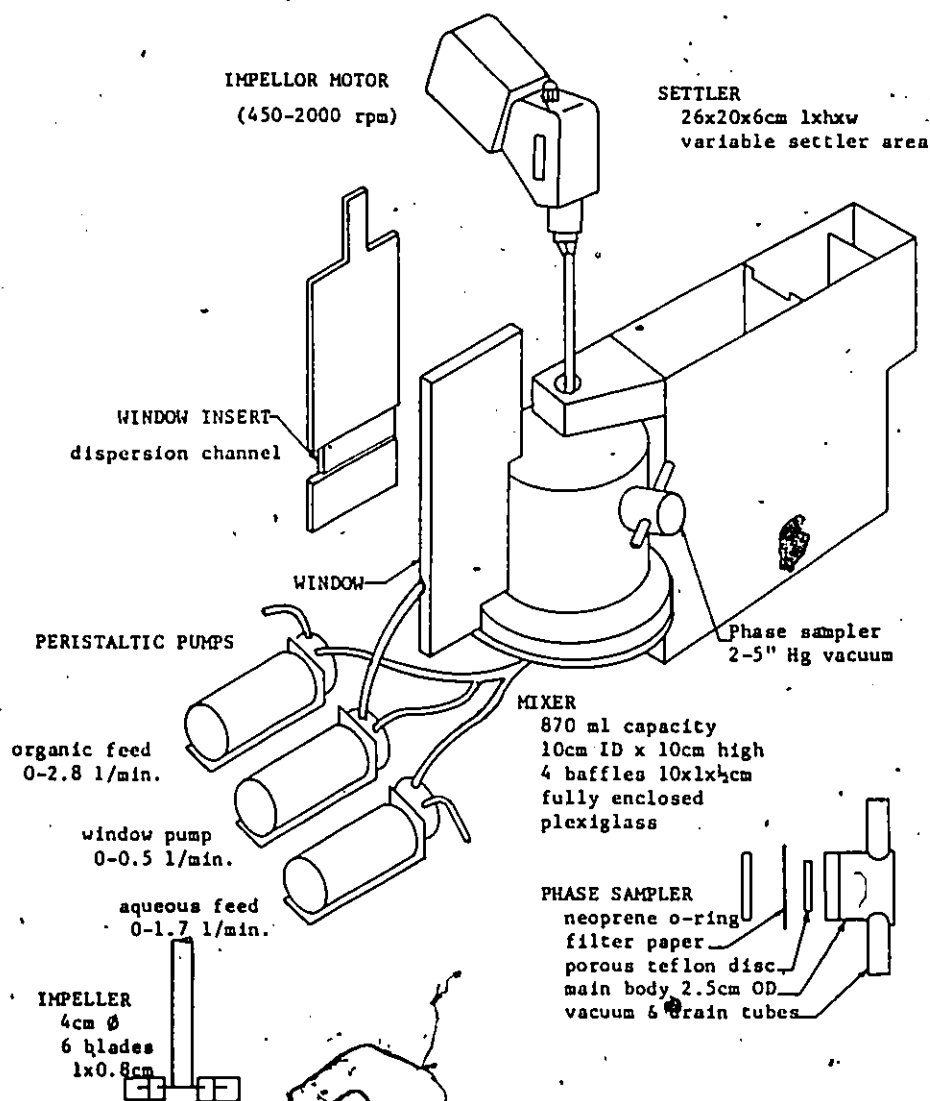


Figure 2.1 EQUIPMENT

the window.

The overflow from the mixer was fed into the mid-height of the settler by a rectangular channel. The settler area could be varied by changing the position of a partition. A 35 mm camera with a 50 mm lens was used to photograph the settler dispersion band and crud formation. Tygon (polyvinylchloride based) tubing was used for service with organic solutions, while silicone tubing was used for aqueous solutions. Peristaltic pumps were employed to feed the phases to the mixer. Earlier types of tubing that were employed deteriorated by contact with the organic phases, possibly by leaching out the plasticizer. The organic phase would therefore have been contaminated to some extent by these materials. Two hundred liter and 20 liter polyethylene containers were used for phase storage and preparations.

2.2.2 Experimental Conditions and Procedures

Table 2.1 lists the important variables and conditions of the mixer/settler runs. The aqueous phase accounted for 40% of the volumetric feed rate and was the dispersed phase in all runs. Synthetic solutions resembling industrial solutions were prepared with tap water and technical grade chemicals. Phase compositions and information concerning chemical equilibrium are given in section 3.

Table 2.1 Experimental Variables
for the Mixer-Settler Runs

Fixed Variables

temperature
mixer geometry
feed O/A ratio

phase continuity
in the mixer

Settings

ambient (22 to 30 °C)

O/A = 1.5:1 or
dispersed phase volume
fraction = 0.40
organic continuous

Independent Variables

settler area
impellor speed
feed rates
phase preparation

Settings

455 to 2700 cm³
7.5 to 33 revolutions/s
870 to 2610 cm³/min
no extraction, fast extraction
slow extraction, stripping

Dependent Variables

drop sizes in the mixer
mass transfer in the mixer/
overall mass transfer
settler dispersion band height
crud/emulsion formation in the settler

The equipment was operated for 10 mixer residence times (from 3 to 10 minutes) in order to allow the establishment of steady state before starting any sampling or physical measurements. Photographs of the drop dispersion were taken after the initial stabilization period. The settler dispersion band height was continually monitored and recorded from the start of the run. Occasional adjustments of the phase outflows were necessary to maintain a constant interface level in the settler. Phase sampling was started immediately after the drop photographs were taken. Any crud formation was noted, and to end the run the separation time of the dispersion in the mixer was measured after the impellor was stopped. Details concerning the conditions for each run may be found in Table A.2.1 of Appendix A.2. Sample drop photographs are included in Appendix A.6.

Chemical analysis were done by the analytical chemistry section at CANMET. The drop photographs were analysed after the completion of all experimental work.

Four distinct series of mixer/settler runs were carried out in this project.

1. No-extraction series- The aqueous and organic phases were pre-equilibrated at a pH of 1.6 before use. No uranium was present in the solutions. This series served to

illustrate the behaviour of the physical processes in the absence of mass transfer.

2. Fast-extraction series- The organic phase was initially equilibrated with a sulfuric acid solution at a pH of 1.6. In the mixer/settler runs it was contacted with an aqueous leach phase containing enough uranium to complex with about 20% of the extractant molecules in the organic phase. This series therefore was a study of extraction for the case where aqueous uranyl complexes were directly exchanged for SO_4 ions attached to the amine extractant. There was no net sulfuric acid exchange.

3. Slow-extraction series- The organic and aqueous phases were suitably prepared before contacting them in the mixer/settler to give an equilibrium pH of 1.6. This time there was sufficient uranium in the aqueous solution to complex with 86% of the extractant molecules in the organic solution. Fine solids were added to the aqueous feed solution. This series represents more closely the industrial extraction circuit, where sulfuric acid and uranium are loaded on to the organic phase, and a high loading of uranium in the organic phase is attained.

4. Stripping series- A fully uranium loaded organic phase was contacted with an ammonium sulphate strip solution. Enough ammonium hydroxide was added to the aqueous

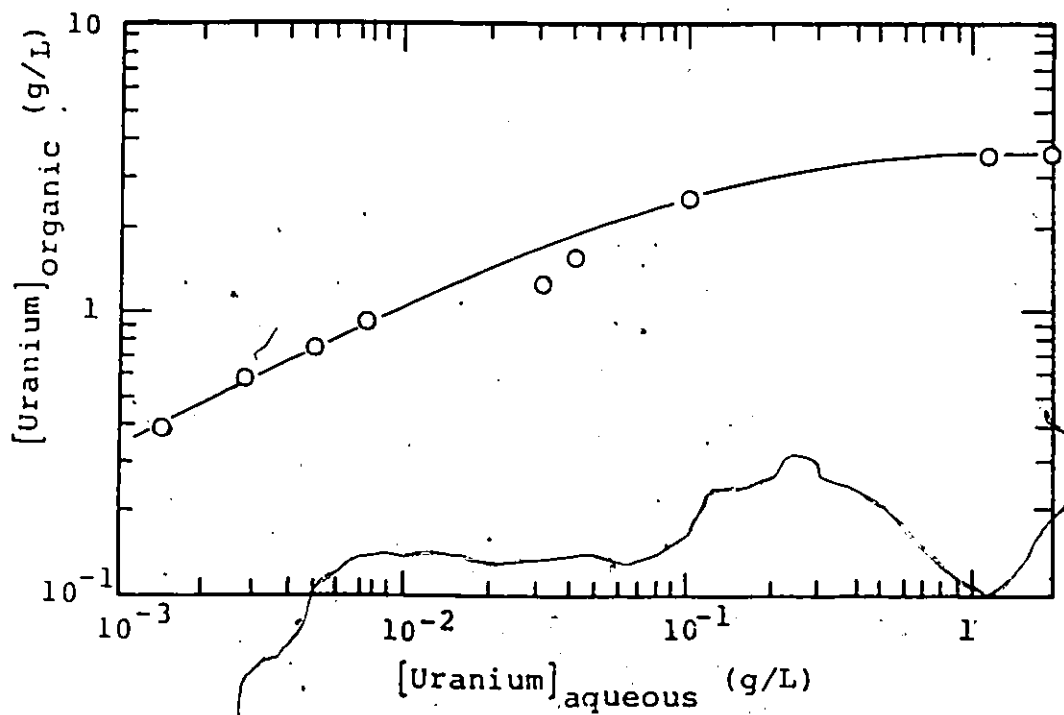
strip to obtain an equilibrium pH of 4.0 in the mixer/settler.

2.3 RESULTS AND DISCUSSION

2.3.1 Chemical Equilibria

Figure 2.2 shows the equilibrium distribution of uranium between the aqueous and organic phases for the conditions of extraction. The maximum loading of uranium and sulfuric acid in the organic phase corresponded to 4.7 and 2.2 molecules of extractant per molecule of uranium and sulfuric acid respectively. This corresponds well to reported literature values of 4 and 2. The great preference of uranium for the organic phase in the case of extraction is well illustrated by the section of the equilibrium curve for low uranium loadings.

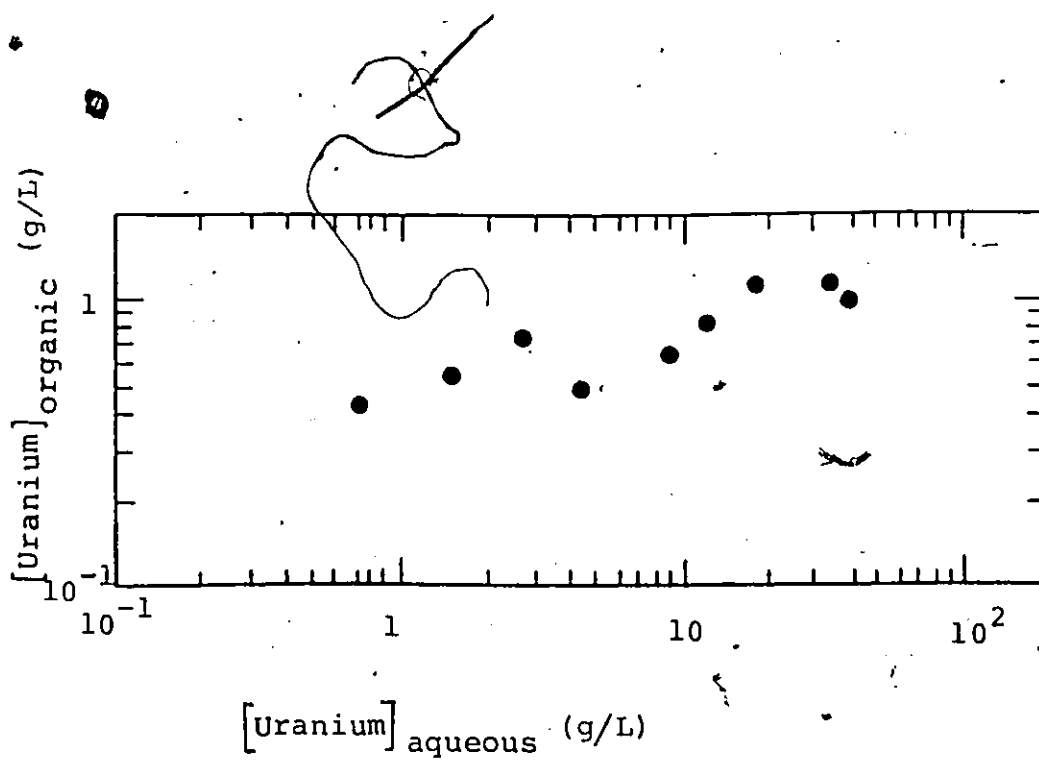
The equilibrium curve for stripping is also given in Figure 2.3. The scatter in the data is thought to be due in part to variations in the equilibrium pH, which varied from 3.9 to 4.4 as compared to the desired pH of 4.0. Calculations of the aqueous phase chemical equilibria are discussed in section 3, which served as an aid in preparing solutions for the runs. The results for stripping indicate the importance of good pH control.



conditions

T - ambient
pH - 1.6
0.07 M Adogen 364
0.1 M Na_2SO_4

Figure 2.2 EQUILIBRIUM DISTRIBUTION OF URANIUM
FOR EXTRACTION



conditions

T - ambient

pH - 4.0

0.07 M Adogen 364

0.9 M $(NH_4)_2SO_4$

Figure 2.3 EQUILIBRIUM DISTRIBUTION OF URANIUM
FOR STRIPPING

2.3.2 Physical Properties

The physical properties of the phases used in this project are shown in Table 2.2. Experimental measurements showed that large changes in the phase densities, the density difference between the phases, and the phase viscosities did not occur during the course of extraction or stripping.

The interfacial tension as measured at phase equilibrium showed an interesting increase from about, 9 or 10 dynes/cm to about 13 or 14 dynes/cm as the uranium concentration in the organic phase increased (Figure 2.3). This was also noted by Kolarik and Pipkin (38) who found (for a uranyl nitrate - TBP system) that the interfacial tension rose from 10 to 19 dynes/cm as the uranium concentration increased. One possible explanation is that increased uranium loadings lead to the formation of organic uranium complexes in the organic phase and the consequent depletion of extractant at the interface between the aqueous and organic phases. The interfacial tension of pure water/kerosene is about 40-50 dyne/cm (Brown and Pitt(12)), which is greater than the results for the solutions in this project. The extractant molecule itself is surface active to a certain extent (as is the phase modifier isodecanol), and would be expected to have some influence on the interfacial tension.

Table 2.2 Physical Properties of the Phases

	Extraction			Stripping		
	ρ	μ	σ	ρ	μ	σ
organic phase	0.80	1.65		0.80	1.85	
aqueous phase	1.03	1.10		1.06	1.23	
mean value for the dispersion	0.89	3.4	11	0.90	3.5	11

μ = viscosity (g/cm/s * 10)

ρ = density (g/cm³)

σ = interfacial tension (dynes/cm)

The mean values for the properties are defined in Section 4.

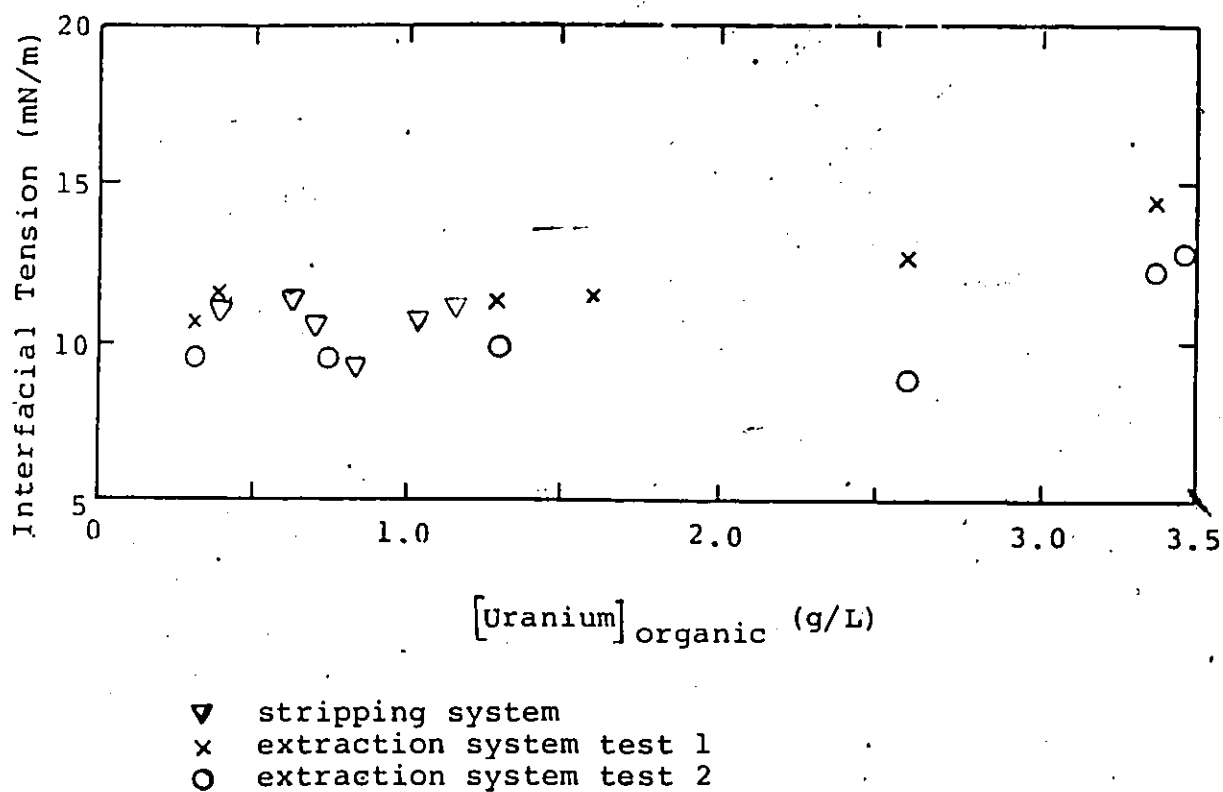


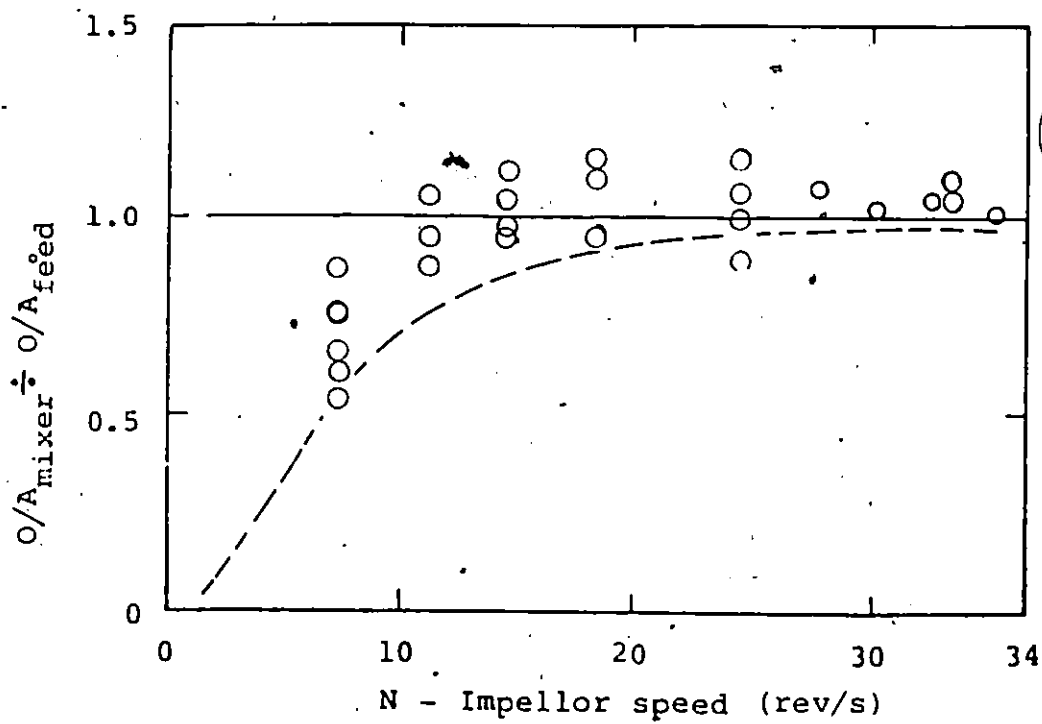
Figure 2.4 INTERFACIAL TENSION AND THE ORGANIC
PHASE CONCENTRATION OF URANIUM

2.3.3 Fluid Flow and Turbulence in the Mixer

The dispersed phase volume fraction in the mixer is not necessarily the same as in the feed stream. Figure 2.4 shows how these two quantities were related in this project, and it shows predictions based on a literature correlation. It is seen that at higher impellor speeds the feed and mixer volume fractions are roughly equal.

Other aspects of fluid flow (and turbulence) are very important to understanding processes such as mixing, drop size distributions, and mass transfer within the mixer. Experimental measurements were not made of these fluid flow variables, but due to the selection of a standard configuration for the mixing cell they may be estimated from correlations in the literature.

The impellor speed was varied from 7.5 to 33 s⁻¹ during the course of experimentation, corresponding to impellor Reynolds numbers in the 3000 to 14000 range. In discussing turbulence in an agitated vessel, it is often assumed that the impellor Reynolds number is sufficiently high (say 20-50,000) such that the effects of the fluid properties may be neglected when calculating power input, and so that the turbulence is "fully developed". That is not strictly the case in this project, due to the small size of the equipment.



--- correlation of Bouyatiotis and Thornton (11)

Figure 2.5 EFFECT OF THE IMPELLOR SPEED ON
THE O/A RATIO IN THE MIXER

The pumping rates, power input, and the "maximum energy dissipating" eddy size as predicted by various correlations are shown as a function of impellor speed in Figure 2.5. The pumping rates suggest that the circulation time of fluid within the mixer was as low as 0.2 seconds at the higher impellor speeds. Predicted values of the length scale of the maximum energy dissipating eddies indicates that they may not be very much smaller than the drops in the mixer dispersion (compare η in Figure 2.5 with drop sizes in Figure 2.6). This means that the commonly assumed relations for the microscale Reynold's number and Weber number (see Shinnar (69)) may be somewhat in error when applied to this project, as they assume that the small eddies are very much smaller than the drops.

2.3.4 Drop Size Distributions in the Mixer

The calculated mean drop sizes are plotted against impellor speed in Figure 2.6. Care must be used when interpreting this plot, as the data accuracy decreases rapidly at higher impellor speeds, largely because of deteriorating picture quality. The droplets are very small and fast moving, while the light scattering by the dense emulsion makes lighting a difficult task (transmission lighting directly into a microscope was used.) The results indicate that the impellor speed has an important effect on drop sizes, but also that other factors such as the presence

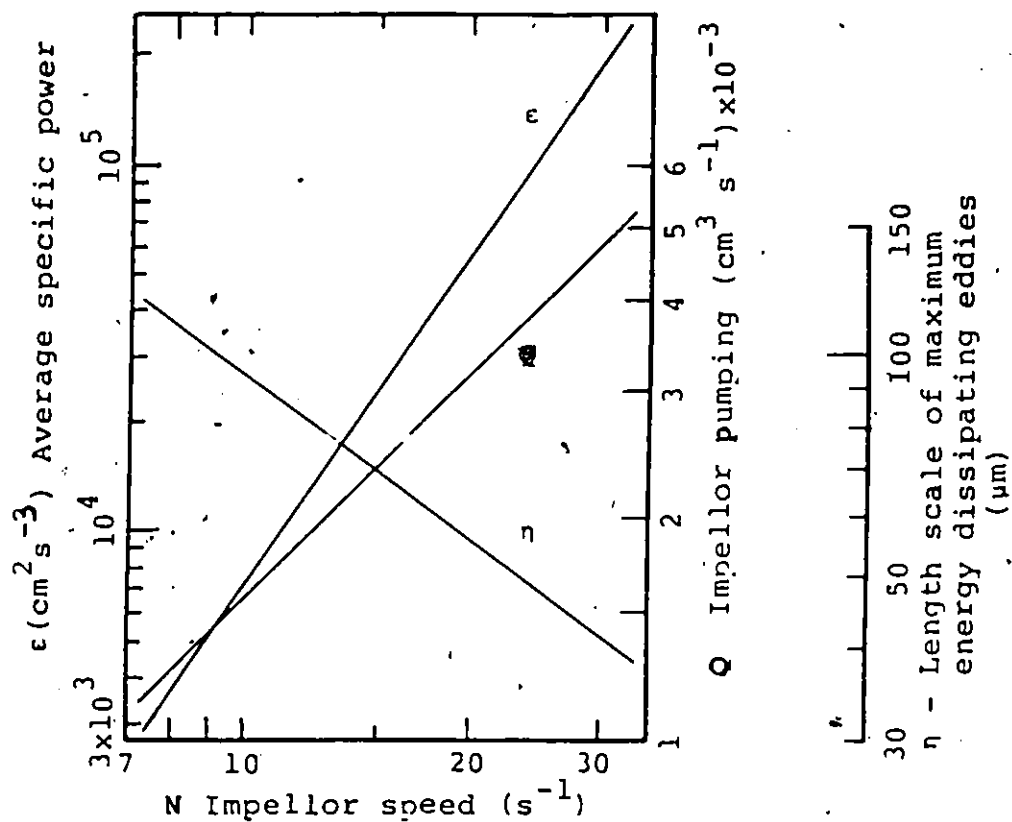


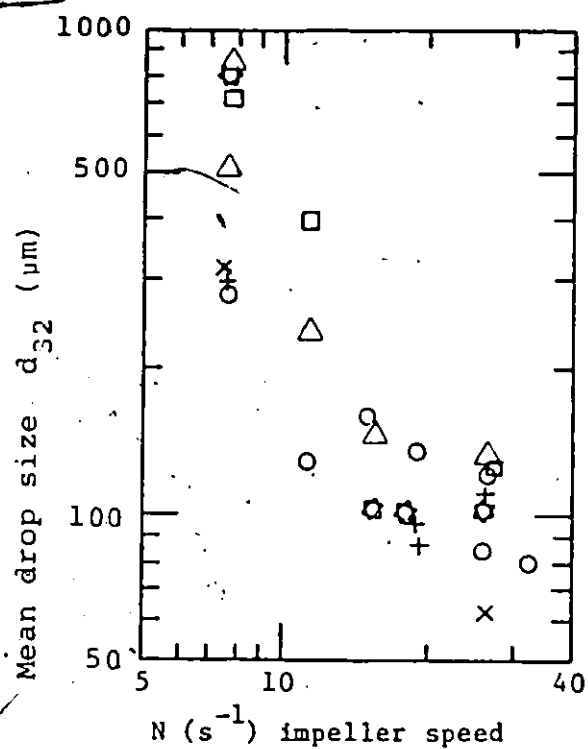
Figure 2.6 CALCULATED ESTIMATES OF AGITATION
AND PUMPING IN THE MIXER

of solids or the system being used have some influence. Figure 2.7 is a plot of selected drop size distributions. The form of the distributions varies from a roughly log-normal distribution to a bimodal distribution.

The mean drop diameter was affected by the impellor speed, however the data is not sufficiently accurate to allow the testing of specific functional relations. Small drops especially would have been underrepresented in the size distributions both because of the measuring technique and due to photographic limitations. According to literature correlations the observed differences in drop sizes from one set of runs to another in this project could not be explained by the measured variations in density, viscosity, and interfacial tension. Possible explanations could be changes in the surface forces of the second kind (acting perpendicular to the interface between the aqueous and organic phases) arising from the effects of fine solid particles, mass transfer, and the different chemical systems. Individual effects could not be distinguished.

2.3.5 Mass Transfer

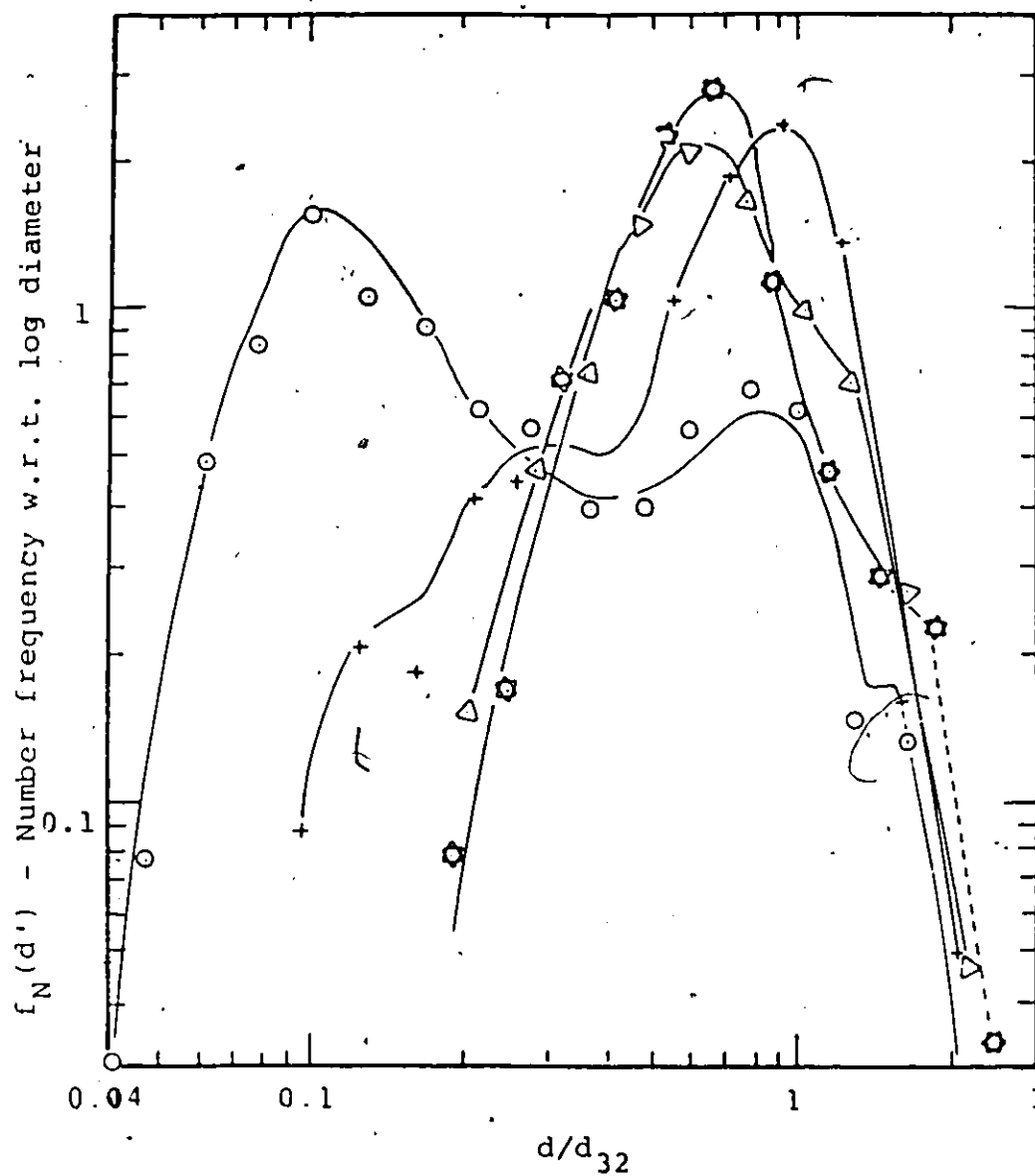
The results for uranium transfer between phases, were badly scattered due to high stage efficiencies for all runs. Selected data from extraction runs are shown in Figure 2.8. All runs gave single state efficiencies greater than 85% as



LEGEND

mixer residence time	1 min	30 secs	20 secs
no extraction	○		
fast extraction	+	×	
slow extraction	⊗		
stripping	△		□

Figure 2.7 APPARENT MEAN DROP SIZE



	Series	Impellor speed (s^{-1})	d_{32}
○	No extraction	25	125
+	Fast extraction	7.5	319
△	Stripping	7.5	504
☆	Slow extraction	14.5	142

Figure 2.8 SELECTED EXPERIMENTAL
DROP SIZE DISTRIBUTION

was observed by Ryon and Lowrie (65) at comparable power inputs. The trend appears to be a greater efficiency as the impellor speed is increased and as the solids content of the feed is increased. Stage efficiencies for the slow-extraction series were lower than those of the fast-extraction series.

There were three main differences between the fast and the slow extraction series;

1. The fast-extraction series involved a preacidified organic phase, whereas in the case of the slow extraction series both sulfuric acid and uranium were loaded onto the organic phase.

2. The amount of uranium that was loaded onto the organic phase at equilibrium amounted to 20% and 86% of the maximum for the fast and slow series respectively.

3. Solids were added to the aqueous phase in the slow-extraction series. Drop sizes, at least for lower impellor speeds, were larger for the slow extraction series.

The above differences would lead one to expect lower stage efficiencies for the slow extraction series.

Increased mixing and smaller drop sizes result from

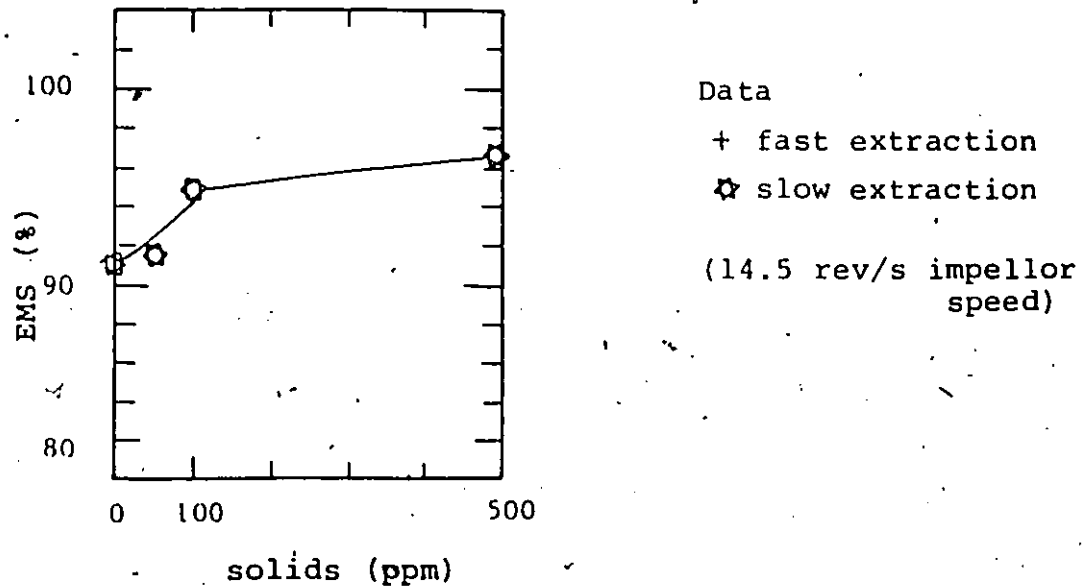
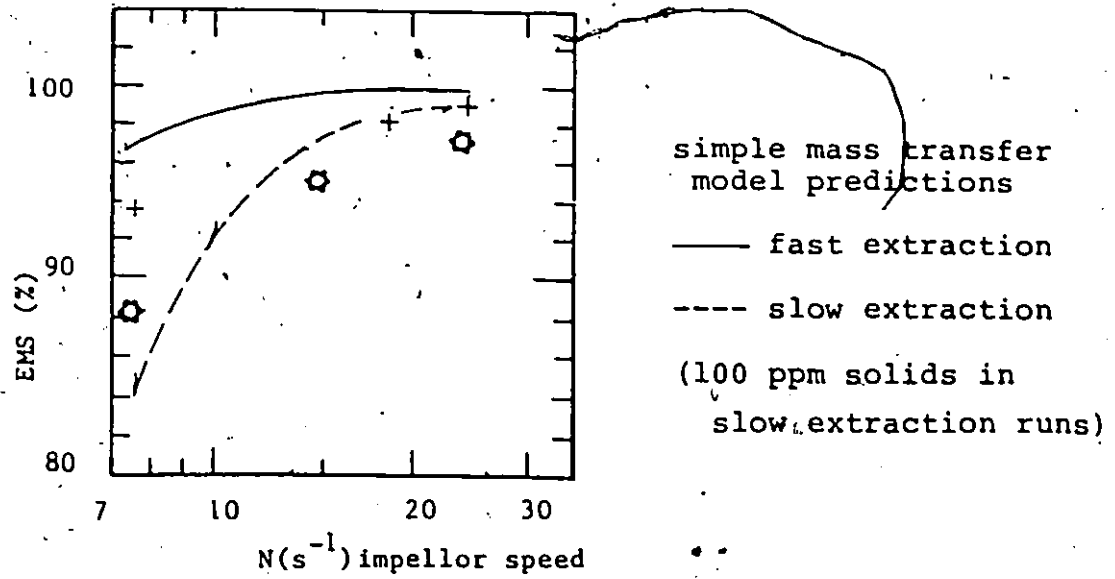


Figure 2.9 MURPHREE STAGE EFFICIENCIES
FOR THE MIXER

higher impellor speeds. Both of these factors would tend to increase the mass transfer and stage efficiencies. The results in Figure 2.8 indicate that increasing the solids content of the feed increased the stage efficiency. This was possibly due to increased coalescence in the mixer, which would lead to enhanced mixing within the aqueous (dispersed) phase and hence improved mass transfer.

2.3.6 Settler Dispersion Band Height and Phase Entrainment

A "normalized" dispersion band height is shown as a function of impellor speed in Figure 2.9 and as a function of solids content of the feed in Figure 2.10. The normalized height gives a relative idea of the ease of separation of the dispersions in the settler. The dispersion band heights were insensitive to the impellor speed in the mixer except at low impellor speeds for the stripping series and the slow-extraction series. Increasing the amount of solids in the slow-extraction series reduced the dispersion band height and improved settler performance. The small dispersion band heights for the stripping and slow extraction series could have been due to the presence of solids. (Local precipitation occurred during the stripping runs.)

A major difference between the behaviour of the settler in this project and the results of Barnea and Mizrahi

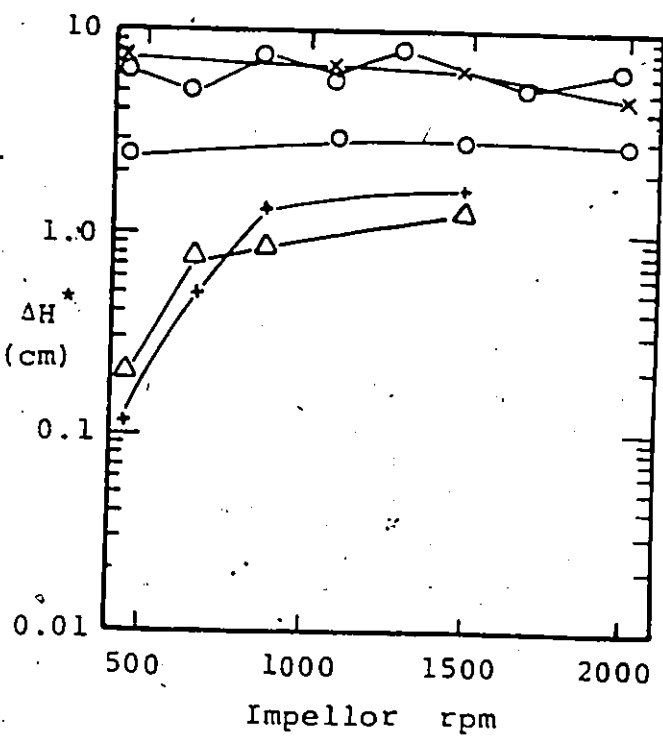


Figure 2.10 THE EFFECT OF
IMPELLOR SPEED ON THE
SETTLER DISPERSION

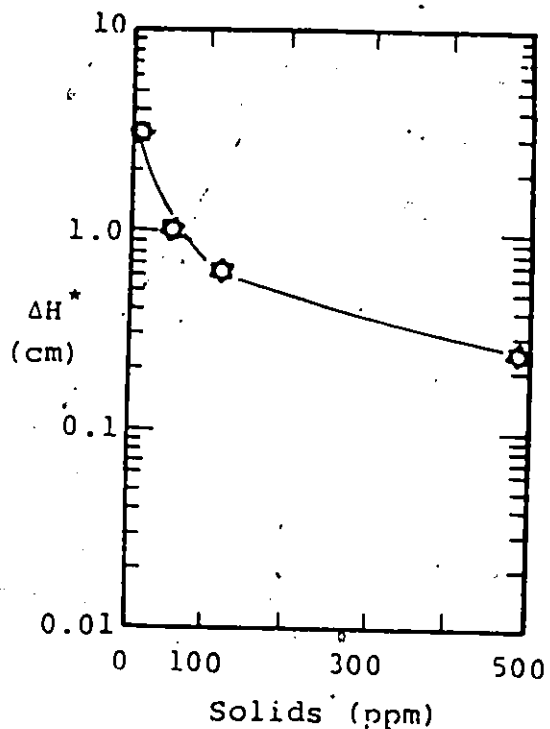


Figure 2.11 THE EFFECT OF
THE SOLIDS ADDED ON
THE SETTLER DISPERSION
(@ 870 rpm).

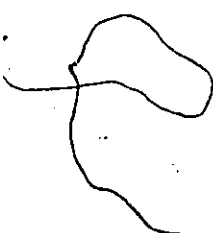
(6) was the path of the "chimney" (which is the band of drops entering the settler from the mixer) through the dispersion band. In their experiments the chimney flowed towards the coalescing front, while in the present case it flowed towards the settling front. This result indicates a fundamental difference in the mode of operation of the settler dispersion band of this project and that of Barnea and Mizrahi. The small equipment size and subsequent low throughputs of this project may account for this difference (see Section 7).

Phase cloudiness and the dispersed phase entrainment generally increased with increasing impellor speeds.

2.3.7 Crud Formation

Table 2.3 summarizes observations of the crud formed during the slow extraction series (for which solids were added). The crud was a brownish loose mass that collected at the coalescence front of the settler dispersion band. The impellor speed and feed concentration of solids did affect the apparent amount of crud (no quantitative measurement of the amount of crud was made) and the behaviour of the crud in the settler. Thus crud did form in the settler in spite of the short run times employed. It is probable that the crud formed in this project was only one type of stable

Table 2.3 Observed Crud Formation in the Settler



Solids in feed (ppm)	0	50	100	500	100	100
Impeller speed (rev/s)	14.5	14.5	14.5	14.5	7.5	25
Thickness of crud (mm)	0	1.2	1.2	F	F	3
% of interface covered (approximate estimate)	0	5-10	30-40	100	20	60

F - fingers of crude extended into the aqueous

emulsion that is encountered in industrial practice. It is possible that the crud may actually be an oil in water emulsion stabilized by the solid particles. (see Section 9)

2.4 CONCLUSIONS

Chemical and physical aspects of the solvent extraction of uranium by a tertiary amine were studied in a one stage mixer-settler. In spite of considerable success in developing equipment for studying the various phenomena, more improvements would be required in the equipment before completely satisfactory results could be obtained.

1. The equilibrium distribution of uranium between the organic and aqueous phases under the conditions of interest to this project was established for the extraction and stripping processes. The equilibrium pH of the stripping process was difficult to control, resulting in erratic data. Procedures were developed for the proper preparation of the aqueous and organic phases for subsequent mixer-settler runs.

2. The density, viscosity, and interfacial tension of the aqueous and organic phases were determined over the range of conditions of this project. Very approximate analyses based on simple models suggested that the observed changes in the physical properties during the course of extraction and stripping would not have caused large variations of the drop size and mass transfer efficiencies in the mixer.

3. The small scale mixer-settler that was developed for this project permitted several processes to be studied during the course of each run. Because the mixer was geometrically similar to standard mixing vessels, estimates could be made of the flow and mixing of the phases in the mixer.

4. The technique developed for photographing drops in the mixer allowed standard equipment for photomicrography to be used for this project. Conditions of lighting and the arrangement of the photographic equipment were easily modified and adapted. The mean drop size data from the experiments was not sufficiently accurate to test specific functional relationships between the mean drop size, physical properties, and turbulence in the mixer.

5. The phase sampling technique that was developed for this project was useful for determining the analysis of each phase in the highly agitated mixer. The filter papers were easily changed when dirty or torn, and allowed samples to be withdrawn in quantities sufficient for analytical purposes. Mass transfer efficiencies for the mixer as determined from the phase samples were found to be greater than 85% for all of the runs. High stage efficiencies were thus obtained over the range of conditions used in this project.

6. The impellor speed only affected the settler dispersion band heights of the slow extraction and stripping series (both of which contained solids). In these series the dispersion band height increased with increasing impellor speeds, but only at the lower range of impellor speeds. The dispersion band heights were reduced by the presence of solids. Qualitative observations indicated that phase entrainment and cloudiness increased with increasing impellor speeds, especially for the organic (continuous) phase.

7. Crud only formed in the settler when solids were present. Preliminary results suggested that higher impellor speeds promote crud formation. However, further work is required to confirm this and to determine the onset of crud formation, the mechanisms of crud formation, the structure of crud, and its effects on settler performance, especially for long operating times.

2.5 RECOMMENDATIONS

The single most difficult experimental technique used in this study was the photomicrography of the dispersed phase droplets. A novel approach was used for the drop photographs - a stream of the emulsion was withdrawn through a side channel where conditions for photography could be optimized. However, the data was scattered and problems with the technique indicated that the following improvements would probably be of help in obtaining better results:

- A much higher quality optical system would be a great improvement over the makeshift system built for this project.
- A coating of optically smooth, continuous-phase wetted material would help to minimize or eliminate the sticking of drops on the dispersion channel window. This problem resulted in the formation of large drops that could have adversely affected results.
- It was very difficult to distinguish very small drops on the photographs, especially when the average drop size was small. The very short interdrop distances may have created this problem. Perhaps a shorter wavelength light or ultraviolet optical system would be better suited for very

small drops. Another technique that might be useful would be to pump a portion of the feed organic through the dispersion channel before feeding it into the mixer. This would greatly decrease the dispersed phase fraction in the channel, leading to reduced coalescence, better droplet separation, and ultimately better lighting conditions and drop photographs.

It would be better to have much larger equipment for the study of the behaviour of the settler dispersion band. Larger equipment would make mass transfer studies much more difficult, however, as the required solution volumes are excessive.

Detailed analysis of the physical and chemical composition of the crud would be of great help to understanding the mechanisms of crud formation. It would also be very interesting to use a wide variety of solids in the feed and study their effect on crud formation. Finally, methods to prevent crud formation, and break up existing cruds would be of practical importance to industrial liquid-liquid extraction circuits.

3. PHASE PREPARATION AND CHEMICAL EQUILIBRIUM

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3. - PHASE PREPARATION AND CHEMICAL EQUILIBRIUM

3.0 OBJECTIVES

As described in section 1 of this report, the objectives of this section were:

To determine the equilibrium distribution of uranium between the aqueous and organic phases under the conditions of interest to this project. Procedures were to be developed for the preparation of the phases for the mixer-settler runs. The information obtained at this stage of the project was of fundamental importance to the mass transfer studies that were later undertaken.

Synthetic solutions were used in this project. The composition of the solutions were intended to resemble industrial process streams in so far as uranium and sulfate concentrations were concerned, but the many impurities present in industrial processes were not duplicated in this project. Procedures for preparing the aqueous phases are described in this section. The organic phase was of necessity reused during the course of the project. Therefore the procedures used for properly cleaning and preparing the organic phase are described. Much of the experimental work is greatly simplified and accelerated by the ability to

the ability to predict by calculations the behaviour of the phases. Therefore, in addition to experimental data on the liquid-liquid distribution of uranium, calculations were made for the adjustment of the aqueous phase pH's. Data and calculations related to this section are given in Appendix 3.

3.1 PHASE PREPARATION

3.1.1 Industrial Solutions vs. Lab Solutions

A typical analysis of the leach liquor from Gulf Mineral's operations of Rabbit Lake is given in Tables 3.1, 3.2, and 3.3. The leach contains significant amounts of iron, aluminum, silica, magnesium, and uranium. Iron, silica, and solids especially seem to affect the dispersion and coalescence of the phases. These impurities were not present in the simple synthetic solutions that were used in this project (also shown in Table 3.1). The considerable costs of preparing an actual ore leach were therefore avoided, and more effort could be devoted to the development of experimental techniques of photography, mass sampling, and mixer settler design. It does mean however that the behaviour of the synthetic solutions may be different from that of an industrial circuit.

As shown in Figure 3.1 (from Coleman et al. (21))

**Table 3.1 A Comparison of Industrial Leach Liquors
With the Synthetic Leach of this Project**

Element	Concentration (g/L)	
	typical Leach	synthetic Leach
U	1.7	14.5
Mo	8×10^{-4}	-
V	$6-25 \times 10^{-3}$	-
Si	0.5-1	-
Fe	1-2	-
Al	2	-
Na	-	5.6
Ca	0.3-0.5	-
Mg	3-10	-
Th	3×10^{-3}	-
Ti	4×10^{-3}	-
Zn	0.02	-
T.D.S.	45-70	23-34
P.S.	<50 ppm	0
pH	1.6-18	1.6

typical leach - from Ritcey (58) and Young (82)
T.D.S. - total dissolved solids
P.S. - particulate solids

**Table 3.2 A Comparison of Industrial Strip Liquors
 With the Synthetic Strip of this Project**

	industrial strip	synthetic strip
$(\text{NH}_4)_2\text{SO}_4$	130 g/L	120 g/L
maximum U loading	25 g/L	5 g/L
pH	3.5 to 4.2	

**Table 3.3 A Comparison of Industrial Organic Phases
 With the Organic Phase of this Project**

	volume %	
	Industrial Organic	Synthetic Organic
Extractant (tertiary amine)	3.5-5%	3.5%
Phase Modifier (isodecanol)	3.5-5%	3.5%
Diluent (aliphatic kerosine)	90-93%	93%

Extractant - Industrially, Alamine 336 and Adogen 364 are commonly used. These are roughly equivalent to tri-octyl-amine.

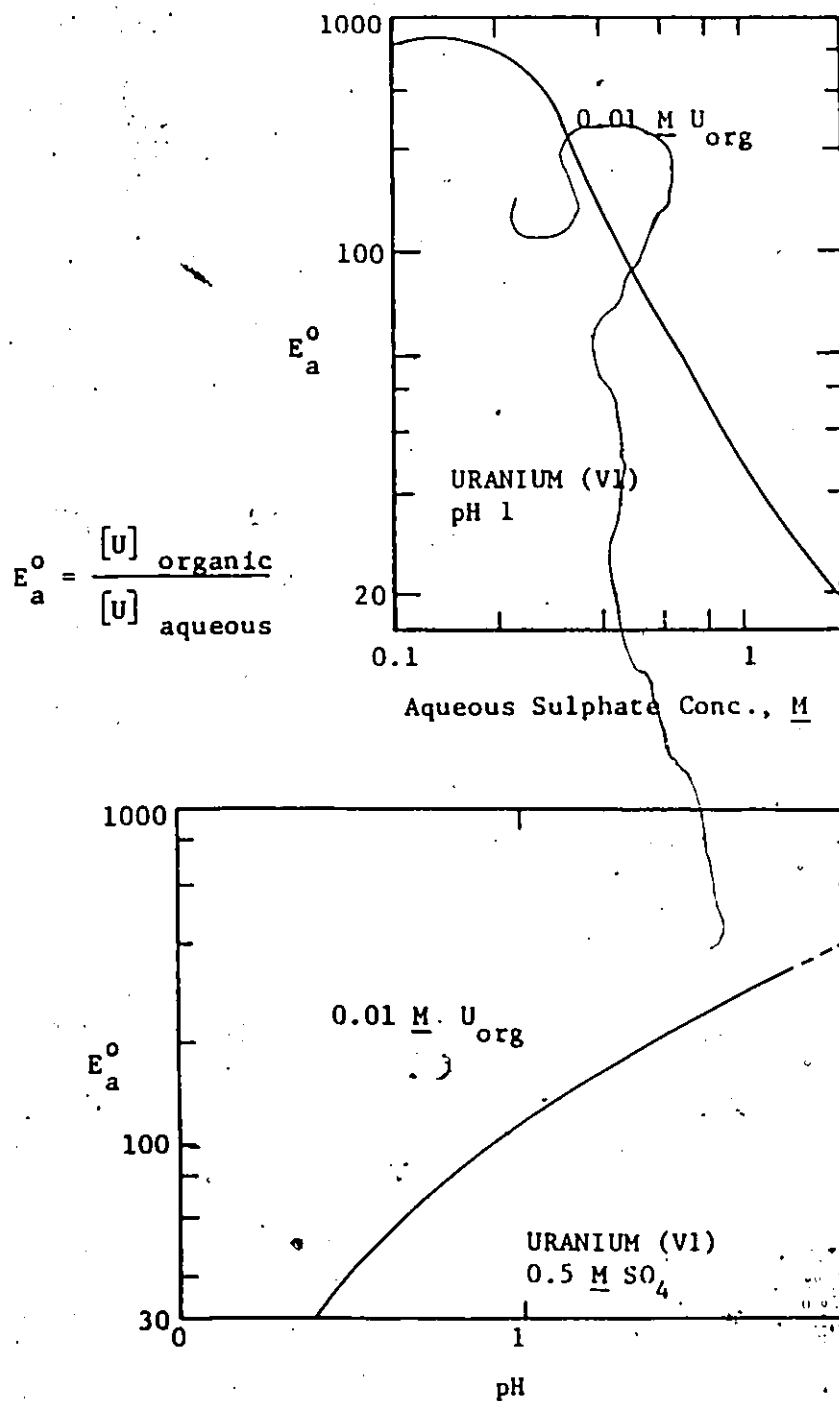


Figure 3.1 EFFECT OF THE pH AND SULPHATE CONCENTRATION ON THE EXTRACTION COEFFICIENT.
(from Coleman et al (16))

both the pH and the sulfate concentration have important effects on the distribution of uranium between the organic and aqueous phases. This is expressed in terms of an extraction coefficient, which is simply the ratio of the organic to the aqueous uranium concentrations for given conditions in the solution and for dilute aqueous concentrations of uranium. In order that the experimental runs resemble industrial conditions, and that the experimental runs have consistent equilibrium values of sulfate concentration and pH, careful preparation of the phases is required. Important deviations of either pH or sulfate concentrations from their desired endpoint values will change the equilibrium distribution of uranium, making it difficult to interpret mass transfer results. Such deviations could possibly affect phase dispersion and coalescence as well.

3.1.2 Phase Compositions

Table 3.4 lists the chemicals that were used in each of the mixer/settler series. The chemicals that were used during the experiments can be found in Table 3.5. The compositions of the phases are given in Table 3.6 along with their method of preparation. The indicated amounts of sulfuric acid and ammonium hydroxide are only approximate as pH control requires a precise adjustment of the phases so as to obtain the desired end point equilibrium. The desired

equilibrium pH would only be obtained for the O/A feed ratios (organic to aqueous volumetric feed ratios) and sulfate concentrations used in this project: ✓

3.1.3 Stripping, Scrubbing, and Cleaning the Organic

The organic phase was reused throughout this project and therefore had to be properly cleaned before recycling. The method adopted was to contact the organic phase with a 5% sodium carbonate scrub solution to remove uranium and any other extracted metals (molybdenum, vanadium, arsenic). An O/A ratio of 2 was used, the procedure being repeated three times, care being taken to remove precipitate and scum from the organic after each contact (a 200 liter polyethylene container was used for the 180 liters of solution). A final scrub with tap water at an O/A of 2 completed the cleaning process, yielding the initial (neutral) organic.

Evaporation, repeated cleaning, and normal use of the organic phase led to losses of the amine extractant. Approximate analysis indicated that the amine concentration decreased from 0.076 to 0.070 molar during the initial course of experimentation. The initial work on chemical equilibrium, physical properties, and the "no extraction" series were all done with organic material from a 60 liter solution. New solution was then prepared and mixed with the

Table 3.4 The Phases Employed for Each Series of Mixer/Settler Runs

Series	O/A	pH	SO ₄	Aqueous Phase	Organic Phase
No Extraction	1.5	1.6	0.18	Acidifier Soln	Acidified Organic
Fast Extraction	1.5	1.6	0.18	Fast Extraction Leach	Acidified Organic
Slow Extraction	1.5	1.6	0.25	Slow Extraction Leach	Partially Acidified Organic
Stripping	1.5	4.0	0.98	Stripping Solution	Fully Uranium Loaded Organic

pH = equilibrium pH

O/A = ratio of the volumetric feed rates of the organic and the aqueous phases

SO₄ = total SO₄ concentration (M)

Table 3.5 Chemicals Used in the Preparation of Phases

	MW	Chemicals and Reagents (Technical Grade)	
U	238	Stein Hall	70% UO ₃
H ₂ SO ₄	98.1	VanWaters & Rodgers	98% liquid
Na ₂ SO ₄	142.1	Anachemia	solid
(NH ₄) ₂ SO ₄	132.1	"	solid
NH ₄ OH	35.1	Allied Chemical Can.	30% soln
Na ₂ CO ₃	106	Anachemia	solid
Shell 140	~140		aliphatic (kerosene) hydrocarbon
isodecanol	158.3	MSS Chemicals	
Adogen 364	364	Sherex Chemicals	tri-C ₈ -C ₁₀ amine

Table 3.6 Principal Solutions Used During the Experiments

	Component	g/L	M	Preparation
Acidifier Solution (pH=1.6)	Na ₂ SO ₄	16.8	0.118	direct
	H ₂ SO ₄	6.1	0.062	
Fast Extraction Leach (pH=1.6)	U	1.4	5.9x10 ⁻³	direct
	Na ₂ SO ₄	16.8	0.118	
	H ₂ SO ₄	5.8	0.059	
Slow Extraction Leach (solids also added)	U	4.9	2.1x10 ⁻³	direct
	Na ₂ SO ₄	16.8	0.118	
	H ₂ SO ₄	12.6	0.128	
Saturation Leach	U	20.6	0.087	direct
	Na ₂ SO ₄	16.8	0.118	
	H ₂ SO ₄	24	0.245	
Stripping Solution	(NH ₄) ₂ SO ₄	120	0.91	direct
	NH ₄ OH	1.7	0.048	
Partial Acidifier (stripping)	(NH ₄) ₂ SO ₄	120	0.91	direct
	H ₂ SO ₄	2.6	0.026	
Scrub Solution (~5% Na ₂ CO ₃)	Na ₂ CO ₃	53	0.50	direct
Initial (neutral) Organic	Adogen 364	3.5%	0.070	direct (scrubbed & recycled)
	isodecanol	3.5%	0.18	
	Shell 140	93%	-	
Partially acidified organic	Initial Org.	-	-	initial org. + partial acid. • O/A 5:1
	H ₂ SO ₄	0.51	0.0052	
Acidified organic	Initial Org.	-	-	initial org. + acidifier • O/A 5:1
	H ₂ SO ₄	2.9-3.4	0.032	
Fully U loaded organic	Initial Org.	-	-	sat'n leach + initial Org. • O/A 5:1
	U	4.4	0.018	
	H ₂ SO ₄	3	0.031	

old solution to get a total solution volume of 120 liters. This altered the amine concentration slightly (from 0.07 M back to approximately the original concentration of 0.076 M).

3.2 CHEMICAL EQUILIBRIUM

3.2.1 Introduction

The adjustment of the phase compositions to obtain specified equilibrium conditions (pH, total sulfate) is considerably simplified if the required amounts of sulfuric acid, ammonium hydroxide, or sodium hydroxide can be estimated. The predominant complexes of the aqueous uranyl ions or the organic extractant molecules are also of interest, as are the effects of changing the O/A ratio, the ionic strength of the solution, or the equilibrium pH. For all these cases a knowledge of the equilibrium behaviour of the aqueous and organic solutions is required.

3.2.2 Chemical Equilibrium within the Aqueous Phases

Attempts to calculate the equilibrium concentrations of all species were limited to the aqueous leach and strip solutions. The results are presented in the form of graphs for assisting the pH adjustment of the solutions (Figure 3.2-extraction, Figure 3.3 - stripping). The calculations are based on literature values of concentration constants (not activity constants) for equilibrium at specified ionic strengths. (see Crockford and Simmons (19), London Chemical Society (41), Randall and Langford (56), Wirth (82)). The

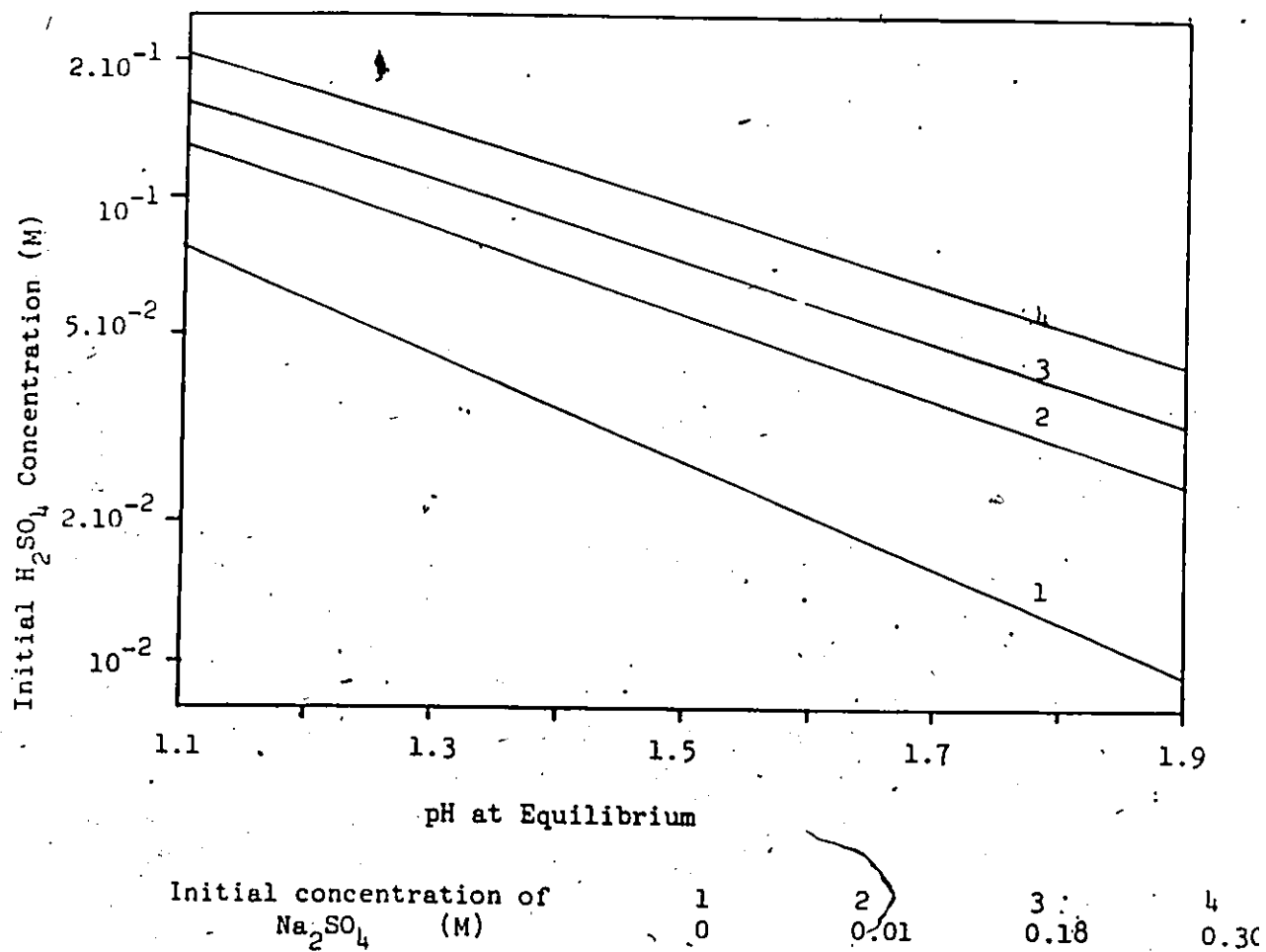


Figure 3.2 pH ADJUSTMENT OF THE ACIDIFIER SOLUTION

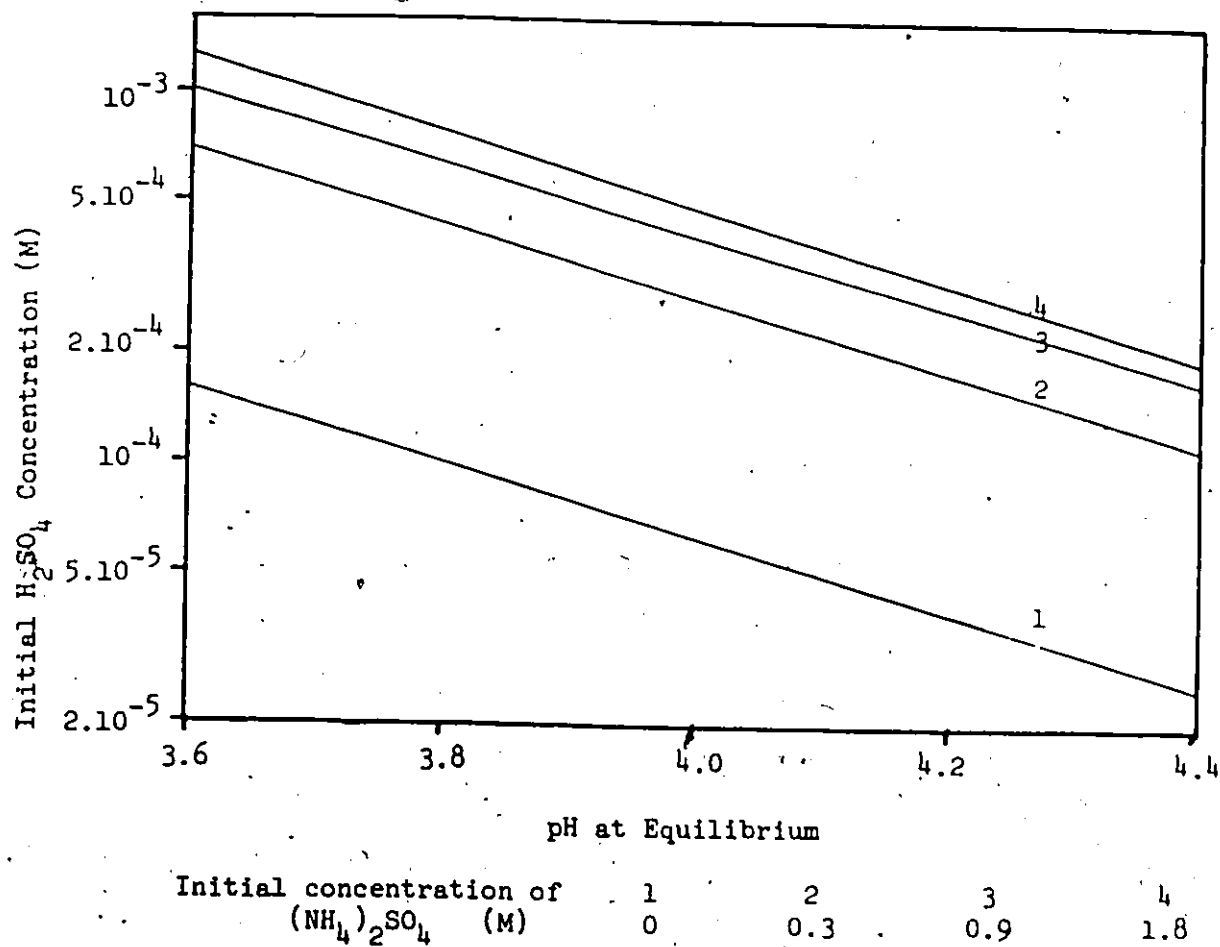


Figure 3.3 pH ADJUSTMENT OF THE STRIPPING SOLUTION

Table 3.7 Reactions within the Acidifier Solution

					K
UO_2^{2+}	+	SO_4^{2-}	=	UO_2SO_4	64
UO_2SO_4	+	SO_4^{2-}	=	$\text{UO}_2(\text{SO}_4)_2^{2-}$	4.9
$\text{UO}_2(\text{SO}_4)_2^{2-}$	+	SO_4^{2-}	=	$\text{UO}_2(\text{SO}_4)_3^{4-}$	16
Na^+	+	SO_4^{2-}	=	NaSO_4^-	1.3
Na^+	+	NaSO_4^-	=	Na_2SO_4	0.006
H_2SO_4	=	H^+	+	HSO_4^-	166
HSO_4^-	=	H^+	+	SO_4^{2-}	0.036

K- equilibrium concentration constants for an ionic strength of 0.5 M

$$K = \frac{\prod [\text{products}]^{P_i}}{\prod [\text{reactants}]^{R_i}}$$

Table 3.8 Reactions within the Stripping Solution

					K
UO_2^{2+}	+	SO_4^{2-}	=	UO_2SO_4	64
UO_2SO_4	+	SO_4^{2-}	=	$\text{UO}_2(\text{SO}_4)_2^{2-}$	4.9
$\text{UO}_2(\text{SO}_4)_2^{2-}$	+	SO_4^{2-}	=	$\text{UO}_2(\text{SO}_4)_3^{4-}$	16
NH_4^+	+	SO_4^{2-}	=	NH_4SO_4^-	3.2
NH_4^+	+	NH_4SO_4^-	=	$(\text{NH}_4)_2\text{SO}_4$	
NH_4^+	+	OH^-	=	$\text{NH}_3 + \text{H}_2\text{O}$	
H_2SO_4	=	H^+	+	HSO_4^-	166
HSO_4^-	=	H^+	+	SO_4^{2-}	0.036
H_2O	=	H^+	+	OH^-	

chemical equilibria between the important species in solution and their corresponding equilibrium constants are shown in Tables 3.7 and 3.8. Extensive measurements were not made to verify these results, however they were found to be of great practical use when adjusting the pH of the phases. Details concerning the calculations are in Appendix A.3.

3.2.3 Acidification of the Organic Phase

Sulfuric acid is extracted from acidic aqueous solutions by the tertiary amine extractant. The reactions are shown in Table 3.9. The predominant form of amine at a pH of 1.6 is the sulfate complex, while for very acidic solutions the bisulfate form of the amine is more important. The bisulfate form does not readily extract uranyl sulfate complexes. This explains the dependence of the extraction coefficient on the solution pH that is indicated in Figure 3.1. As the pH decreases below 1, the bisulfate form of the amine becomes predominant, effectively reducing the amount of uranium that may be held in the organic phase. In fact, stripping the uranium from the organic may be accomplished by the use of strong acid solutions instead of using weakly acidic solutions (pH=4.0) as in this project.

The experimentally determined amounts of sulfuric

Table 3.9 Acidification of the Organic Phase

Reactants	Product	Name of Product	pH
	R_3N	free amine	>3.5
$2R_3N + H_2SO_4 \rightleftharpoons$	$(R_3NH)_2SO_4$	sulfate salt	1.6-1.8
$R_3N + H_2SO_4 \rightleftharpoons$	$(R_3NH)HSO_4$	bisulphate salt	<<1

pH - Range of aqueous phase pH for which the product is the predominant form of amine

Table 3.10 pH Control Requirements
(Experimentally Determined)

Process	pH		pH Control	$\frac{\text{moles extractant}}{\text{moles pH control}}$
	in.	end		
Extraction	7.0	1.6	$3.2 \times 10^{-2} H_2SO_4$	2.2
Partial Acidification	7.0	4.0	$5.1 \times 10^{-3} H_2SO_4$	-
Stripping	1.6	4.0	$8.6 \times 10^{-2} NH_4OH$	0.81

pH - pH of the aqueous solution in equilibrium with the organic phase
in. - initial state
end - final state

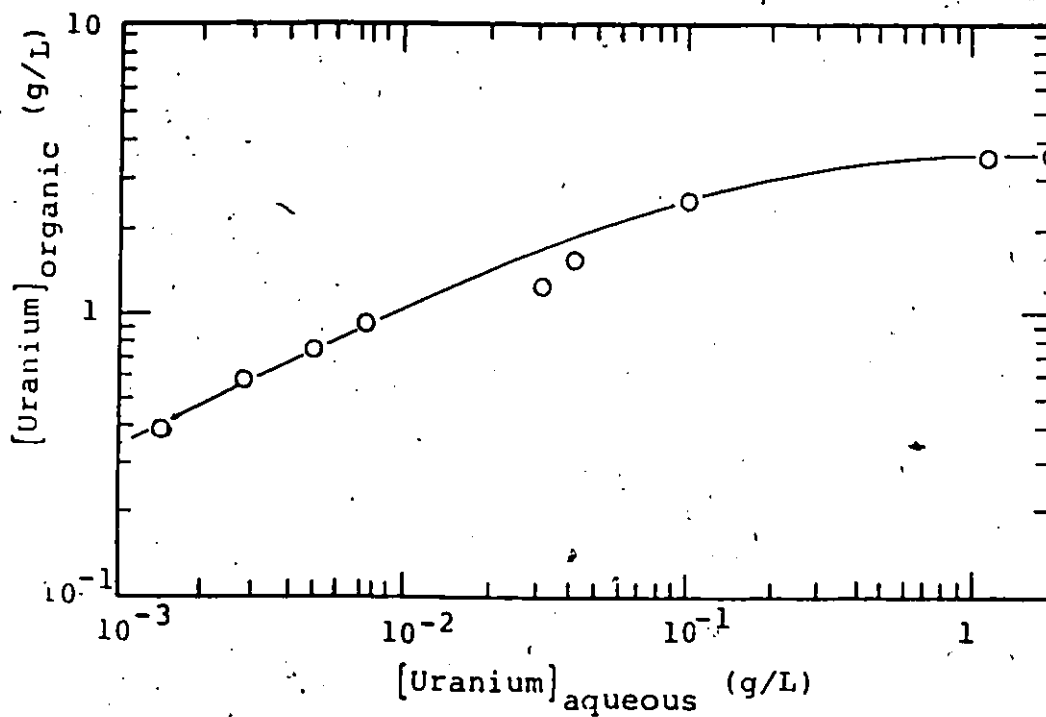
pH control - moles of the indicated pH control reagent per liter of organic
This does not include pH control requirement for the aqueous phase (see figures 3.2 and 3.3).

acid and ammonium hydroxide required to obtain the desired equilibrium pH (1.6 for extraction, 4.0 for stripping) are given in Table 3.10. The number of moles of extractant per mole of sulfuric acid in the organic phase can be estimated from those results. At a pH of 7 there was very little H_2SO_4 in the organic phase. When the pH was lowered from 7 to 1.6, the acid extraction was 0.032 moles H_2SO_4 per liter of organic. From Table 3.6 the measured concentration of extractant in the organic phase was 0.07M. This gave a ratio of extractant molecules to sulfuric acid molecules of 2.2.

3.2.4 Extraction Equilibrium

In order to determine the equilibrium conditions for extraction standard shake-out tests were performed. The fast extraction leach and the acidified organic phases were put into separatory funnels at varying O/A ratios. The funnels were shaken three times for 15 seconds at five minute intervals, left overnight at room temperature, and shaken in the same manner the next day to ensure that equilibrium was attained. Each phase was then analysed by an x-ray fluorescence technique to determine its uranium content.

The data are plotted in Figure 3.4, and may also be found in Table A.3.1 of Appendix 3. The limiting concentration of uranium in the organic phase was 3.5 g/L or 0.015 M. When compared with the concentration of extractant



conditions

T - ambient
pH - 1.6
0.07 M Adogen 364
0.1 M Na_2SO_4

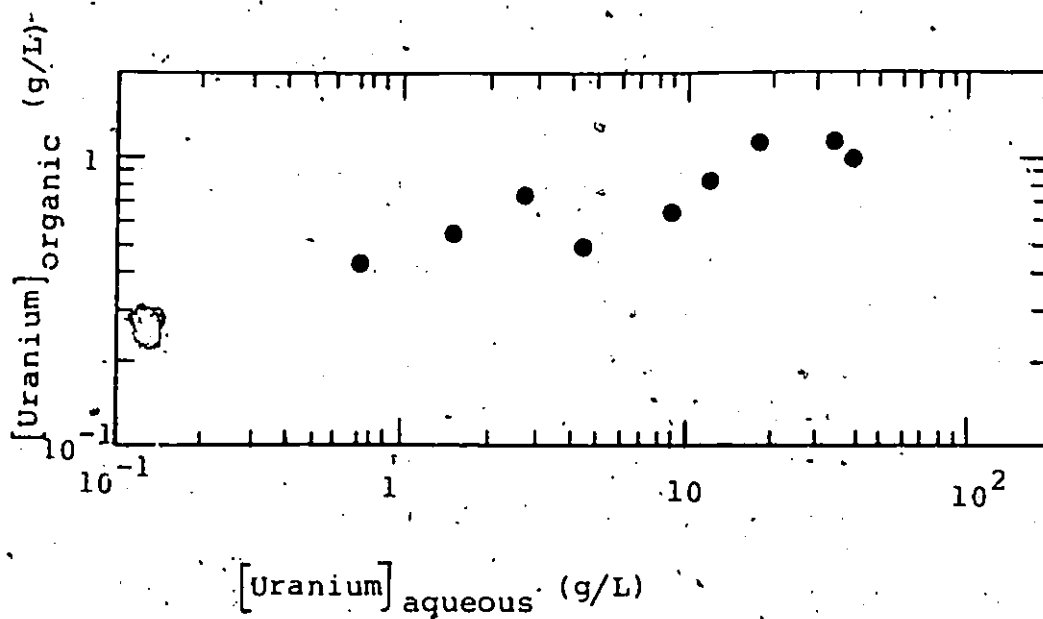
Figure 3.4 EQUILIBRIUM DISTRIBUTION OF URANIUM
FOR EXTRACTION

in the organic phase (0.07 moles/liter- Table 3.6) this indicates a limiting ratio of 4.7 extractant molecules per uranium atom.

3.2.5 Stripping Equilibrium

Equilibrium studies of the stripping process were slightly different from the extraction shakeout tests. The stripping solution (without NH_4OH) was mixed with the fully uranium loaded organic in an agitated beaker at different O/A ratios. A pH control solution containing NH_4OH was added until the equilibrium pH of 4.0 was attained. Fifteen minutes were required after each pH adjustment to allow the pH electrode reading to stabilize. Solutions with a very high equilibrium concentration of uranium formed precipitate after several days even though the pH readings were normal (approximately 4.0).

The equilibrium data for stripping is plotted in Figure 3.5 (see also Table A.3.2 in Appendix 3). The results were not as good as those obtained for the extraction equilibrium, as seen by the scatter of the stripping data in Figure 3.5 and by the range of equilibrium pH values shown in Table A.3.2.



conditions

T - ambient
 pH - 4.0
 0.07 M Adogen 364
 0.9 M $(\text{NH}_4)_2\text{SO}_4$

Figure 3.5 EQUILIBRIUM DISTRIBUTION OF URANIUM
 FOR STRIPPING

3.3 DISCUSSION - PHASE PREPARATION AND CHEMICAL EQUILIBRIUM

Figures 3.2 and 3.3 are plots of the pH at equilibrium of leach and strip solutions of specific makeup based only on literature values for equilibrium constants. Figure 3.2 for extraction proved to be especially useful in conjunction with Table 3.10 (for the acidification of the organic phase) when making pH adjustments for extraction.

The problem of pH control for stripping is well illustrated by Table 3.10 and Figure 3.3. The amount of sulfuric acid that is released per liter of organic in raising the pH from 1.6 to 4.0 is about 0.032 moles. At an O/A ratio of 1.5 this means that the concentration of sulfuric acid released into that aqueous strip solution is 0.048 moles. Figure 3.3 shows that the sulfuric acid content of the stripping solution at a pH of 4 is only about 4×10^{-4} M. The sensitivity of the pH control is therefore obvious as errors of less than 1% in the amount of NH_4OH added for pH control will greatly affect the equilibrium pH of the stripping section.

As discussed previously there was a limiting value of 2.2 extractant molecules for each sulfuric acid molecule in the organic phase. Coleman et al (21) and Carino (19) suggest that the predominant form of amine at a pH of 1.6 should be the sulfate complex, which would give a ratio of

moles of extractant to moles of acid of about 2, which is in agreement with the experimental value above.

Figure 3.4 shows that the limiting value of the moles of extractant to the moles of uranium at high uranium loadings was found to be 4.7. Both Carino (19) and Coleman (21) suggest that the limiting ratio is 4 for extraction, which also agrees with the experimental value.

It is felt that the scatter in the stripping equilibrium data was largely due to variations in the equilibrium pH from the desired value. This is important because pH control is quite difficult to attain, especially for continuous flow experiments. Variations in the pH might therefore be expected to affect the results of mass transfer measurements, which are discussed in Section 7.

3.4 CONCLUSIONS

The equilibrium distribution of uranium between the organic and aqueous phases under the conditions of interest to this project was established for the extraction and stripping processes. The equilibrium pH of the stripping process was difficult to control, resulting in erratic data. Procedures were developed for the proper preparation of the aqueous and organic phases for subsequent mixer-settler runs.

4. PHYSICAL PROPERTIES OF THE PHASES

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4. PHYSICAL PROPERTIES OF THE PHASES

4.0 OBJECTIVES

As described in Section 1 of this report, the objectives of this section were:

To measure the density, viscosity, and interfacial tension of the phases over a range of equilibrium concentrations of uranium. This would provide information about the physical properties of the system as commonly required when analyzing physical processes such as turbulence, drop breakup, and phase separation in the mixer-settler. This information would also reveal the changes of the physical properties during extraction and stripping.

The formation of organo-metallic complexes during extraction often has the effect of drastically changing the physical properties of the organic phases. In extreme cases this may lead to an excessively high viscosity or even to the formation of a third phase. It is therefore important to know if the physical properties vary enough during the extraction and stripping processes to have an important effect on drop sizes and mass transfer in the mixer, or phase separation and entrainment in the settler. Data and calculations related to this section are given in Appendix 4.

4.1 INTRODUCTION

Knowledge of the physical properties of the phases that were used in this project should permit some comparisons between the phase dispersion characteristics of this study and of other studies. It should also indicate any significant changes in the physical properties that might occur in the course of the solvent extraction process. Finally, there are many correlations in the literature dealing with drop sizes and mass transfer in dispersions for which the physical properties must be known.

Liquid-liquid extraction involves both mass and momentum transfer within bulk phases and across their interfaces. Any heat of reaction or heat of mixing effects for this project are assumed to be negligible because of the dilution of reaction species within the bulk phases. Also, it was found during experiments that temperature increases for the single stage extraction or stripping runs were only about 1°C.

In this project the bulk viscosity, bulk density and interfacial tension were actually measured. For the study of mass transfer estimates of the mass diffusivities are required. The mass diffusivity of uranyl species is discussed in Section 7. A number of other physical properties are also of importance to interfacial phenomena,

but they were not measured or estimated in this project. For example, the interfacial elasticity and viscosity are commonly referred to in studies of the behaviour of liquid interfaces, and the properties of solid particles determine the effect that they will have on drop coalescence in a dispersion. Zeta potentials are often measured in studies of emulsion stability. (See Section 8 for a more complete discussion of emulsion stability and the factors that affect it.)

4.2 SOLUTION DENSITIES

The aqueous phase had a density close to 1.0 g/cc while organic phase density was about 0.8 g/cc. The difference between the two, about 0.2 g/cc, is a variable often appearing in correlations. A relative error of less than 5% would be acceptable in this value (in order to keep it to the same general level as many of the other errors in the experimental measurements), meaning that an error of about 1% or 2% would be acceptable in the estimates of bulk phase densities.

Both hydrometer tests and tests using 250 mL, 50 mL, and 25 mL volumetric flasks were used for the measurements of density. Temperatures of the fluids were recorded but not controlled. Table 4.1 shows results for the density of water, which are in close agreement with literature values. Phase densities are shown in Table 4.2 for the feed solutions used in the runs (see Section 3) and for extreme cases of extraction and stripping equilibria. Changes in the density with extraction and stripping were less than 11% for the aqueous phase and less than 2% for the organic phase. The density difference between the aqueous and organic phases varies by as much as 65% from the fast extraction case to the stripping case.

Table 4.1 Verification of the Density Measurement Technique
(Density of Water @ 21.9 to 22.1 °C)

volumetric flask measurement	
50 mL	0.9952
250 mL	0.9965
hydrometer measurement	0.9989
literature value	0.9978
(deaerated H ₂ O-22°C Lange's Handbook of Chemistry)	

Table 4.2 Solution Densities

A. Initial Phases

	T (°C)	ρ (g/mL)
Aqueous Phases		
Acidifier Solution	21.4	1.029
Fast Extraction Leach	22.0	1.033
Stripping Solution	22.0	1.066
Organic		
Neutralized	21.9	0.799
Acidified	21.9	0.804
Fully U Loaded	22.0	0.809

B. Equilibrated Phases

Equilibrated Phases	O/A	ρ_{aqueous}	ρ_{organic}	$\Delta\rho$	$\frac{\rho_{\text{max}}}{\rho_{\text{min}}}$
Fast Extraction and Acidified Org.	0.25	1.023	0.800	0.227	1.12
	8.0	1.017	0.796	0.203	
Stripping Solution and Fully U Loaded Org.	0.25	1.056	0.791	0.334	1.29
	20.0	1.125	0.797	0.259	

$$\Delta\rho = \rho_{\text{aqueous}} - \rho_{\text{organic}}$$

4.3 SOLUTION VISCOSITIES

A Brookfield viscometer was used to determine the phase viscosities. An adapter for the instrument allows the testing of low viscosity fluids. The viscometer consists of a solid cylinder rotating inside of a stationary cylinder, the annulus being filled with the liquid being tested.

Three liquids were used to check the instrument operation; distilled water, and two viscosity standard fluids from the company Brookfield. The results (Table 4.3) indicated two problems; a significant error in the results and a problem in maintaining constant temperatures during the measurements. The temperatures indicated in the table are the average temperatures for all liquid in the apparatus. Local temperatures in the annulus of the viscometer were probably higher than the 1°C temperature rises indicated. To overcome the problem with temperature variations, further tests were done at a high and a low temperature in order to provide information about the temperature dependence of the phase viscosities. Temperatures were taken before and after each test. Before each test the solution, container, and viscometer parts were placed in a constant temperature bath so as to be in thermal equilibrium at the start of the test.

From five to seven readings were taken to get the

average viscosities shown in Table 4.4. There is only a 21% increase in viscosity when comparing the lowest aqueous phase viscosity (1.10 cP for the synthetic leach) with the highest viscosity aqueous phase (1.33 cP for the fully loaded strip) at room temperature. Likewise, only a 5% increase is noted between the lowest and highest viscosity organic phases. The very important effects of metal loading that occur in some liquid-liquid extraction systems do not occur with the phases used in this project.

Table 4.3. Verification of the Brookfield Viscometer

Fluid	Temperature (°C)	Viscosity (cP)	Error (%)
Viscosity Standard (5 cP at 25°C)	22.0-23.0	5.1	2%
Viscosity Standard (10 cP at 25°C)	21.8-22.9	9.5	5%
Distilled Water	21.9-22.4	1.07	12%
	25.5-26.5	1.02	17%

Literature values for water (Lange Handbook of Chemistry)
 Temp. °C 22 24 26
 viscosity H₂O (cP) 0.953 0.910 0.870

Table 4.4 Measured Phase Viscosities

Fluid	Temperature (°C)	Viscosity (cP)
Syn. Aqueous Leach	22.5-23.0	1.10
	30.3-29.8	0.98
Acidifier	21.1-21.4	1.12
	28.0-28.2	0.98
Aqueous Strip	21.3-22.2	1.23
	28.0-27.9	1.15
Fully Loaded Strip	21.4-22.0	1.33
	30.2-30.0	1.17
Fully Loaded Organic	21.9-?	1.66
	28.0-25.2	1.55
Acidified Organic	21.9-23.8	1.65
	29.5-26.7	1.46
Neutralized* Organic	21.7-21.9	1.59
	27.7-27.3	1.46

* Neutralized here means that the acidified organic was equilibrated with strip solution at a pH of 4

4.4 INTERFACIAL TENSIONS

4.4.1 Methods of Measurement

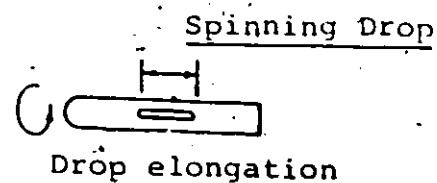
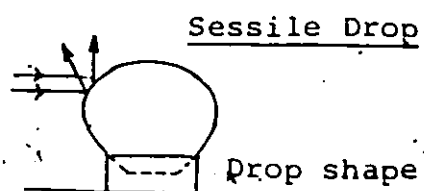
Several methods exist for the measurement of interfacial tension. A partial list is given below. A more complete discussion is given by Davies and Rideal (21) and Bikerman (9). Figure 4.1 illustrates the methods.

Sessile Drop Method- This method calculates the interfacial tension from shape measurements of a drop resting on a solid surface. The value of interfacial tension so calculated is independent of the nature of any solid surface. Slow changes in interfacial tension may be studied.

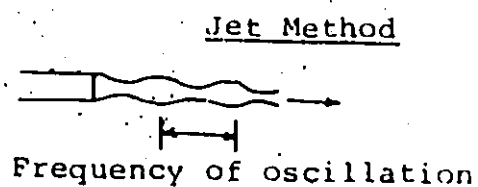
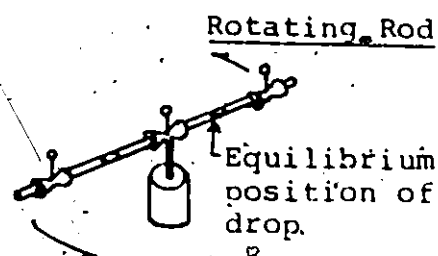
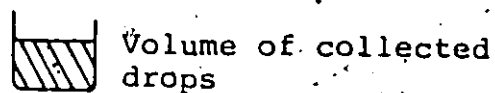
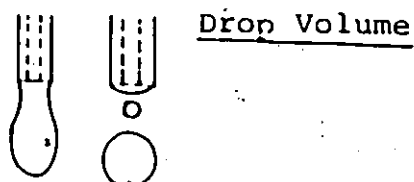
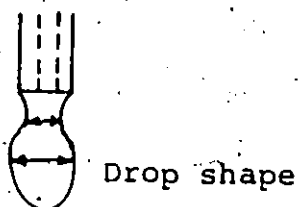
Pendant Drop Method- Measurements are made of the shape of a drop suspended from a plane, circular surface. The drop must wet all of the circular surface.

Drop Volume Method- Similar to the pendant drop method in construction, drops are allowed to form slowly, break off and collect in a container.

Jet Method- A fluid is injected into another fluid through an elliptical orifice. The odd cross section tends to become circular because of interfacial tension, but overshoots the circular configuration and becomes elliptical



Pendent Drop



De Nuoy Ring Tensiometer

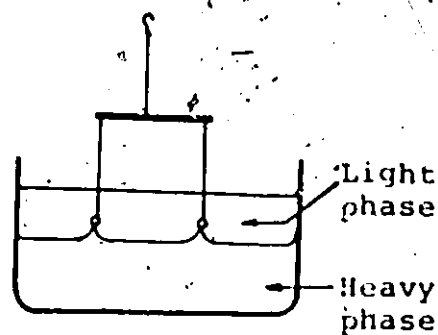
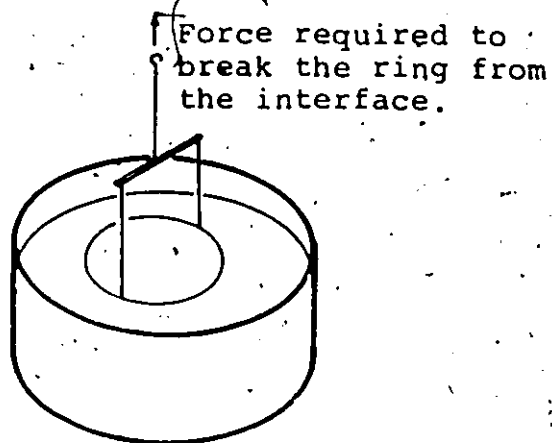


Figure 4. EXPERIMENTAL METHODS - FOR THE DETERMINATION OF INTERFACIAL TENSIONS.

again, this time perpendicular to its original orientation. It continues to oscillate in this manner, allowing the frequency of oscillation to be established and hence the interfacial tension. Interfacial tensions that change rapidly due to reactions or adsorption of impurities at the interface may be measured in this manner.

De Nuoy Ring Tensiometer- This method makes use of a platinum-iridium ring which is "perfectly" wetted by one of the liquids (contact angle of zero). The force necessary to break the ring away from the interface is measured. This is related to the phase densities, ring diameter and thickness, and the interfacial tension.

Spinning Drop Method (Cayius et al. (15))- A glass tube is spun around its axis, causing the lighter phase to form an elongated drop within the heavier phase in the tube. From the angular velocity, density difference, and drop elongation the interfacial tension may be determined.

Rotating Rod Method (Baird and Nirdosh (2))- A long glass capillary is rotated about its mid-length in a direction perpendicular to its axis. The capillary is full of the heavier phase and has a drop of the lighter phase in each end. The drops will migrate towards the center of the rod to a position depending on the angular velocity of the rod, the fluid densities, and the interfacial tension.

The sessile drop, pendant drop, and jet methods are felt to have distinct advantages due to their non-dependance on solid surfaces and also because they may be used to study transient effects on interfacial tension. The ring tensiometer method was used in this study, due to its ease of use and the availability of the equipment.

4.4.2 Verification of the De Nuoy Ring Tensiometer

The ring tensiometer was tested by measuring both surface and interfacial tensions of standard liquids. The selected liquids were distilled water, carbon tetrachloride, and heptane. Average results for several measurements are shown in Table 4.5. The results for the surface tensions agree well with literature values. Interfacial tensions were 12 to 22% lower than the literature values. The discrepancy in the values for interfacial tensions may be due to surface contamination, insufficient contact time (24 hours for $\text{CCl}_4\text{-H}_2\text{O}$, 10 minutes heptane- H_2O) for the establishment of equilibrium, or errors arising from the technique of measurement. The ring method assumes perfect wetting by one of the phases. This is probably the case for surface tensions, but does not appear to be correct for interfacial tensions. That conclusion is supported by differences in values for approach to the interface from both directions (Table 4.6).

Other verification tests included:

-The Effect of the Dish Diameter- Both 45 mm and 80 mm diameter dishes were used. There was a 5% difference in the values obtained, therefore the larger dishes were used in subsequent experiments.

-Effect of Ring Shape- An old distorted platinum iridium ring was used to measure the surface tension of water. The ring perimeter was planar and hung parallel to the liquid surface, but it was elliptical in shape. In spite of its elliptical, kinked perimeter, it gave essentially the same results as a new, circular ring. Therefore, minor bending and distortion of the ring which occurred during the experimentation would not have greatly affected the results.

-Effect of Aging the Interface- It was observed that the measured interfacial tensions decreased with time. For the rest of the experiment the interface was cleaned before each measurement by vacuuming material from the interface with a pipette and a vacuum pump.

-Effect of Changing the Direction of Approach to the Interface- It is possible with the ring tensiometer to approach the interface from above or below. When this was done for surface tensions wide discrepancies resulted. For interfacial tensions, smaller differences were noted.

Table 4.5 - Verification of the Ring Tensiometer

Lower Fluid	Upper Fluid	Temp °C	Interfacial Tens. (dynes/cm)	
			Exper.	Liter.*
H ₂ O	Air	23.2	70.8	71.2
Tap Water	Air	-	70.3	-
H ₂ O (Sat'd CCL ₄)	Air	23.0	68.5	-
H ₂ O (Sat'd Heptane)	Air	20.0	60.1	-
CCL ₄	Air	24	27.7	26.9
CCL ₄ (Sat'd H ₂ O)	Air	21.2	27.7	-
Heptane (Sat'd H ₂ O)	Air	20	20.3	20.3
CCL ₄	H ₂ O	23	35.2	45.0
H ₂ O	Heptane	20	44.0	50.4

*Literature values are for 20°C

Table 4.6 Effect of the Direction of Departure From the Interface on the Measured Values of Surface and Interfacial Tensions

lower fluid	upper fluid	Apparent Interfacial Tension (dynes/cm)	
		downward	upward
fast extraction leach*	air	40	72
fast extraction leach*	air	21	66
emulsified organic**	air	3.5	14
leach or strip soln\$	organic phase	11	11

* two similar solutions

** neutralized organic for which the pH was raised to form a stabilized "emulsion". The organic was filtered and tested.

\$ results were essentially the same for a range of

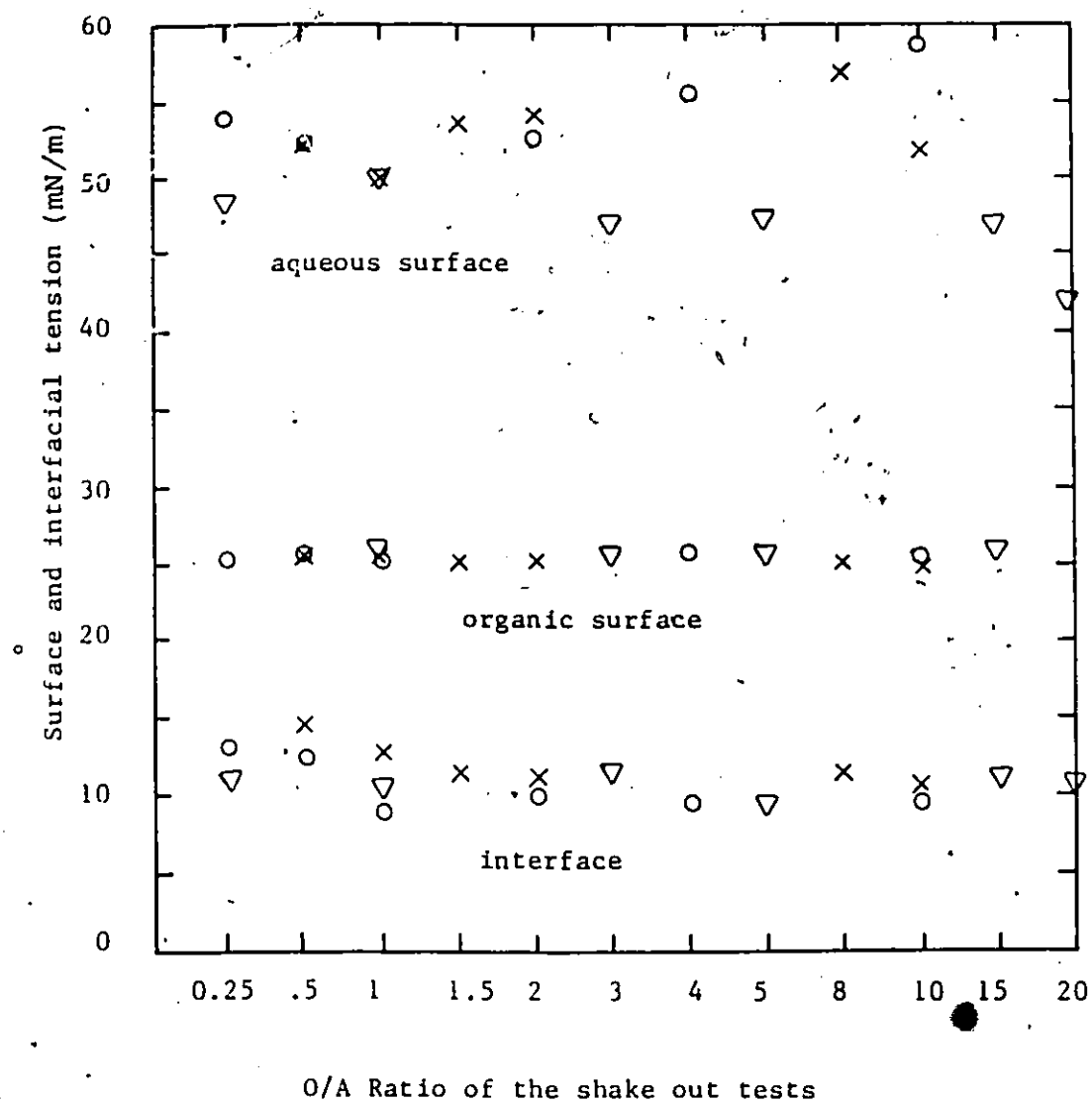
4.4.3 Results

Surface and interfacial tension measurements for equilibrated extraction and stripping phases are shown in Figures 4.2 and 4.3. The average value for interfacial tension was 10.6 ± 1 dynes/cm for both extraction and stripping when the organic phase concentration of uranium was less than 2 g/L. At higher uranium concentrations the interfacial tension appeared to increase, reaching a high of about 13 to 14 dynes/cm. The organic surface tension was a constant 25.5 ± 1 dynes/cm for both cases, while the average aqueous phase surface tension was 47.0 ± 2.4 dynes/cm for stripping and 53.8 ± 2.8 dynes/cm for extraction.

Further results included;

1) The Effect of the Direction of Approach to the Interface- In the cases of the calibration tests and measurements on the extraction phases, the interfacial tension measured in going from the light phase to the heavy phase was about 0.4 dynes/cm greater than the measurements in going from the heavy to the light phase.

2) Surface/Interfacial Tensions of a Neutralised Organic- The organic phase was scrubbed and contacted with water at a pH of 7. Tests were made with two samples. The surface tensions for the aqueous and the organic phases were



▽ stripping system
 × extraction system test 1
 ○ extraction system test 2

Figure 4.2 INTERFACIAL TENSION MEASUREMENTS

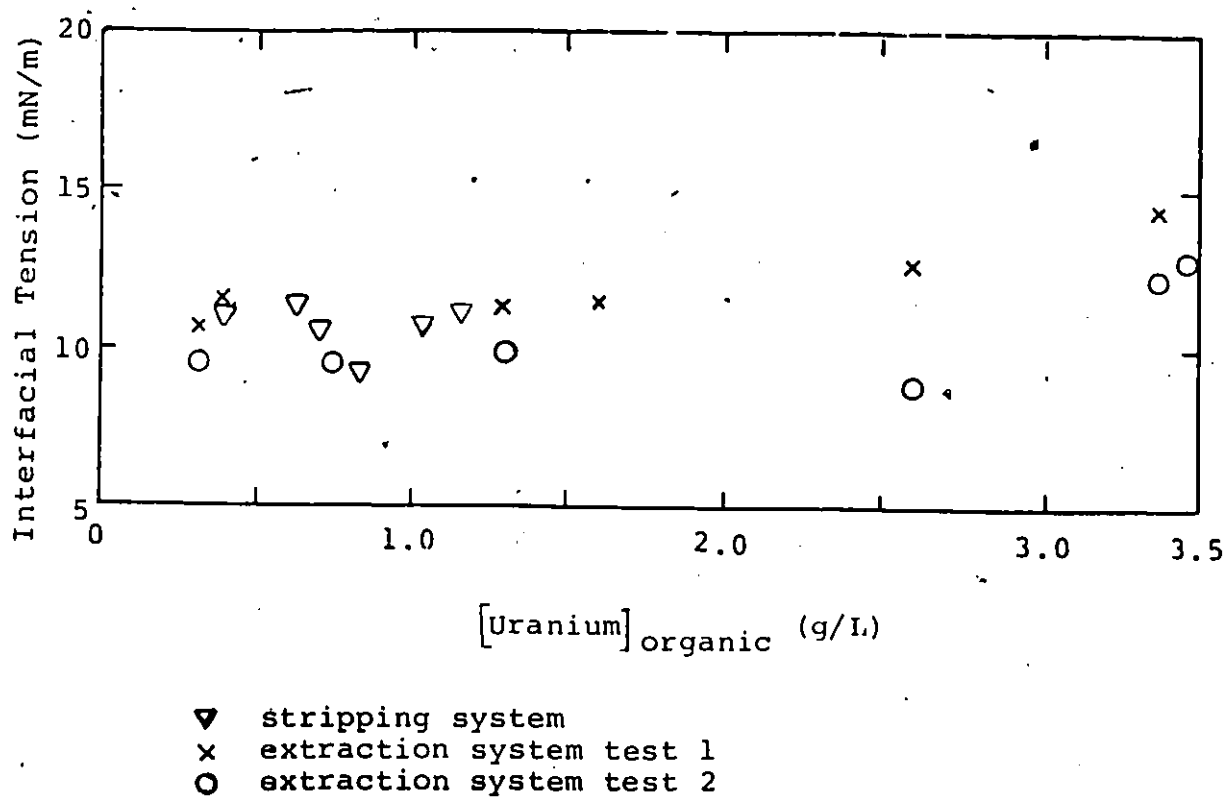


Figure 4.3 INTERFACIAL TENSION AND THE ORGANIC
PHASE CONCENTRATION OF URANIUM

(43.6, 37.7) dynes/cm and (25.1, 25.7) dynes/cm respectively. The measured interfacial tension was (13.1, 13.7) dynes/cm for the two tests.

4.4.4 Discussion - Interfacial Tension Measurements

In theory, the lower phase should perfectly wet the De Nuoy ring when making measurements of interfacial tensions by raising the ring. Conversely, the upper phase should perfectly wet the ring when making measurements by lowering the ring. The large discrepancy for surface tensions when raising or lowering the ring suggests that the liquids gave near perfect wetting of the ring. When measuring the interfacial tensions however, neither phase appears to perfectly wet the ring as measurements were similar when raising or lowering the ring. There may have been some systematic error associated with the non-perfect wetting of the ring during the measurement of interfacial tensions. The errors in the interfacial tensions as shown in the verification tests were in fact much greater than the errors of the surface tension verifications.

In contrast to the aqueous surface tension and the interfacial tension, the organic surface tension was constant throughout extraction and stripping. Differences in the aqueous surface tensions may have been due to the

presence of small amounts of the organic phase that could form a film on the surface of the aqueous phase, altering the measured value of surface tension.

The interfacial tension seems to rise with an increasing uranium concentration in the organic phase. A possible explanation for this is that the mildly surface active extractant salts are being depleted at the interface (along with the isodecanol modifier). If these mild surfactants tend to lower the interfacial tension, their depletion would lead to the observed rise in interfacial tension. A change in interfacial tension from 9 to 13 dynes/cm represents a 45% increase.

4.5 DISCUSSION - PHYSICAL PROPERTIES

The physical properties as measured in this section are later used in correlations for analysing fluid flow, drop sizes, and mass transfer. The question arises as to whether the changes in the physical properties become important to those processes as uranium is either added to or removed from the organic phase during extraction or stripping. As a basis for the discussion below, percentage changes in the physical properties for the aqueous and organic phases are assumed to be 10% for the density, 65% for the density difference between phases, 20% for the viscosity, and 45% for the interfacial tension. These values are similar to the experimental changes observed in this section.

A correlation presented in Section 5 for the root mean square fluctuating velocity in isotropic turbulence is:

$$u^2(r) = c_1(\xi r)^{2/3} \quad (5-8)$$

The power per unit mass of dispersion, ϵ , is independent of the physical properties under highly turbulent conditions (Equation 5-2), so that $u^2(r)$ is unaffected by the changes in the physical properties. Circulating times and pumping rates (Equations 5-4 and 5-5) are likewise unaffected.

In Section 6 the maximum stable drop size in a turbulent dispersion is given as:

$$d_{\max} = \frac{c_1 \sigma^{0.6}}{\rho^{0.6} N^{1.2} D^{0.8}} \quad (6-6)$$

A density change of 10% would affect $d_{\max}$ by 6%, while the impact of a 45% change in σ would be 25%. The predicted changes in $d_{\max}$ are much less than the differences in drop sizes from one series of tests to another as discussed in Section 6.

The impact of changes in the physical properties on mass transfer rates in the mixer is more difficult to estimate. Two simple mass transfer coefficient-based models are presented in Section 7. These models were used to predict the stage efficiency for the fast extraction and the slow extraction series of mixer/settler runs. At an impeller speed of 10 revolutions/second (1 W/kg power dissipation, which is similar to some industrial conditions - Perry (55p21-67)) Table 7.1 shows predictions of 98.5% and 92% stage efficiencies for the fast and slow extraction series respectively. The drop size assumed for the slow extraction series was double that of the fast extraction series. Assuming that the major effect of changes in physical properties (not including diffusivity) is to affect drop

size, then the 25% drop size difference estimated in the last paragraph is going to have an effect on the stage efficiency of less than 5%.

4.6 CONCLUSIONS - PHYSICAL PROPERTIES

The density, viscosity, and interfacial tension of the aqueous and organic phases were determined over the range of conditions of this project. Very approximate analyses based on simple models suggest that the observed changes in the physical properties during the course of extraction and stripping would not have caused large variations of the drop size and mass transfer efficiencies in the mixer.

5. POWER AND PUMPING IN AN AGITATED VESSEL

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5. POWER AND PUMPING IN AN AGITATED VESSEL

5.0 OBJECTIVES

As described in Section 1 of this report, the objectives of this section were:

To design and build a mixer-settler unit that would allow the study of drop sizes and mass transfer in the mixer and phase separation in the settler. The unit was to be geometrically similar to equipment used by other researchers, such that estimates of power dissipation, drop sizes, and mass transfer in the mixer could be made based on correlations in the literature.

Measurements of the power input to the mixing vessel and of turbulent velocity fluctuations of the mixer dispersion were not included in the objectives of this project. Because of the fundamental importance of power and turbulence to the processes of drop breakup and coalescence and mass transfer in the mixer, the bulk of this section is concerned with theory and calculations of power, pumping, and turbulence in the mixer. Not only is this information used in calculations in later sections, it will also be of use to other workers who wish to compare the conditions in this project with their own experiments. However, the

dispersed phase volume fraction was measured at the end of each run, which gave an idea of the degree of mixing of the phases. Data and calculations for this section are given in Appendix 5.

5.1 LITERATURE SURVEY

5.1.1 Specific Power

Specific power is the energy dissipation per unit mass of fluid in a dispersion. The local specific power, ϵ , varies greatly from point to point within a mixing vessel (Nagata (52)), but in many analyses a knowledge of the average specific power, $\bar{\epsilon}$, is all that is required. For a mixing vessel the average specific power may be calculated from the following expression derived by dimensional analysis (Rushton et al. (63) or McCabe and Smith (43p237)):

$$N_p = N_p(Re_{imp}, Fr, S_1, S_2, \dots, S_6) \quad (5-1)$$

$$\text{where } N_p = \frac{P}{N^3 D^5} = \text{power number,}$$

$$Re_{imp} = \frac{ND^2 \rho}{\mu} = \text{Reynold number (for the impellor),}$$

$$Fr = \frac{N^2 D}{g} = \text{Froude number,}$$

$S_1 \dots S_6$ are shape factors for the mixing vessel geometry, and

P = total power input to the mixing vessel.

In the case of a mixing vessel of fixed geometry, the above expression simplifies to:

$$\epsilon = 4/\pi N_p N^3 D^2 \quad (5-2)$$

where ϵ = energy dissipation per
unit mass of dispersion,
 N = impellor speed,
 D = " diameter, and
 N_p = power number.

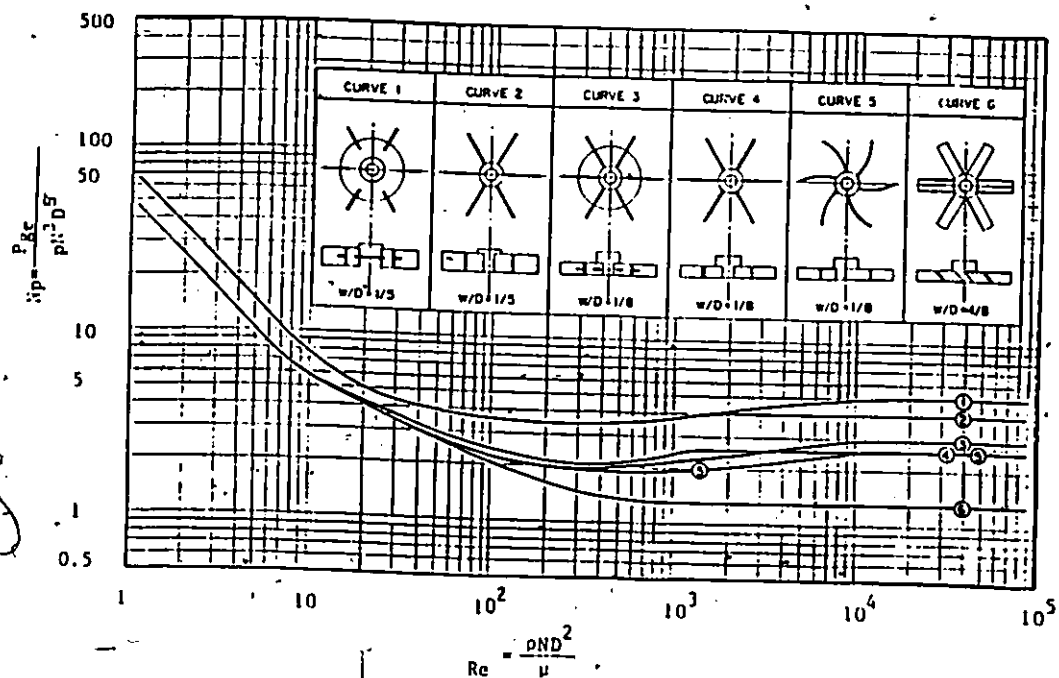
The power number, N_p , is correlated in terms of the impellor Reynolds number:

$$Re_{imp} = \rho N D^2 / \mu \quad (5-3)$$

Examples of N_p - Re_{imp} relationships for diverse mixing vessel and impellor geometries are illustrated in Figure 5.1. Note that for very high Re_{imp} ($>10^4$) the power number is nearly constant. This is because the fluid viscosity becomes less and less important at higher Reynolds numbers. Turbulence is considered to be fully developed in this region.

5.1.2 Fluid Pumping

The circulation of fluid within a mixing vessel was studied by Holmes et al (31), who found the average time of circulation of a fluid element from the impellor through the



Note: Curve 1 is appropriate for this project.

Figure 5.1 POWER NUMBER - REYNOLDS NUMBER
CORRELATIONS IN NEWTONIAN FLUIDS
FOR VARIOUS IMPELLOR DESIGNS
(Bates et al. (7))

vessel and back to the impellor to be :

$$t_c = [0.85N(D/T)]^{-1} \quad (5-4)$$

where t_c = circulation time, and

T = mixing vessel diameter.

Therefore, the pumping rate, Q_c , is given by:

$$Q_c = V/t_c = 1.7 N D^3 \quad (5-5)$$

where V is the volume of the mixer.

The results of Holmes et al. apply to a standard baffled cylindrical vessel that is geometrically similar to the one used in the present study.

5.1.3 Turbulent Flow within a Mixing Vessel

The following discussion of turbulence is based on work of Taylor (76), Kolmogoroff (19), Shinnar (68) and others. The subject is reviewed by Tavlarides and Stomatoudis (75), Shinnar and Church (68), Hinze (30), and Batchelor (6).

Mixing, drop break-up, drop coalescence, and mass transfer are affected by the degree of agitation of a dispersion. For a highly turbulent dispersion these processes will be statistical in nature, and there are at least two approaches to their analysis. The first of these involves the use of the Navier-Stokes equations for fluid motion in a turbulent environment (see Hinze (30)). A second, less rigorous approach, is to use approximate dimensional analysis. Dimensional analysis was employed in this study.

Dimensional analysis of processes occurring in a dispersion require a knowledge of the relative velocity between points within the dispersion. For example, the Reynolds number for a pipe makes use of the average flow velocity, which is approximately the relative velocity between fluid in the pipe channel and fluid at the pipe wall. The relative velocity is also required to calculate a Weber number, which is the ratio of inertial to surface stresses for a drop.

In the case of turbulence the appropriate relative velocity to use is the time averaged root mean square of the velocity fluctuations between two points. Larger eddies are anisotropic, meaning that the velocity fluctuations between two points separated by a distance comparable to the length scale of the eddy will depend on the orientation of the

points. However, Kolmogoroff (39) proposed that directional information is lost as energy is passed from larger eddies to successively smaller eddies. In this case eddies that are much smaller than the largest eddies are isotropic in nature. In addition it is assumed that energy enters the system by transfer from the vessel boundaries to the largest eddies only, and is converted to heat by small energy dissipating eddies. Intermediate sized eddies only transfer energy from larger to smaller eddies.

For this case of local isotropy $\sqrt{u^2(r)}$ (the root mean square velocity fluctuation between two points a distance r apart) should be some function of ϵ_1 (the local specific power dissipation), μ/ρ (the kinematic viscosity of the fluid), and r (the length scale being considered). Furthermore, if the distance r is much greater than the scale of maximum energy dissipating eddies, denoted by η , the kinematic viscosity μ/ρ should have no effect on $\sqrt{u^2(r)}$. This is assuming that in all cases r is much less than L (the length scale of the main flow). Dimensional analysis leads to:

$$u^2(r) = c_1(\epsilon r)^{2/3} \quad \eta \ll r \ll L \quad (5-6)$$

$$u^2(r) = c_2(\epsilon \mu / \rho) r^2 \quad r \ll \eta \ll L \quad (5-7)$$

The calculation of the microscale Reynolds number and Weber

number are shown below (from Shinnar and Church (68)). Substitutions for ϵ in terms of N (impellor speed) and D (impellor diameter) are made according to equation (5-2).

For $L \gg r \gg \eta$ (inertial subrange)

$$We = \frac{u^2(r) \rho r}{\mu} = \frac{c_1^{1/2} \epsilon^{2/3} r^{5/3}}{\mu} = \frac{K_1 N^2 D^{4/3} r^{5/3} \rho}{\mu} \quad (5-8)$$

$$Re = \frac{\rho u^2(r) r}{\mu} = \frac{c_1^{1/2} \rho \epsilon^{1/3} r^{4/3}}{\mu} = \frac{K_1^{1/2} \rho N D^{2/3} r^{4/3}}{\mu} \quad (5-9)$$

For $r \ll \eta \ll L$ (viscous subrange)

$$We = \frac{c_2 \rho \epsilon r^3}{\mu \sigma} = \frac{K_2 N^3 D^2 r^3}{\mu \sigma} \quad (5-10)$$

$$Re = \frac{c_2^{1/2} \rho \epsilon^{1/4} r^2}{\mu} = \frac{K_2^{1/2} \rho N^{3/2} D r^2}{\mu} \quad (5-11)$$

Most viscous dissipation of energy occurs within eddies whose Reynolds number is less than 1. Thus, from the expression for Re in the viscous subrange above:

$$\eta = \left[\frac{\mu^3}{\rho^3 \epsilon} \right]^{1/4} \quad (c_2^{1/4} \approx 1) \quad (5-12)$$

Howell et al (40) have developed an analogy between Kolmogoroff's theory of locally isotropic turbulence and the familiar relations for the drag coefficient of a solid sphere submerged in a stream.

5.1.4 The Apparent Viscosity of a Dispersion

Kolmogoroff's theory of local isotropy as outlined above was developed with a homogeneous medium in mind. In the case of liquid-liquid dispersions some consideration must be made for the presence of a second phase and its effect on turbulence.

Extensive work has been done on the determination of the apparent viscosity, μ_m , of emulsions, for which dispersed phase fractions, ϕ_d , vary from less than 0.01 to greater than 0.80. Becher (8) and Sherman (67) have reviewed this work in detail. A number of factors affect the apparent viscosity of a dispersion, including the viscosities of the component phases, the dispersed phase fraction, drop sizes, and the presence of surfactants or solids. Many correlations have been proposed. For very dilute dispersions Einstein's relation applies:

$$\mu_m / \mu_c = 1 + 2.5 \phi_d \quad (\phi_d < 0.01) \quad (5-13)$$

where μ_m is the mean dispersion viscosity,
 μ_c is the continuous phase viscosity, and
 ϕ_d is the dispersed phase volume fraction.

The relation chosen for this project ($\phi_d=0.4$) was that of Vermeulen et al (78):

$$\frac{\mu_m}{\mu_c} = \frac{1}{(1-\phi_d)} \left[1 + \frac{1.5\mu_d\phi_d}{\mu_d+\mu_c} \right] \quad (5-14)$$

The mean density of a dispersion is defined as:

$$\rho_m = \rho_d\phi_d + \rho_c(1-\phi_d) \quad (5-15)$$

5.2 EXPERIMENTAL WORK AND CALCULATIONS

5.2.1 Details - Equipment and Procedures

The mixer and impellor were chosen so as to be geometrically similar to those used by many other workers in the fields of mixing and drop studies. The mixer was, however, smaller than those typically used in laboratory studies (10 cm diameter as compared to perhaps 15 to 40 cm). The impellor was situated halfway between the top and the bottom of the mixer, instead of 1/3 off the bottom as is commonly the case in industrial practice. This arrangement permitted an organic phase continuous operation of the mixer. The impellor speed was calibrated with a stroboscope. Flowrates were controlled by the use of peristaltic pumps and were adjusted at the beginning of each run.

5.2.2 Results and Discussions

The volume fraction of the dispersed phase within the mixer is not necessarily the same as that of the feed, due to density differences of the phases. For example, if the mixer was not agitated, then the lighter phase would rise rapidly and exit the mixer. Most of the mixer volume would then be taken up by the heavier phase. A comparison between the two is presented in Figure 5.2, where the quotient of the mixer and the feed O/A ratios is plotted against

Mixer

- plexiglass
- 10cm ID x 10cm high
- fully enclosed
- four 10cm x 1cm x 0.3cm baffles
- feed into centre bottom
- overflow at centre top

Impellor

- stainless steel
- 6 flat blade disk turbine
- 4cm overall diameter
- 1cm x 0.8cm blades
- 3cm diameter disc

impeller at half
the mixer height

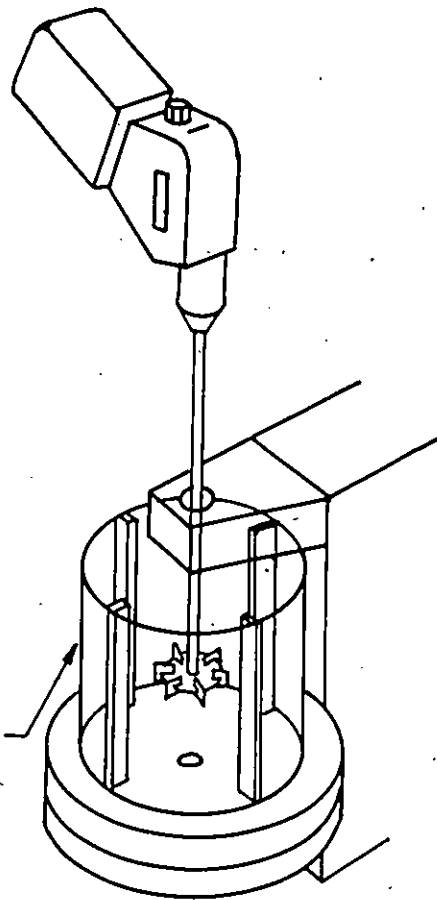
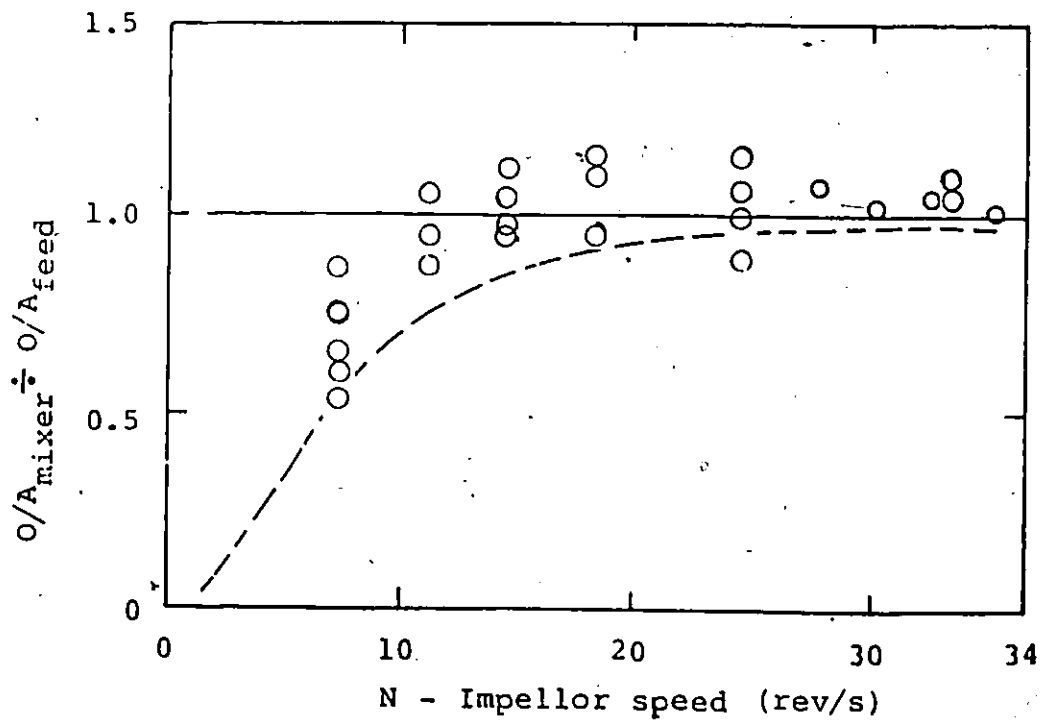


Figure 5.2 MIXER CONSTRUCTION

impellor speed. (The O/A ratio is the ratio of the organic to aqueous phase volumes.) The relation of Bouyatiotis and Thornton (11) is plotted alongside the experimental data in Figure 5.3. It has the same form as the experimental data, but it gave values that are slightly low. Errors in the measured O/A ratio in the mixer and errors in the flow rate measurements were found to be the principal causes of the scatter.

Physical properties of the extraction and stripping phases are shown in Table 5.1. Mean values of density and viscosity were calculated using Equations 5-14 and 5-15, assuming a constant dispersed phase holdup in the mixer of 0.40. A power number of 5.3 was assumed for this project, based on data for similar geometries summarized by Nienow (53) and Bates et al. (7). No measurements were made of the power input or of circulation times. Therefore estimates of the specific power, pumping, Re , We , and η are based on correlations in the literature for homogeneous, isotropic turbulence, and a constant power number. Results are summarized in Figures 5.4 and 5.5.

The impellor Reynolds number was normally less than 10^4 during this project, indicating that turbulence was not necessarily fully developed (Shinnar and Church (68)). The total power input to the mixing vessel that is predicted for an impellor speed of 33.3 revolutions per second is 17



--- correlation of Bouyatiotis and Thornton (11)

Figure 5.3 EFFECT OF THE IMPELLOR SPEED ON
THE O/A RATIO IN THE MIXER

Table 5.1 Physical Properties of the Dispersions

	Extraction			Stripping		
	ρ	μ	σ	ρ	μ	σ
organic phase	0.80	1.65		0.80	1.85	
aqueous phase	1.03	1.10		1.06	1.23	
mean value for the dispersion	0.89	3.4	11	0.90	3.5	11

μ = viscosity (g/cm/s * 10)

ρ = density (g/cm³)

σ = interfacial tension (dynes/cm)

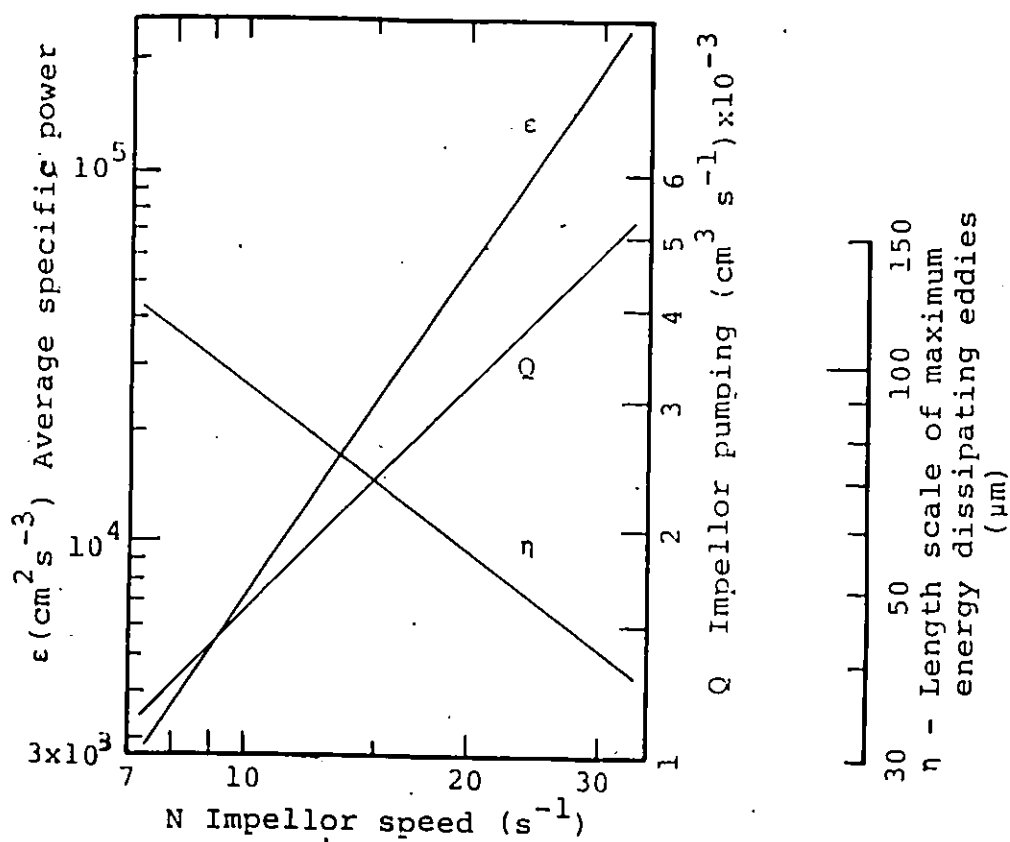
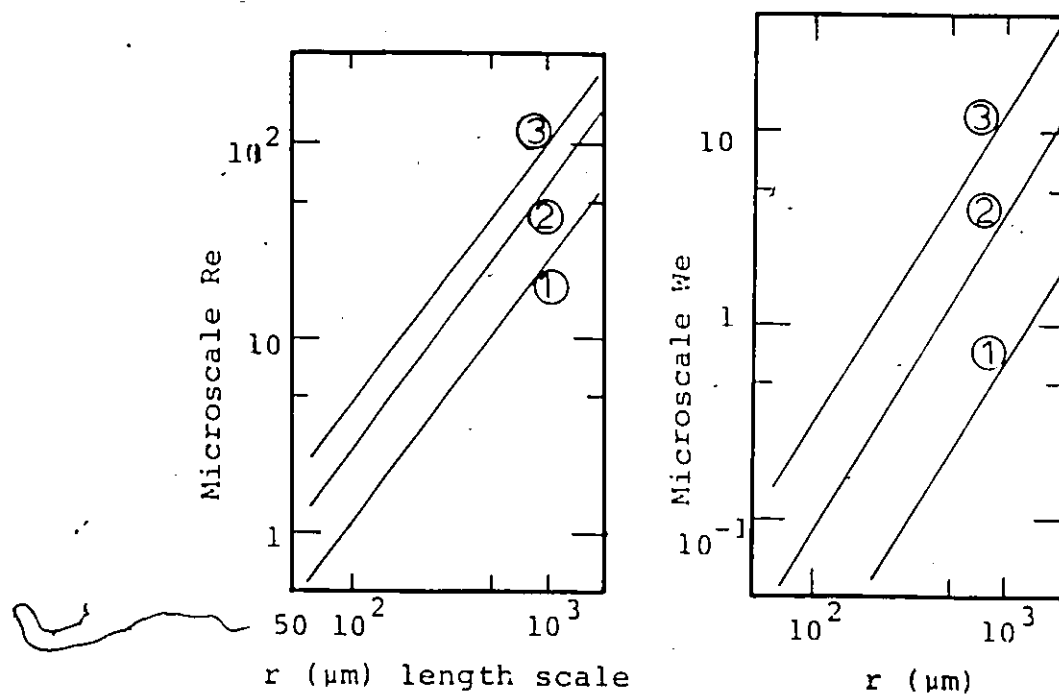


Figure 5.4 CALCULATED ESTIMATES OF
AGITATION AND PUMPING IN THE MIXER



impellor speed (rev/s)

① 7.5

② 18

③ 33

Figure 5.5 SHINNAR'S We AND We FOR THIS PROJECT

(Calculated assuming $r \gg \eta$)

Watts. This seems to be at least of a reasonable order of magnitude. The calculated impellor pumping rates in the mixer are surprisingly high, as they predict at higher impellor speeds that 5 to 6 times the mixer volume is pumped each second of operation. Maximum feed flowrates (to 44 cm^3/s) and the flow of fluid through the photography "window" (to 6 cm^3/s) only amount to 2% of the minimum impellor pumping rate. Therefore they are not expected to have had a significant influence on flow within the mixer.

5.3 CONCLUSIONS

The small scale mixer-settler that was developed for this project permitted several processes to be studied during the course of each run. Because the mixer was geometrically similar to standard mixing vessels, estimates could be made of the flow and mixing of the phases in the mixer.

6. DROP SIZE DISTRIBUTIONS IN AN AGITATED VESSEL

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6. DROP SIZE DISTRIBUTIONS IN AN AGITATED VESSEL

6.0 OBJECTIVES

As described in Section 1 of this report, the objectives of this section were:

To develop photographic techniques for the determination of drop size distributions in the mixer. The resulting data could then be compared to correlations in the literature, making use of the measured physical properties and estimates of turbulence.

Much research has been done to describe and model the processes of drop breakup and coalescence in agitated vessels. In this section a review is made of literature concerned with physical descriptions of drop breakup, maximum, minimum, and average drop sizes, and experimental techniques commonly used to study drop dispersions. The experimental determination of drop size distributions was of basic interest to this project. Drop sizes are also of importance in later sections of this report, especially with respect to mass transfer in the mixer. Data and calculations for this section are given in Appendix 6.

6.1 LITERATURE SURVEY

Turbulent conditions within a liquid-liquid system tend to break up one of the liquid phases into drops, which may then coalesce. The processes of dispersion and coalescence are affected by the physical properties of the phases and the intensity of the turbulence. Current understanding of these processes is summarized in the following sections.

6.1.1 The Maximum Stable Drop Size in Locally Isotropic Turbulence

Several important processes of the dispersion of one phase in another are illustrated in Figure 6.1. Within a mixing vessel it is likely that the dispersed phase is broken up by a combination of the illustrated mechanisms. Different mechanisms would apply to different stages in the breakup process. Several detailed analysis of whether a given, well defined flow condition will result in interfacial instabilities and the dispersion of one phase into the other are described by Gopal (see Sherman (67p23)).

The stresses affecting drop deformation in locally isotropic turbulence are listed below. The expressions are only approximations that are based on simple mechanical models as explained by Arai et al.(1) and Howell et al.(35).

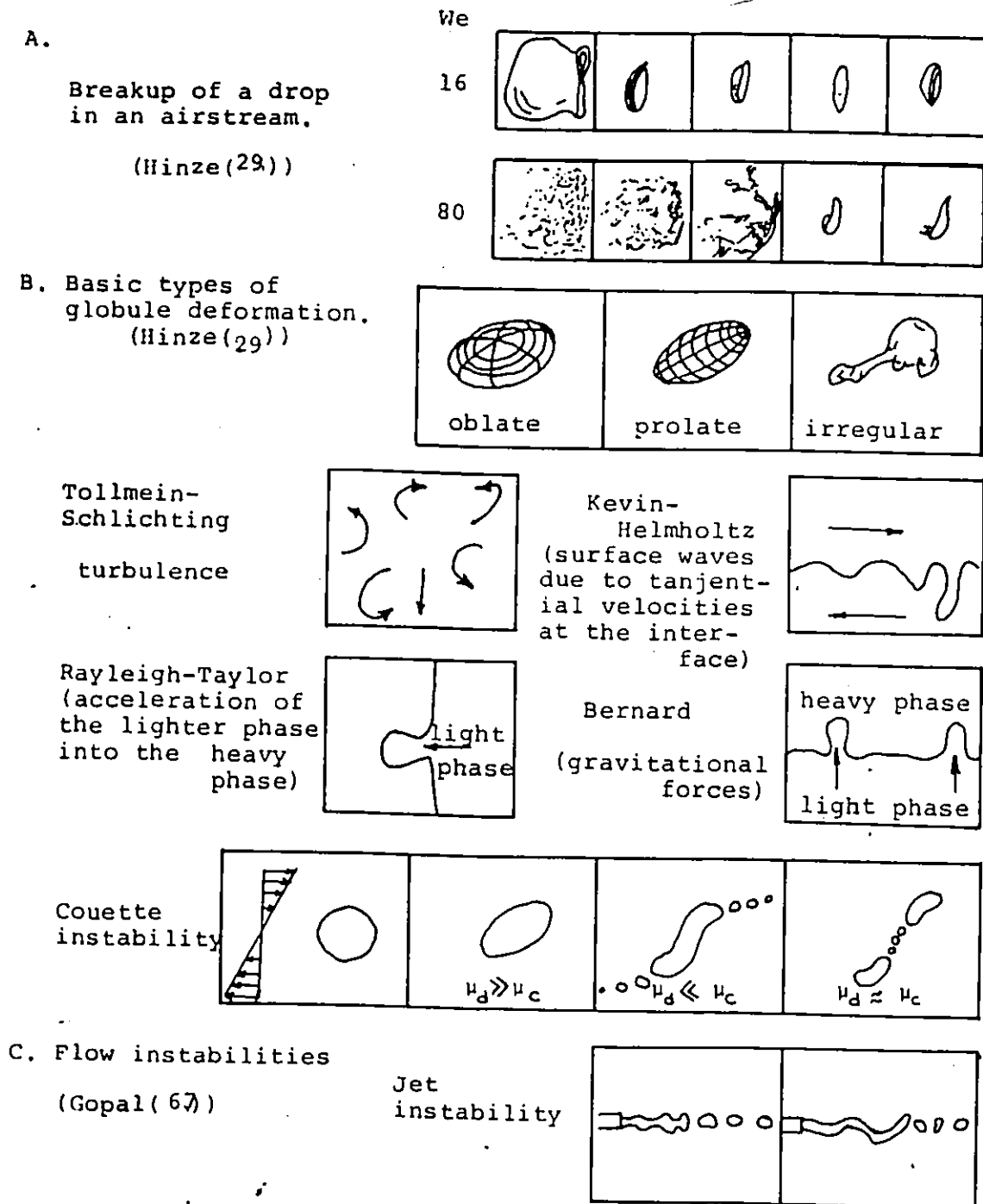


Figure 6.1 ILLUSTRATION OF PHASE DISPERSION PROCESS

As shown below, the relations assume that the drops are much larger than ξ , the length scale of maximum energy dissipating eddies (equation 5-12).

$$\tau_{pe} = \text{external inertial stresses} \propto \rho u^2(d) \quad (6-1)$$

$$\tau_{\sigma} = \text{interfacial stresses} \propto \sigma \theta / d \quad (6-2)$$

$$\tau_{\mu i} = \text{internal viscous stresses} \propto \mu_d \frac{d\theta}{dt} \quad (6-3)$$

$$\tau_{pi} = \text{internal inertial stresses} \propto \rho_c \frac{d^2\theta}{dt^2} \quad (6-4)$$

$$\text{where } \theta = \text{drop deformation} = \frac{L-d}{d} \quad (6-5)$$

L = major axis of ellipsoidal drop

d = undeformed diameter

For the purpose of illustrating the general principles of drop breakup, only the stresses τ_{pe} and τ_{σ} need be considered. Their ratio forms a dimensionless Weber group, which should be a constant for the maximum stable drop size in a dispersion according to this simplified dimensional analysis. This is equivalent to assuming that drop breakup occurs when the inertial stresses due to turbulence exceed

the surface stresses holding the drop together. Reexpressing in terms of the impellor speed and diameter using relations from section 5:

$$We_{critical} = \frac{\tau_{pe}}{\tau_{\sigma}} = \frac{K_1 N^2 D^{4/3} d^{5/3} \rho}{\sigma} = \text{constant} \quad (6-6)$$

$$d_{max} = 61 \rho^{-0.6} N^{-1.2} D^{-0.8} \sigma^{0.6} \quad (6-7)$$

An alternate form of the expression is:

$$\frac{d}{D} = \text{constant} * We_{imp}^{-0.6} \quad (6-8)$$

where

$$We_{imp} = \frac{\rho N^2 D^3}{\sigma} \quad \text{is the impellor Weber number.} \quad (6-9)$$

6.1.2 The Minimum Stable Drop Size in Locally Isotropic Turbulence

The processes affecting drop coalescence are discussed in detail in section 8. Shinnar and Church (68)

discussed the minimum drop size that would be stable in an agitated dispersion. Denoting the force of adhesion of two drops of unit diameter separated by a distance h as $A(h)$, they reasoned that in order to prevent coalescence the kinetic energy of the drops would have to be greater than the energy of adhesion between them.

$$\text{kinetic energy} \propto r^3 \rho_d u^2(d) = \rho_d \epsilon^{2/3} d^{5/3} \quad (6-10)$$

$$\text{adhesion energy} \propto d * A(h_o) \quad (6-11)$$

where h_o = separation distance between drops at which point coalescence occurs

For conditions of the minimum stable drop size (using Equation 5-6):

$$\frac{\text{kinetic energy}}{\text{adhesion energy}} \propto \left[d * \frac{\epsilon^{1/4} \rho_d^{3/8}}{A(h_o)^{3/8}} \right]^{-3/8} = \text{constant} \quad (6-12)$$

For homogeneous turbulence in a mixing cell where it is assumed that $\epsilon_{\text{local}} = \epsilon_{\text{average}}$ (using Equation 5-2):

$$d_{\min} = \text{constant} * N^{-0.75} D^{-0.5} \rho^{-3/8} A(h_o)^{3/8} \quad (6-13)$$

If it is assumed that $A(h_o)$ is proportional to the interfacial tension, then:

$$d_{\min} = \text{constant} * \rho^{-3/8} N^{-0.75} D^{-0.5} \sigma^{3/8} \quad (6-14)$$

Note that the minimum stable drop diameter has the same dependency on the impellor speed as η , the length scale of the maximum energy dissipating eddies (combine equations 5-2 and 5-11).

6.1.3 The Sauter Mean Drop Diameter, d_{32}

It can be seen by comparing equations (6-7) and (6-14) that the maximum and minimum stable drop sizes in a dispersion are different functions of the impellor speed. As illustrated in Figure 6.2, at low impellor speeds there is a large range of stable drop sizes that are between the minimum stable drop size where coalescence occurs and the maximum stable drop size where breakup occurs. As the impellor speed increases this range decreases. Eventually no drops within the dispersion are stable. Coalescence, redispersion then affect the whole drop population. This effect is discussed by Shinnar (69).

The Sauter mean drop diameter, d_{32} , is defined in terms of the ratio of the total volume of the dispersed phase divided by its total surface area:

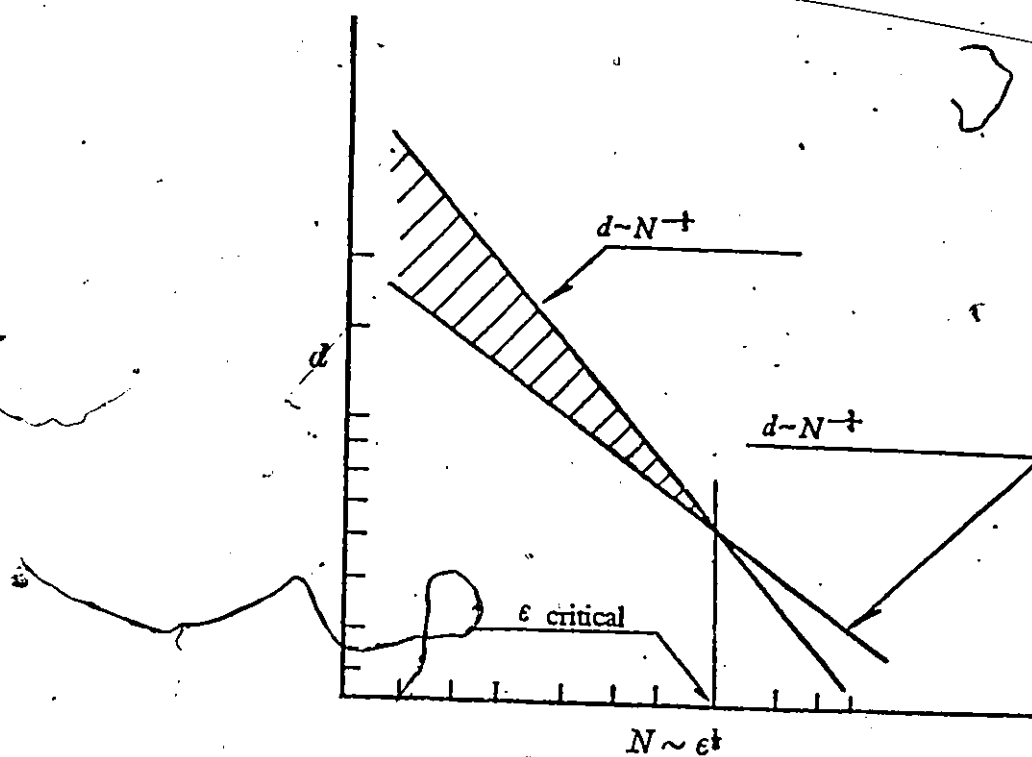


Figure 6.2 STABLE DROP SIZES IN AN AGITATED
DISPERSION (From Shinnar (69))

$$d_{32} = \frac{\sum d_i^3}{\sum d_i^2} = 6 * \frac{\text{total volume of the dispersion}}{\text{total area of the dispersion}} \quad (6-15)$$

In a dispersion one would expect the mean drop diameter to lie within the extremes of the maximum and the minimum stable drop sizes as illustrated in Figure 6.2. It would therefore be proportional to the impellor speed to the -0.75 to -1.2 power, depending on the relative importance of drop breakup and drop coalescence. In very dilute dispersions ($\phi < 0.01$), coalescence will be negligible as it is unlikely that drops will collide frequently enough to change the drop size distribution. In that case drop breakup will be controlling. Breakup may also be controlling in dispersions of higher to which surfactants have been added to inhibit coalescence (Shinnar (69)). Drop coalescence would become controlling in dispersions with high . . . These conclusions, obtained by dimensional reasoning, are supported by published results of experimental work (Tavlarides and Stamatoudis (75), Doulah (23), Giles et al. (25), Hinze (30), Kolarik and Pipkin (38), Mylněk and Resnick (47), Van Heuven and Beek (77), Vermeulen et al. (78), Röger et al. (61)). The relations for the mean drop diameter, d_{32} , are summarized in Table 6.1.

6.1.4 The Rates of Drop Breakup and Coalescence

Semi-theoretical models for the rates of drop breakup

Table 6.1 - Expressions for the Mean Drop Size
in a Dispersion

Controlling regime	range of ϕ	d_{32}	d_{32}/D
Breakup	$\phi < 0.01$	$\frac{c_1 \phi^{0.6}}{P_c^{0.6} N^{1.2} D^{0.8}}$	$c_1 We_{imp}^{-0.6}$
Breakup and Coalescence	$0.01 < \phi$ and $\phi < 0.1$		$c_1 (1 + c_2 \phi) We_{imp}^{-0.6}$
Coalescence	$0.3 < \phi$	$\frac{c_3 \phi^{3/8}}{P_c^{3/8} N^{3/4} D^{0.5}}$	$c_4 We_{imp}^{-3/8} D^{-11/8}$

$c_1 \sim 0.045$ to 0.06
 $c_2 \sim 2.5$ to 9

and drop coalescence have been proposed that reduce to the expressions for the maximum and minimum stable drop sizes as discussed in the previous section (Tavlarides and Stomatoudis (75)). Drop breakup models require estimates of the probable number of small drops formed during the breakup process and the drop size frequency distribution. Coalescence models require estimates of the frequency of collisions between drops and the probability that collisions between drops of different diameters will lead to a coalescence. At the present time these models must be considered to be very approximate, partially due to the difficulty of obtaining data concerning coalescence and breakup phenomena.

Experimentally determined correlations for coalescence frequencies are reviewed by Tavlarides and Stomatoudis (75). Investigators have related the coalescence frequencies to impellor speed, the dispersed phase volume fraction, and physical properties of the phases. The correlations vary widely in form and in the predicted effects of variables on the coalescence frequency.

6.1.5 Modelling Drop Dispersion Dynamics -

. Population Balance Equations

The population balance equation (PBE) modelling approach provides a framework for the analysis of dispersion

dynamics that may also be extended to mass transfer and heat transfer in dispersions. As applied to the interaction of drops in a dispersion, population balance techniques amount to a modelling of the rate of change of drop size distributions. There are three processes that affect the distributions;

1) Breakup- Drops of a particular size are created by the breakup of larger drops and are lost by their own breakup.

2) Coalescence- Drops of a particular size are created by coalescence of smaller drops, and are lost by coalescence with other drops.

3) Inflows and outflows from the control volume will in general involve the gain and loss of drops of a particular size.

An example of the analytical application of population balance equations (PBE) is provided by Bajpai et al. (3). They made a number of assumptions regarding the above processes that led to a simple expression for the drop size distribution. This has been plotted in Figure 6.3. To avoid the problems in finding analytical solutions to the PBE's, Monte Carlo simulation techniques have been used (Tavlarides and Stomatoudis(75)). Figure 6-4 illustrates the interesting

results obtained for equilibrium and transient modelling of drop size distributions from several workers.

6.1.6 The Form of the Drop Size Distributions

Several empirical relations for the form of the drop size distributions are shown in Figure 6.3 (from Mugele (55) and Bajpai and Ramkrishna (3)). Most of the relations will give linear plots on graph paper whose axis are appropriately scaled. However, in order to facilitate comparison they were plotted on the same graph using a special scaling of the axis. Figure 6.3 is a plot of $\log(f_N(d'))$ versus d' , where:

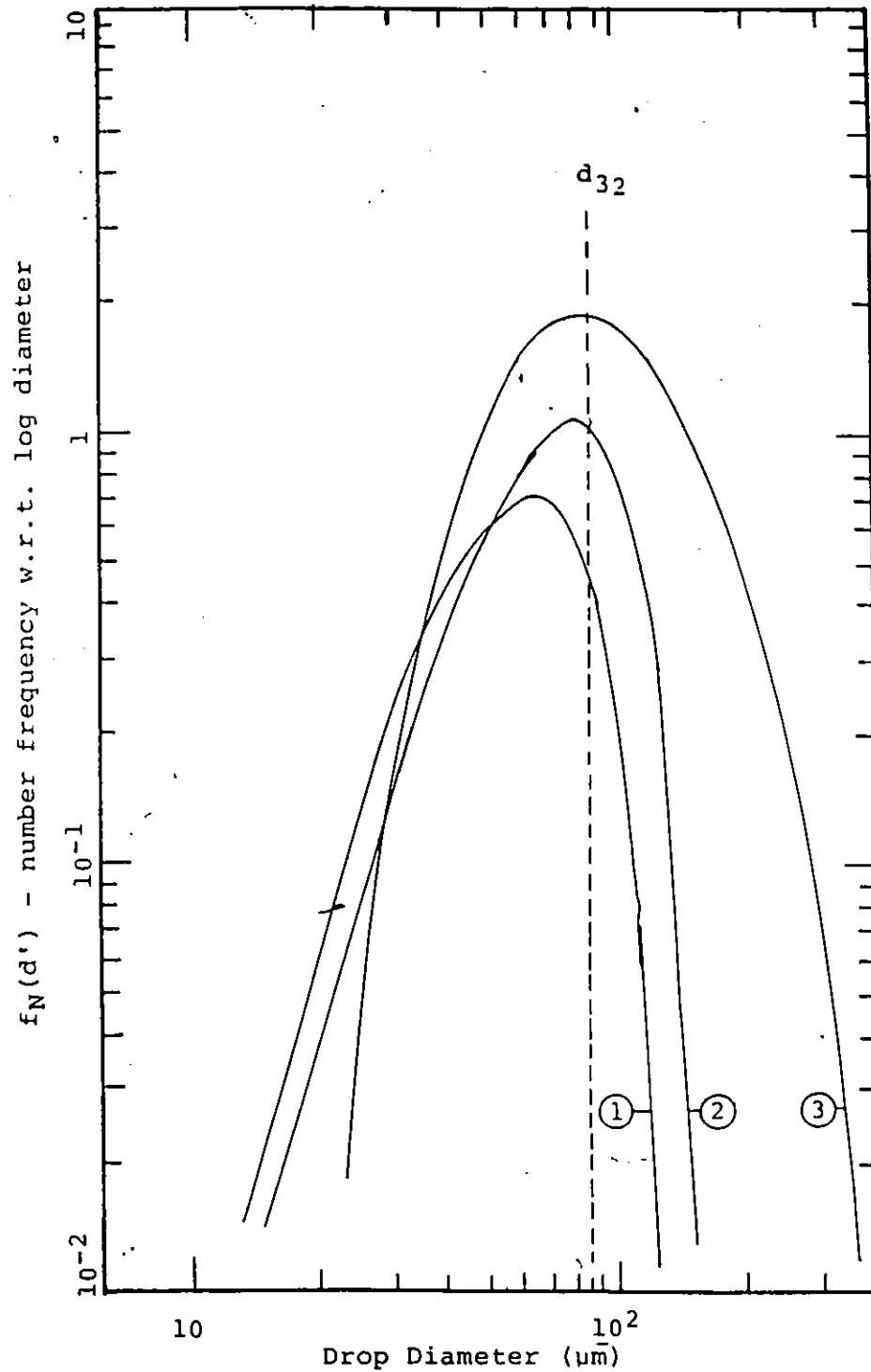
$$d = \text{drop diameter} \qquad d' = \log(d)$$

$$N = \text{number of drops} \qquad N_T = \text{total number of drops}$$

$$f_N(d') = \frac{1}{N_T} \frac{dN}{dd'} \qquad (6-16)$$

This format has the following advantages;

-There may be great differences between the smallest and largest drops present in the dispersion. A horizontal axis that is linear in d (as typically employed in the literature) tends to "hide" the smaller drops. These drops



- ① Mugele (49) ② Bajpai - Ramkrishna (3)
 ③ Gaussian in log diameter.

Figure 6.3 GENERAL CORRELATIONS FOR THE FORM OF DROP SIZE DISTRIBUTIONS

may be of importance to phase entrainment and crud formation.

-Because of the log scaling of the drop diameter, plots of volume or area frequency distributions will have exactly the same shape as the number frequency distributions shown (with a "compressed" log axis).

That there is some error in the transformation of the relations to this "standard" form can be seen from the fact that the integral of $f_N(d')$ with respect to d' does not equal 1.0 for all of the relations (as required of a probability density function). Bajpai and Ramkrishna's semi empirical relation is particularly interesting because it is based on a population balance model of drop distributions as discussed in the preceding section.

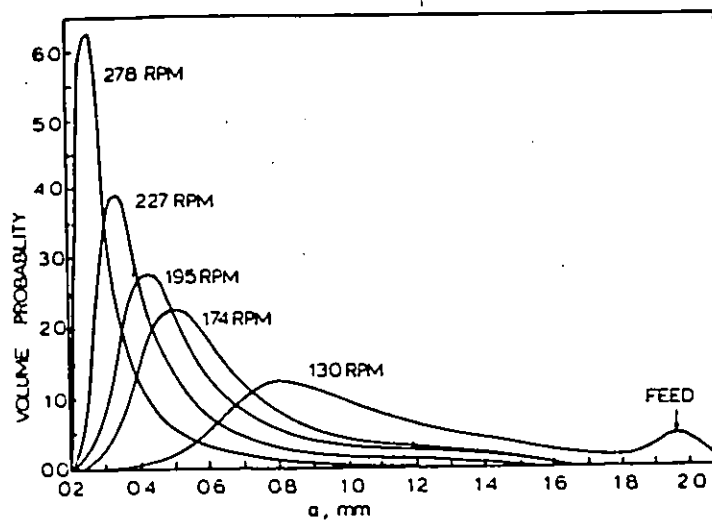
6.1.7 Further Factors Affecting Drop Distributions

The local specific power dissipation will vary from point to point within a mixing vessel. Significant differences of drop sizes at different points within the mixing vessel may (Mok and Treybal (48)) or may not (Coulagloglu and Tavlarides (17)) arise in practice. Coulagloglou suggested that a criteria for determining whether drop sizes will vary significantly would be the

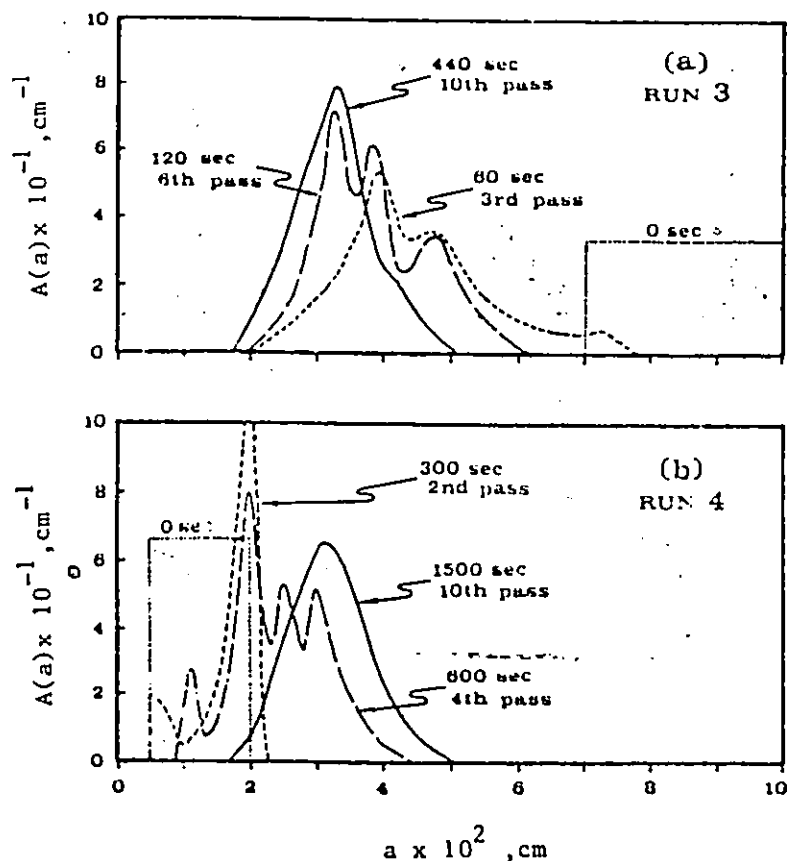
ratio of the coalescence frequency of the drops to the circulation frequency within the cell. The population balance equations may be applied if the dispersion flow within the mixing vessel and the coalescence and breakup phenomena are sufficiently well known.

Some researchers (Bouyatiotis and Thornton (11), Mok and Treybal (48)) have found that drop sizes do not differ between batch and continuous operation of a mixer. However, simulations by Ross et al. (62) as shown in Figure 6.4 predict an effect of the feed drop size distribution especially at lower impellor speeds. It might be the case that the importance of the feed drop size distribution depends on the feed flow rate, the internal fluid circulation, the residence time in the mixer, the coalescence frequency, and the mean drop diameter.

Relatively little work has been done at high dispersed phase fractions (see for example Kolarik and Pipkin (38), Rodger et al. (61)) for which the processes are more involved than for dilute dispersions. As the dispersed phase fraction increases the average distance between drops decreases dramatically. The structure and behaviour of thin continuous phase films may have some effect on the assumption of locally isotropic turbulence. At high dispersed phase fractions the relative importance of coalescence should increase.



Theoretical drop size distributions for breakage only for continuous-flow operation with uniform feed and $\psi = 0.5$ (Ross et al (62))



Evolution of the drop size probability density for two different initial drop size probability densities. (Hsia(37)).

Figure 6.4 POPULATION BALANCE MODELS OF DROP SIZE DISTRIBUTIONS.

Industrial dispersions will contain surfactants, solids, and involve mass transfer, all of which can significantly alter the surface phenomena that are important to drop breakup and coalescence. A discussion of these variables appears in section 8.

6.1.8 Techniques Used in the Study of Liquid-Liquid Dispersions

MEASUREMENT OF DROP SIZES

The basic technique of measuring drop sizes involves the taking of photomicrographs of the actual dispersion within the mixer. Fiber optics have been employed for this purpose (Park and Blair (54)) as well as conventional optical systems. Other techniques of measuring drop sizes are calibrated or verified by direct photography. Disadvantages of the technique include the tedium and effort required to obtain information, and the problems associated with taking high magnification photographs of dense, fast moving dispersions. There is also a tendency to underrepresent small drops when analysing such photographs.

To obtain better quality photographs and to be able to carefully study smaller drop sizes, it is possible to "freeze" drops in a sample withdrawn from a dispersion. This

may be accomplished by actually lowering the temperature for high melting point dispersed phases (Shinnar (69)), or by the addition of suitable surfactants or surfactant-forming monomers either to the whole dispersion or to the withdrawn sample. It is obvious that surfactants should preferentially be added to the withdrawn sample where possible, as their presence in the mixing vessel may alter the dispersion itself. Some success has been attained with this technique (Mylnek and Resnick (47)).

For dilute organic-in-aqueous dispersions a Coulter counter has been used to measure drop sizes (Sprow (73)).

The average drop diameter d_{32} may be related to the transmission of light in a dispersion (Calderbank (13)). This method has the advantage that results are immediately known and require less effort than photographic techniques once they are calibrated. The disadvantages are that the actual drop size distributions cannot be determined, and that the technique does not work well with phases that have a residual cloudiness after mixing.

The direct photography method was used in this project. With modern image analysis systems, the measurement of large numbers of drops is made much more rapid and reliable. Several innovations were also made to the photographic technique of drops in an agitated dispersion

with the hope of obtaining reliable data.

COALESCENCE FREQUENCIES

Direct high speed photography has not been successful in measuring drop coalescence frequencies, partly because frequencies are usually so low as to require an excessive amount of film to find even a few coalescence events. Indirect methods have therefore been used to determine average coalescence frequencies. These methods may be based on chemical reactions (Madden and Damerall (42)), dye tracing (Miller et al. (45)), and the change in light transmission with time after a change in impellor speed (Howarth (33)). These may all be used with appropriate models to estimate coalescence frequencies. A much simpler estimate of a lower bound of the coalescence frequency was developed by Schindler and Treybal (66) by taking into account the change in drop size from the impellor discharge region to the circulating region of a mixing vessel.

6.2 EXPERIMENTAL WORK DROP SIZE DISTRIBUTIONS

WITHIN THE MIXER

6.2.1 Equipment and Procedures

Drop size distributions were determined from photomicrographs of a stream continuously being pumped from the mixer, through a "window" and back into the mixer via the feed stream. The arrangement of the equipment is shown in Figure 6.5. The rectangular slit that formed the dispersion channel through the window was located behind one of the baffles at the mid height of the mixer. The window pumping rate was set to minimize the number of drops sticking to the window. Higher pumping rates were avoided to reduce photographic problems associated with high drop speeds.

Lighting was found to be particularly important when taking photographs. The best results were obtained by flashing light through the dispersion directly into the microscope objective. A light aperture was placed between the flash unit and the dispersion channel. Its diameter (2 to 3 mm) was just large enough to allow a full field of view through the camera at lower magnifications. This aided contrast and detail.

A binocular microscope (Wilde) with a monocular

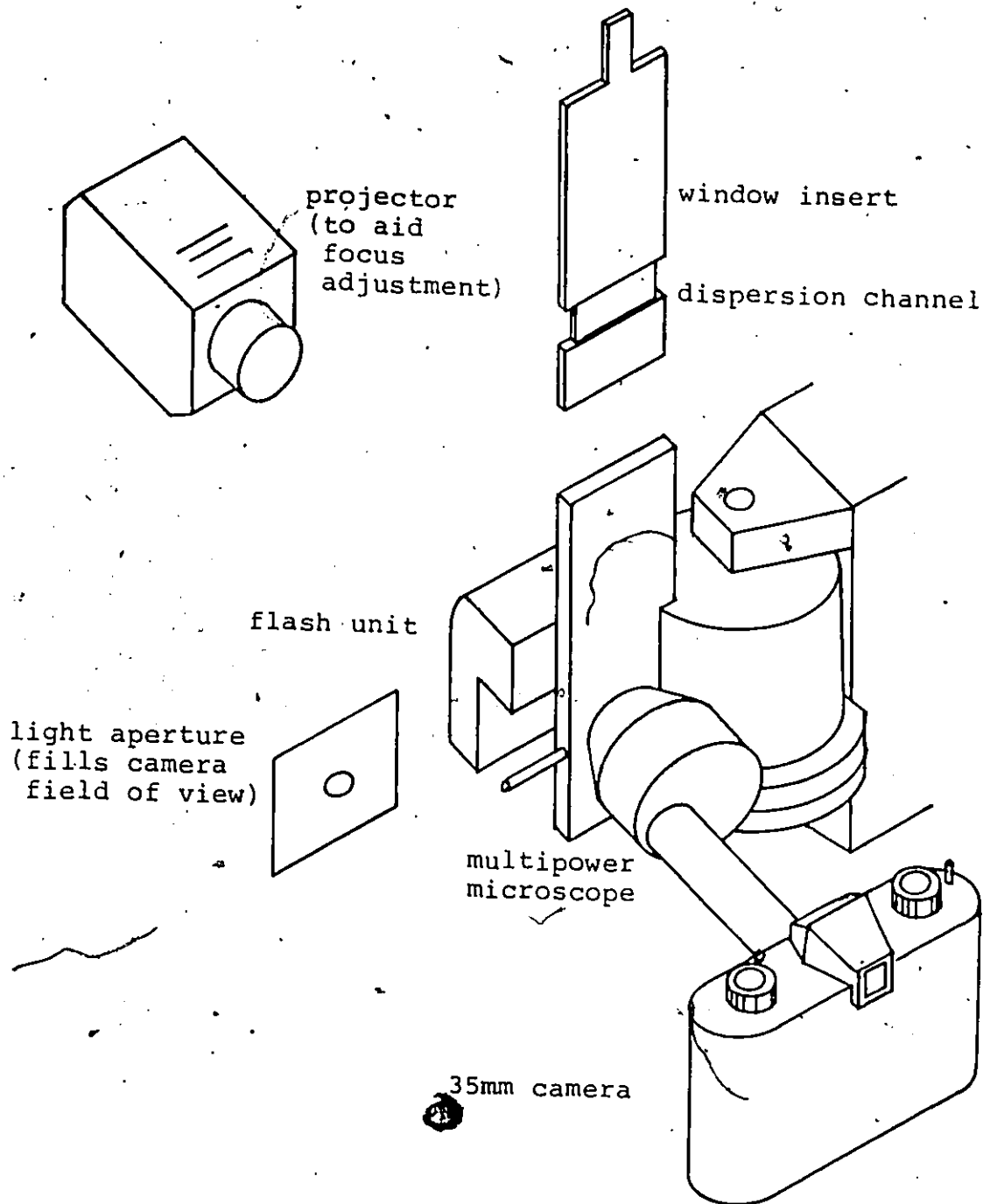


Figure 6.5 ARRANGEMENT OF PHOTOGRAPHIC EQUIPMENT

fitting for mounting a camera was used in conjunction with a Canon F-1 35 mm camera. Nominal magnifications on the microscope were 6X, 12X, 25X, 50X. Magnification onto the negative was about half the nominal value. Only the highest three magnifications were used. Kodak plus X Pan ASA black and white film was used.

Photographs were analysed by projecting the negatives onto an image analysis tablet that was part of a Zeiss micro computer based system (Video-Plan). Merely by encircling drops with a special pen, the area, diameter, and volume were immediately calculated. Data was easily treated with the system's classification and statistics programs. The error in drop diameters so measured is roughly estimated to be less than 20%. Better results could be expected by making enlarged prints of the negatives.

6.2.2 Data and Observations

Examples of drop photographs and pertinent information concerning the drop size distributions for each run is included in Appendix 6.

There was a tendency for large drops to hide smaller drops in a photograph of a dispersion, leading to an understatement of smaller drop sizes. In hydrometallurgical applications smaller drop sizes may be important because of

their potential impact on settler performance, phase entrainment, and crud formation. Drops smaller than about 25 micrometers could not be resolved by the optical system.

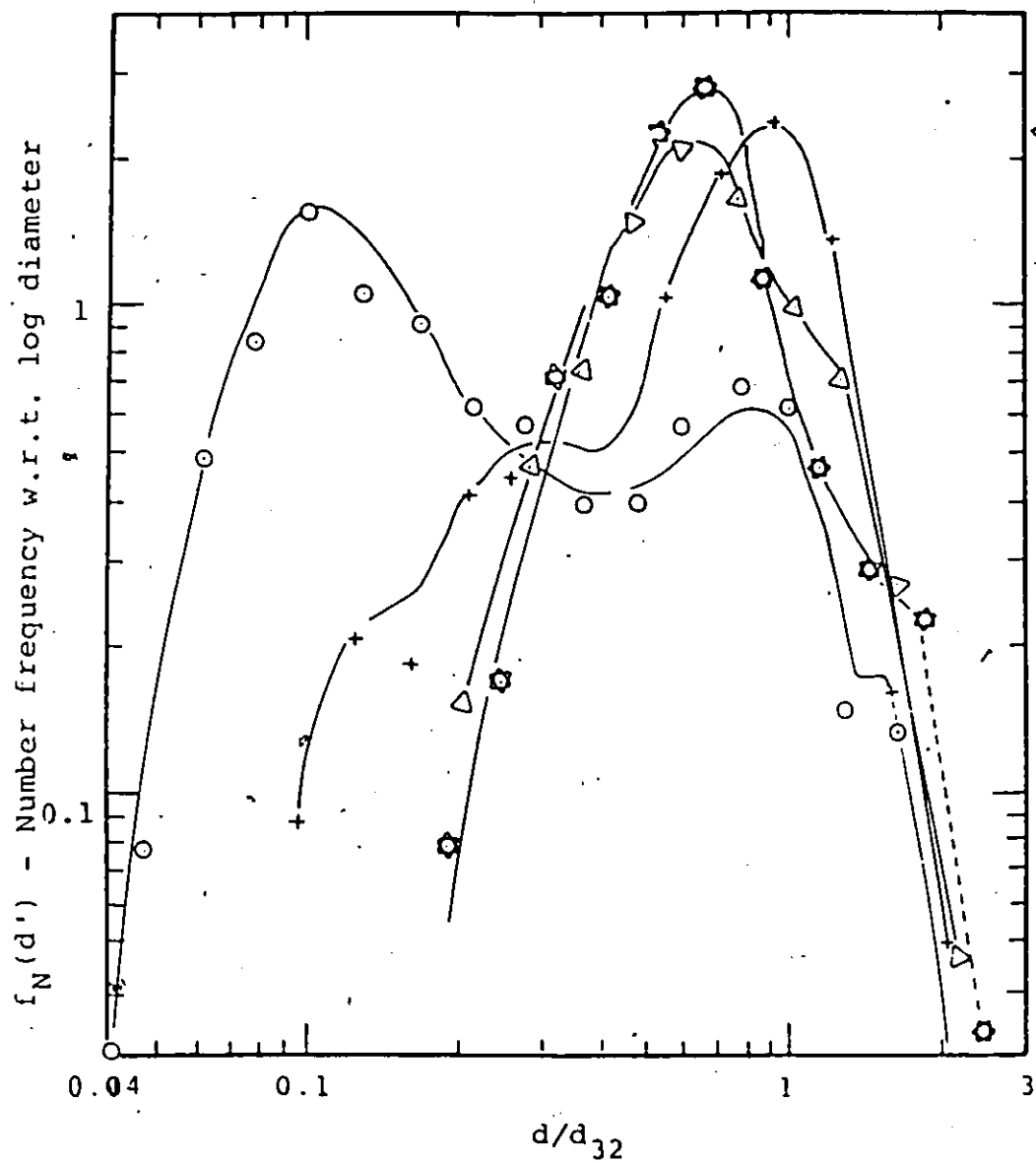
The taking of photographs through a "window" in this study led to the particular problem of drops sticking to the wall of the window where they coalesced and grew. It was difficult to distinguish drops stuck against the wall from drops within the dispersion, which could have led to serious errors in the frequencies of the large, important drops. Some correction was made by taking photographs a few seconds apart and eliminating drops that appeared on successive photographs. The nominal magnification of the microscope was adjusted to yield about 200 drops per photo. However, on some photographs only a very few drops could be distinguished. This was particularly noticeable at higher impellor speeds, and is partially explained by smaller drop sizes, severity of the lighting problems, and optical limitations of the equipment that was used. Data at impellor speeds above 18 to 20 revolutions per second are therefore considered to be less accurate. The quality of the distribution measurements is indicated in Table A.6.1 of Appendix A.6. Up to 400 drops were analysed for each mean diameter when good photographs were obtained of the dispersion. Normal practice (Kolarik and Pipkin (38), Mylnek and Resnick (47)) is to analyse from 600 to perhaps 1000 drops for each data point.

A variety of forms of drop distributions are illustrated in Figure 6.6, where the log diameter frequency distribution (as discussed in section 6.1.6) is plotted as a function of the log of a normalized drop diameter (the actual drop diameter divided by the Sauter mean diameter). Two of the distributions shown resemble the literature correlations in Figure 6.3. One of the others is definitely bimodal, and the last has an extended tail of smaller drop sizes.

In Figure 6.7 the average drop size is plotted as a function of the impellor speed for each of the series of runs. The lines on the graphs are for comparison with theoretical trends, and are explained in Section 6.2.3. Appendix A.6 contains diagrams of typical drop photograph analysis as carried out on the graphics tablet.

Photographs were taken after 10 and 20 residence times of operation. A comparison of the mean diameter at the two times is shown for four runs in Table A.6.2 in Appendix A.6. Three of the four runs indicated a decrease in mean diameter with operating time.

The organic phase remained hazy for a day or two after being contacted with the aqueous phase. Higher impellor speeds led to pronounced haziness of both phases. No phase inversion (reversal of phase continuity in the



Series		Impellor speed (s^{-1})	d_{32}
○	No extraction	25	125
+	Fast extraction	7.5	319
△	Stripping	7.5	504
⊗	Slow extraction	14.5	142

Figure 6.6 SELECTED EXPERIMENTAL
DROP SIZE DISTRIBUTION

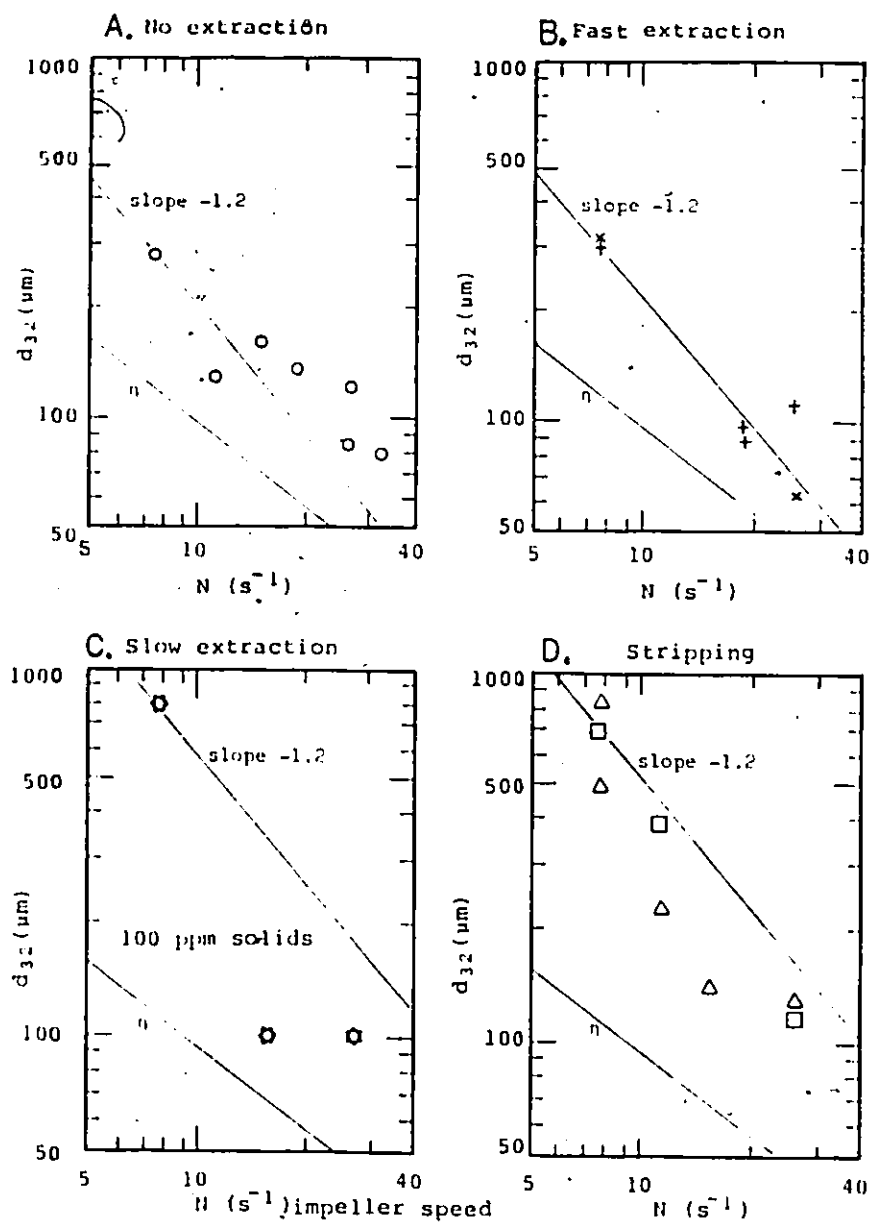


Figure 6.7 APPARENT MEAN DROP SIZE

mixer) was observed.

6.2.3 Calculations and Results

Lines of slope -1.2 and -0.75 are shown in Figure 6.7 as a comparison to the experimental data (see equations 6-7 and 6-15 for the functional relation between the impellor speed and the maximum and minimum stable drop sizes in a dispersion). The lower line (of slope -0.75) on the graphs shows the estimates of η (the size of the maximum energy dissipating eddies, or Kolmogoroff length), while the upper line has a slope of -1.2. The slope of the upper line corresponds to the trend of the maximum stable drop size in a dispersion (section 6.1.1). The slope of the lower line corresponds to the trend of the minimum stable drop size in a dispersion (section 6.1.2). Note that all the measured average drop sizes are larger than η .

6.2.4 Discussion

As seen from Figure 6.7 there is not a smooth decrease in the mean drop size with increasing impellor speed, as observed by other workers. These imprecisions are due to problems with the experimental technique that have already been discussed, that are especially severe in the present

work due to the wide range of impellor speeds that were employed and the high dispersed phase fraction. The photographic techniques were inadequate for impellor speeds greater than 20 rev/s, but consistently good photographs were obtained for speeds less than about 15 rev/s.

Comparison of Figures 6.6 and 6.3 shows that the experimental distributions sometimes showed significant fractions of smaller drop sizes that are not predicted by common correlations. This effect is noticeable at lower impellor speed and could be present but not accounted for at higher speeds due to the difficulty in distinguishing small drops. The distribution at higher speeds is fairly well represented by correlations of Bajpai and Ramkrishna, Bayer, and Mugele that appear in Figure 6.3. Bajpai's correlation is doubly attractive because of its' simple mathematical form and because it was derived from a population balance analysis.

Experimental bimodal distributions have been reported by several workers (Kolarik and Pipkin (38)), Brown and Pitt (12)) and are predicted at low impellor speeds by population balance equations (Ross et al. (62), Hsia and Tavlarides (37)). Their experimental work was for batch mixing. The ratio of the drop diameter of the upper mode to that of the lower mode was about 1.3 to 1.8. Kolarik suggested that this might be due to a coalescence-redispersion mechanism, for which

the ratio 1.8 indicates the breakup of drops approaching the maximum stable drop size into five or six smaller drops. The models of drop distributions, such as Figure 6.4 from Ross, assume that only two drops are formed by breakup, but they take into account continuous operation, so the upper mode corresponds to the drop size of the feed, and the lower mode perhaps corresponds to the mode of a batch operation. In this case from Ross, the ratio of upper mode to lower mode diameters is about 2.5. The bimodal distributions obtained in this experiment at lower impellor speeds yield a ratio of as much as 8 to 10. It is possible that the two modes correspond to the minimum and maximum stable drop sizes in the dispersion, resulting from the coalescence of small drops to the minimum stable drop diameter, and the breakup of large drops to the maximum stable drop diameter.



Data in Figure 6.7 show a definite if irregular decrease in mean drop size with increasing impellor speed. The mean drop sizes are larger than the calculated Kolmogoroff length scale, η , (lower line on the graphs). Because of the scatter in the data, no conclusion can be made as to whether the trend in drop sizes follows the predicted trend for the maximum stable drop size (the line of slope -1.2) or the predicted trend for the minimum stable drop size (the slope of the lower line). Because of the high dispersed phase fraction and consequent increase in coalescence in the dispersion, one might expect a trend that

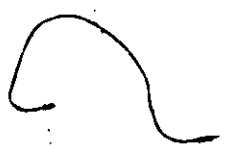
lies between the two extremes.

It is seen by comparing Figures 6.7a, b, c and d that the mean drop diameter varied from one series of runs to the next. Drops were largest in the slow extraction runs, followed by the stripping runs, then the fast extraction/no extraction runs. In comparing drop sizes for the different series of runs it is helpful to predict the effect that different physical properties could have on the results. A short and simple analysis was carried out in Section 3, where at most a 25% change in drop sizes might be expected due to differences in physical properties for the different series of runs. This cannot account for the observed difference of a factor of five in Figure 6.7 between the d_{32} values between the series. Possible explanations for the differences are the presence of solids, mass transfer, or possibly some form of contamination that affected surface properties. In Figures 6.7c and d the effects of solids and mass transfer cannot be entirely separated, as both were present in the slow extraction and the stripping series. However, series with a combination of solids and mass transfer may be compared to series little or none of both. At lower impeller speeds, drop sizes are much larger for series with mass transfer and solids.

6.3 CONCLUSIONS

The technique developed for photographing drops from the mixer allowed standard equipment for photomicrography to be used for this project. Conditions of lighting and the arrangement of the photographic equipment were easily modified and adapted. The mean drop size data from the experiments was not sufficiently accurate to test specific functional relationships between the mean drop size, physical properties, and turbulence in the mixer.

A



7. MASS TRANSFER

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7. MASS TRANSFER

7.0 OBJECTIVES

As described in Section 1 of this report, the objective of this section was:

To develop a phase sampling technique for the determination of mass transfer efficiencies in the mixer. The resulting data would then be studied in light of information and estimates of chemical equilibrium, physical properties, turbulence, and drop size distributions.

Uranium transfer between the aqueous and organic phases occurs within both the mixer and the settler. The majority of the transfer takes place within the mixer for the system being studied in this project. This section deals only with processes affecting uranium transfer in the mixer.

Two simple mass transfer models were developed as a basis of comparison to the experimental data for mass transfer during extraction. Predictions of the effect of different variables on mass transfer efficiencies can be made with the models. Data and calculations for this section are given in Appendix 7.

7.1 LITERATURE SURVEY

7.1.1 Stage Efficiency in the Mixer

The Murphree stage efficiency of uranium transfer is defined as;

$$E_{MS} = \frac{\text{amount of uranium actually transferred}}{\text{amount transferred at equilibrium}}$$

$$E_{MS} = \left[\frac{x - x_f}{x_e - x_f} \right] = \left[\frac{y - y_f}{y_e - y_f} \right] \quad (7-1)$$

where x and y denote the aqueous and organic concentrations of uranium and the subscripts f and e refer to feed and equilibrium concentrations respectively. Some of the factors that affect the stage efficiency are discussed in the following paragraphs.

Molecular diffusion and turbulence promote mixing within the bulk phases. This also ensures that all reactive complexes come in contact with interfaces where exchange of materials between phases may take place. Molecular diffusion for small drops is a rapid process because diffusional paths are very short and interfacial areas are large.

Physical properties at and near the interface will

affect processes such as the breakup/coalescence of drops and mixing close to the interface. These physical properties in turn are affected by the presence of surface active agents (such as the extractant molecules, phase modifier, solids, breakdown products of the organic materials in the leach, and contaminants). High rates of mass transfer across an interface have been reported to affect the local values of interfacial tension (through the Gibb's and Marangoni effects that are explained in section 8) and the local mass transfer coefficients (Bird, Stewart, and Lightfoot (10p656)).

The probability that a given fluid element will rest within the mixing vessel for a given length of time is described by the residence time distribution (RTD) for the operating conditions being considered. The RTD has an important effect on the stage efficiency, E. In the case where high efficiencies are desired, fluid elements that stay in the vessel for times much less than the average residence time can reduce the actual efficiency. The RTD of highly agitated vessels approaches the ideal relation (Levenspiel (40p260)):

$$\delta(t) = \frac{\exp^{-t/\tau}}{\tau} \quad (7-2)$$

where $\Phi(t)$ = fraction of fluid elements that are leaving the reactor whose residence time was between t and $t+dt$ within the reactor

τ = average residence time (space time)

Even though fluid "packages" within a stirred vessel may be very well mixed together the fluid within the individual packages is not necessarily well mixed, especially for high viscosity/low diffusivity systems. In the case of liquid-liquid extraction, this is of particular importance for the dispersed phase, for even in highly agitated vessels the small drops may act as rigid spheres and have very little internal circulation of fluid. It is sometimes assumed when modelling mass transfer for liquid-liquid systems that perfect mixing occurs in the continuous phase, but that mixing within the dispersed drops only occurs with drop interactions (coalescence and breakup). (Tavlarides and Stamatoudis (75)).

Drop size distributions will affect the completion of mass transfer. For example, the mass transfer out of very large drops is slower than for average sized drops, which will tend to reduce efficiencies.

7.1.2 Modelling Mass Transfer in the Mixer

Two simple models were considered for the prediction of the efficiency of uranium transfer within the mixer. Papers that are concerned with mass transfer in liquid-liquid dispersions include Curl (20), Miller et al. (45), Spielman and Levenspiel (72), and Flynn and Treybal (24), and Howell et al. (36). Mass transfer studies of uranium complexes that are especially interesting to this project include Murdoch and Pratt (50) and Horner et al. (31a). Literature covering mass transfer in liquid-liquid dispersions is reviewed by Tavlarides and Stomatoudis (75).

The following assumptions have the effect of reducing the models to a simple mass transfer process of a hypothetical uranium complex from one phase to the other. This would hopefully give some idea of the efficiency of uranium transfer that could be expected from simple mass transfer alone. A comparison with the actual results could then indicate that either the process is well represented by a simple mass transfer model, or that one of the neglected steps is important to the overall transfer process.

- 1) The dispersed phase forms uniform drops immediately upon entering the mixer and coalescence/dispersion effects are assumed to be negligible.

- 2) Any changes in bulk phase acid or extractant concentrations can be neglected.
- 3) The interfacial reactions, interfacial resistances, adsorption and desorption of complexes are assumed to be fast in relation to bulk phase mass transfer, so that the aqueous and organic species are in equilibrium at the interface.
- 4) Assume the material flux across the interface to be too low to affect mass transfer coefficients.
- 5) Assume that aqueous and organic components, other than the hypothetical uranyl complex, remain in their respective phases, and that the phases are immiscible.
- 6) Assume no volume changes during mass transfer.

MOLECULAR DIFFUSION MODEL

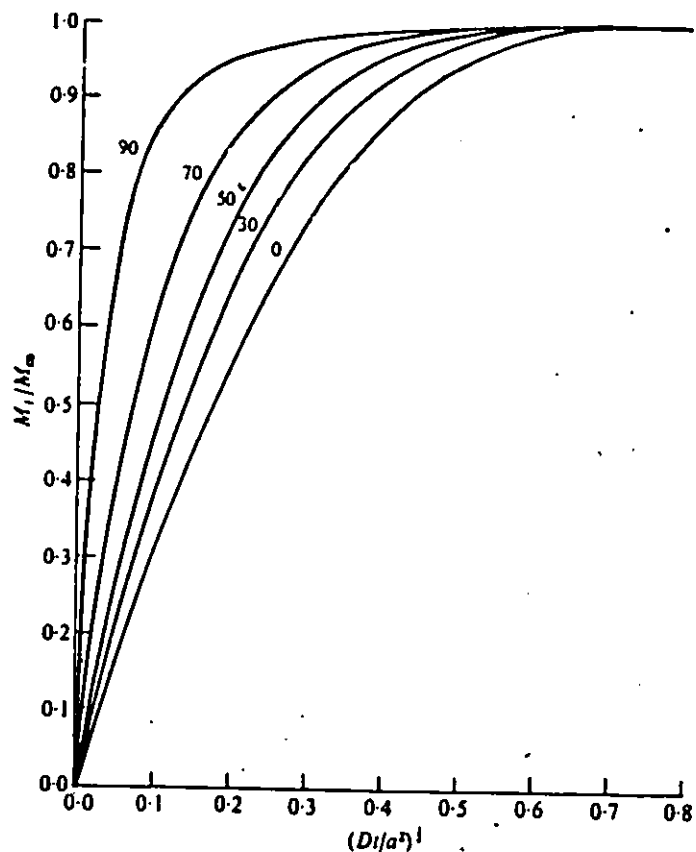
In this model, it is assumed that each drop is surrounded by a shell of continuous phase that rests with it for the duration of its stay in the mixer. The continuous phase shell is assumed to be completely mixed. Mass transfer within the drops is by molecular diffusion, and the residence time distribution is that of a well-mixed vessel.

(equation (7-2)).

The degree of completion of mass transfer for a drop resting a given time within the mixer is then described by the relationship in Figure 7.1, which is presented by Crank (18). This may be combined with the residence time distribution to give the overall efficiency:

$$E_{MS} = \int \bar{Q}(t)E(t)dt \quad (7-3)$$

Calculations of the Murphree stage efficiency, E , are summarized in Table 7.1. For details of the calculations refer to Appendix 7. An estimate of $9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used for the diffusivity of the aqueous uranium complex $\text{UO}_2(\text{SO}_4)_3$. The curve in Figure 7.1, for 100% transfer of uranium from the aqueous to the organic phase (that is labelled 0, referring to the percentage of material that is not transferred) was used in the calculations. This curve closely approximates the high extractions obtained in the experimental work.



Numbers on the curves refer to the percentage of material that is not transferred from one phase to the other at time $t = \infty$.

M_t - amount of solute transferred from a drop at time t

M_∞ - amount of solute transferred as t approaches infinity

D - diffusivity of the solute in the drop

a - drop radius

t - time

Figure 7.1 UPTAKE BY A SPHERE FROM A SOLUTION
OF LIMITED VOLUME (From Crank (18))

MASS TRANSFER COEFFICIENT MODEL

Mass transfer coefficients have been obtained for a number of systems, and may be useful for predicting coefficients in equipment similar to that used in the original studies. Correlations of mass transfer coefficients applicable to liquid-liquid extraction are reviewed by Perry (55p21-62), Hanson (27p386), and Glasser et al. (26). Two such studies for the continuous phase mass transfer coefficients are Harriot's (28) work on suspended solids and Mok and Treybal's results (48) for liquid-liquid systems, which is related to Harriot's work. These studies involved systems for which the interfacial concentration was known (negligible mass transfer in the dispersed phase and a constant interfacial concentration).

The calculation of the stage efficiency involved finding the bulk phase concentrations and average interfacial concentration that resulted in the appropriate overall mass transfer for the given stage efficiency. The approach resulted in the solution of four simultaneous equations which are listed below. Detailed explanations of the approach are given in Appendix A.7.

$$\begin{array}{ll} \text{continuous phase} & \text{Sh} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3} \quad (7-4) \\ \text{coefficient} & \end{array}$$

dispersed phase coefficient

$$k_d = \frac{-d}{6} \ln \left[\frac{3}{8} \beta_n^2 \exp \left[\frac{-\alpha_n 64 D d}{d^2} \right] \right] \quad (7-5)$$

interfacial aqueous concentration

$$x_{ao} = \frac{-k_y}{k_x} (1-x_{ao}) \left[\frac{g(x_{ao})-h(x_{ao})}{1-g(x_{ao})} \right] + x_{ao} \quad (7-6)$$

mean residence time

$$\tau = \frac{c_{aq} (1-x_{ao})}{S k_x (1+O/A)} \left[\frac{x_{ai}-x_{ab}}{x_{ao}-x_{ab}} \right] \quad (7-7)$$

The mass transfer coefficient approach involves many assumptions and judgements. It is an approach that does not readily incorporate factors such as the residence time distribution.

PREDICTIONS OF THE MASS TRANSFER MODELS

The stage efficiency predictions of the two models for the fast and the slow extraction runs are summarized in Table 7.1. They are also shown alongside experimental data in Figure 7.4. The first surprising thing to note about the results is that two very different approaches yielded similar results. Both models predict that stage efficiencies for the fast extraction runs would be greater than for the slow extraction runs, largely because of the difference in the assumed drop sizes. The mass transfer coefficient analysis predicts that the aqueous (dispersed) phase

Table 7.1 Predicted Mass Transfer Efficiencies
Diffusional Model and Mass Transfer Coefficient Model

Impellor Speed (s ⁻¹)	Fast Extract.			Slow Extract.		
	d ₃₂ (μm)	E _D (%)	E _{MT} (%)	d ₃₂ (μm)	E _D (%)	E _{MT} (%)
7.5	300	97.1%	97.5	850	83.1%	81.0
8	285	97.3	97.8	800	84.6	83.1
9	245	97.9	98.3	640	89.3	89.2
10	225	98.1	98.6	540	92.0	91.6
12	175	98.6	99.1	410	95.0	95.0
15	135	98.9	99.5	275	97.4	97.6
20	97	99.0	99.7	170	98.7	99.0
25	74	99.0	99.8	120	98.9	99.5

E_D - stage efficiency predicted by the diffusional model
E_{MT} - stage efficiency predicted by the mass transfer model
d₃₂ - assumed average drop sizes for the two

resistance is controlling because of the great preference of the uranyl species for the organic phase. For much higher aqueous phase concentrations of uranium the continuous phase resistance would become more important as the equilibrium curve "flattens out" (see Figure 3.4).

7.2 EXPERIMENTAL WORK - URANIUM TRANSFER

7.2.1 Equipment and Procedures

Sampling of the aqueous and organic phases within the mixer was carried out by the use of phase preferentially wetted filter paper supported on porous teflon discs. The discs were installed flush with the mixer wall in the upper half of the mixing vessel, and permitted the independent sampling of each phase directly from the mixer dispersion. Each sampling unit was connected to a vacuum system that allowed the controlled withdrawal of fluid. The arrangement of the mixer sampling system is shown in Figure 7.2.

Five to ten 10 minutes of sampling time was required to get a 50 ml. sample of each phase, allowing only one sample to be taken per run. With excessive vacuum or incorrect selection or installation of the filter papers, entrainment of the unwanted phase would occur in the phase samples. This was especially true of the aqueous phase sampler, possibly because ordinary filter paper was used instead of a strongly aqueous wetted material. The filter papers were changed frequently between runs, especially for stripping runs, when precipitates collected on the aqueous paper, or for runs which contained suspended solids.

An important question is how representative the

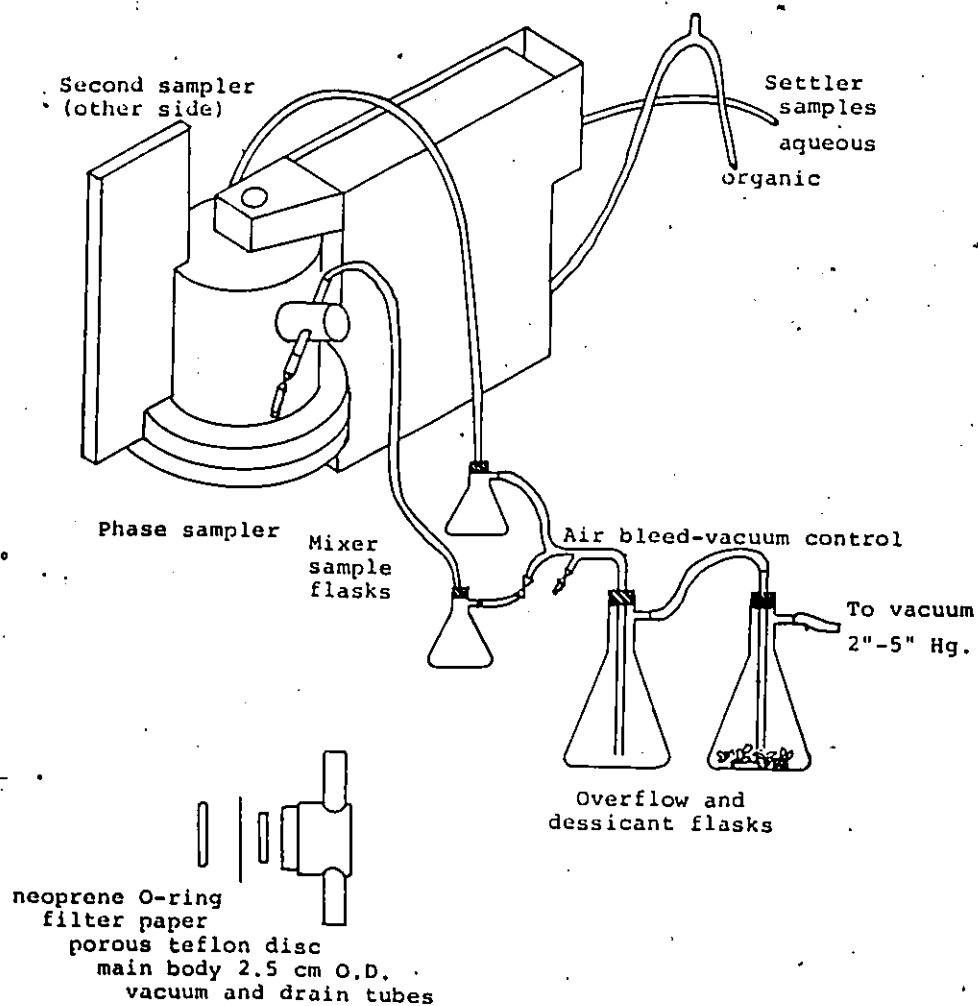


Figure 7.2 PHASE SAMPLING EQUIPMENT

samples were of the contents of the mixer. No tests were performed to check this (eg. changing the position of the phase samplers, varying the sampling conditions, etc.). Due to the good agitation within the mixing vessel it is probable that fluid coming into contact with the samplers was fairly representative of the mixer contents. The mechanism of phase withdrawal does allow for some error, especially for the dispersed phase. Figure 7.3 illustrates that as a droplet breaks and spreads onto the aqueous wet filter paper, it would be well contacted with the surrounding organic phase, giving rise to a certain amount of mass transfer that may be significant for large drops. The drop contents would also rest on the filter paper for some time before passing to the other side of the paper. For this experiment, assuming an aqueous film thickness of 50 to 250 μm (0.05 to 0.25 mm), a 50 ml phase sample taken in 5 minutes, and a 3.8 cm^2 filter paper area, the mean residence time is 0.12 to 0.58 seconds. This is small in comparison to the average residence time in the mixer (60 seconds).

Phase samples were also taken at the outlets of the settler. For selected runs portions of the settler samples were mixed together at the feed O/A ratio 1.5:1 to allow a double check of the equilibrium endpoint of the extraction.

All phase samples were filtered in order to remove traces of the unwanted phase (eg. organic films in aqueous

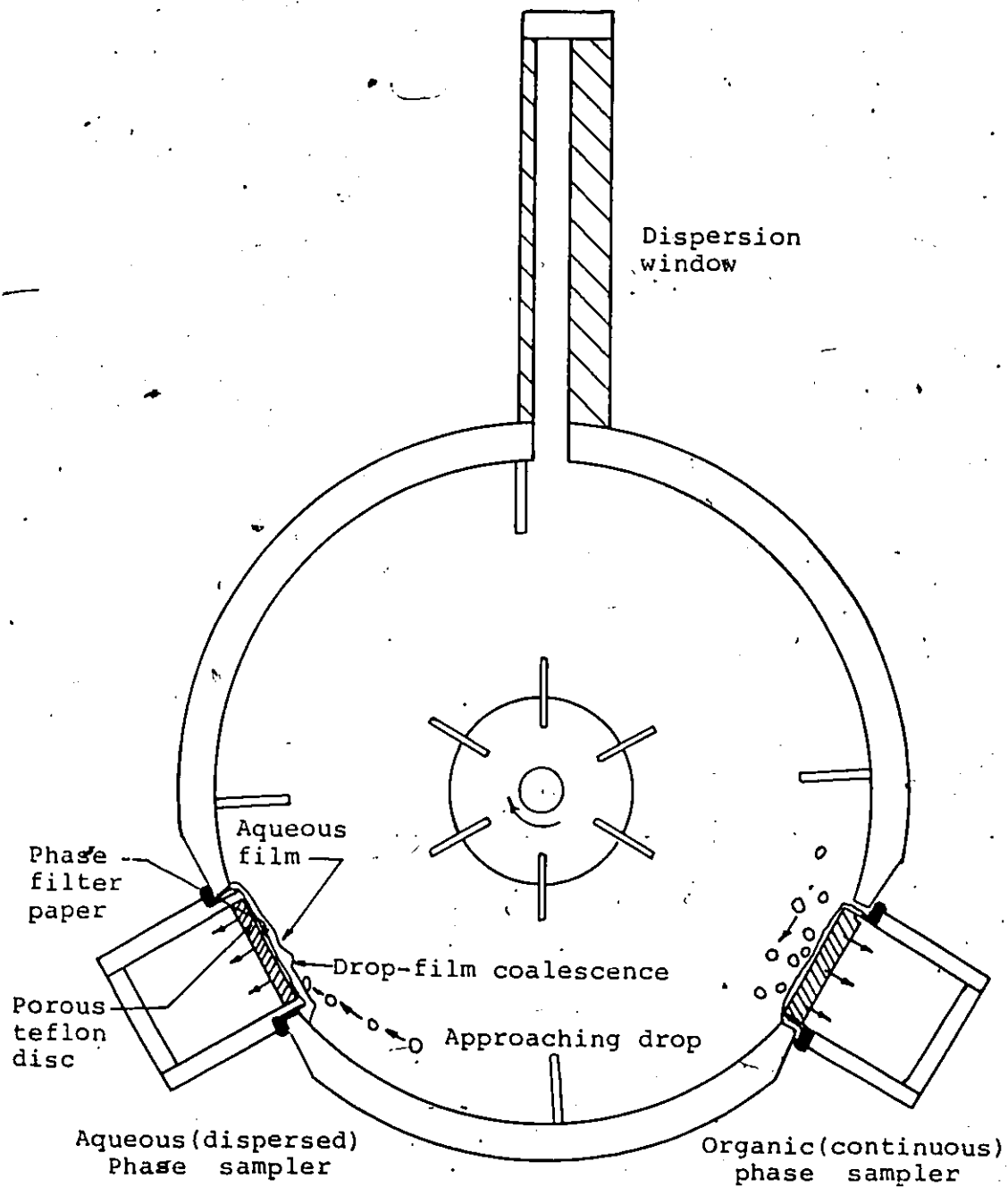


Figure 7.3 DETAILS OF THE PHASE SAMPLING FROM THE MIXER

phase samples). They were then analysed for uranium concentration at CANMET's analytical laboratory by an X-ray fluorescence technique. The analytical technique should give results accurate to 5%, but larger errors may result from sample preparation (dilutions error and sample withdrawal error). (See Snell and Ettre (71) for details about the uranium analysis.)

7.2.2 Data and Observations

Tables A.7.1 to A.7.3 in Appendix A.7 summarize the measured uranium concentrations for both phases in the mixer, in the settler, and for equilibrium. Consistency of the results was checked by mass balance calculations, which indicated errors of up to 39% in an extreme case and 11% on average.

To a very limited extent, the completion of uranium transfer could be followed visually during the runs by noting the colour of the two phases in the settler. Uranium concentrations above 1 g/L gave a yellow colour to a phase. Only runs carried out at the lowest impeller speed showed signs of incomplete mass transfer, and then only for the cases for the cases of stripping and "slow" extraction.

When the initial aqueous strip phase and the loaded organic phase first come into contact, there was a temporary formation of precipitate due to the high initial aqueous phase pH. As stripping progressed the pH was lowered by the release of sulfuric acid into the aqueous phase, redissolving the uranium. Experimentally this was observed when the aqueous and organic phases were initially introduced to the mixer prior to starting a run. Also, in the stripping run with the slowest impellor speed and shortest residence time, aqueous drops coalescing with the separated aqueous phase in the settler gave small "bursts" of precipitate which subsequently tended to dissolve. The formation of a certain amount of solids in the dispersion during stripping could have affected drop coalescence and therefore mass transfer. (See section 9 for a more complete discussion of the effect of solids on coalescence.)

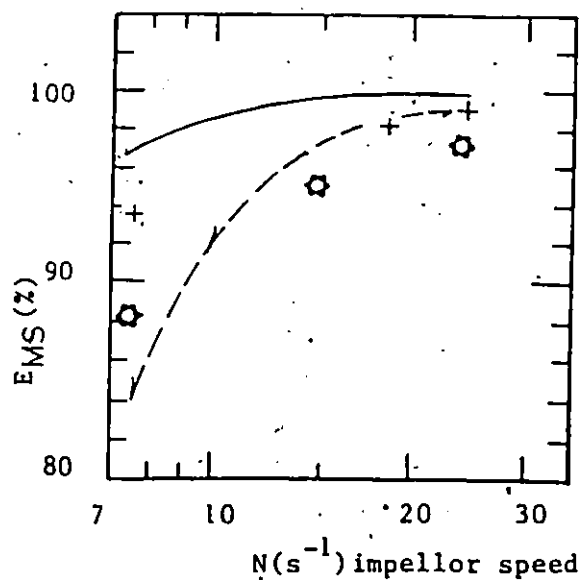
7.2.3 Calculations and Results

The equilibrium uranium loading in the organic phase was 0.9 g/L for the fast extraction series and 3.8 g/L for the slow extraction series. When compared with the maximum uranium loading in the organic of 4.4 g/L this means that the degree of organic loading was 20% and 86% for the fast and slow series respectively. Calculated values of the Murphree stage efficiency of uranium transfer within the

mixer are shown in Figure 7.4. Also shown are efficiencies calculated for the extraction runs based on the simple mass transfer models that are summarized in Table 7.1. It is immediately apparent from Figure 7.4 that uranium transfer was substantially ($>85\%$) completed within the mixer for all runs. Data from the phase samples from the settler indicated that mass transfer was essentially completed in the settler dispersion band (Tables A.7.2 and A.7.3).

Figure 7.4 indicates a trend of increasing efficiency with increasing impellor speed for the extraction series. Increasing solids content in the feed also appears to have resulted in increased efficiencies, possibly as a result of improved droplet coalescence which more than compensated for the larger drop sizes associated with the higher solids concentrations.

The calculated results for mass transfer in the case of stripping were in the range of 88 to 110% efficiency, (there was obviously a fair amount of error in the results) indicating high efficiencies even at low residence times. The error in the stripping results was greater than for the extraction runs (see Table A.7.6 in appendix A.7). It is thought that this was largely due to pH control problems as discussed in section 3.3.

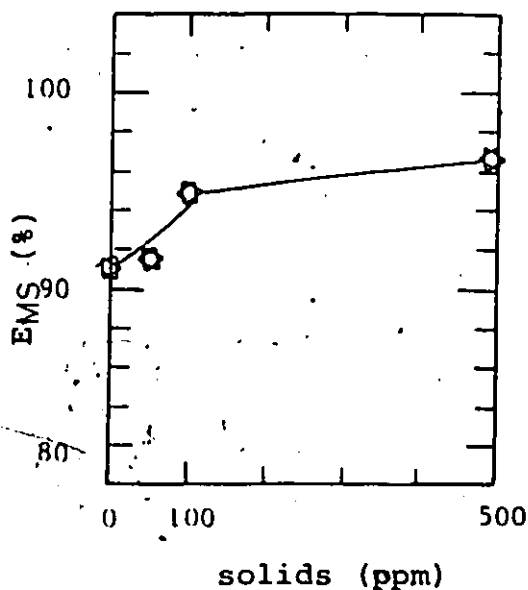


simple mass transfer
model predictions

— fast extraction

--- slow extraction

(100 ppm solids in
slow extraction runs)



Data

+ fast extraction

☆ slow extraction

(14.5 rev/s impeller
speed)

Figure 7.4 MURPHREE STAGE EFFICIENCIES
FOR THE MIXER

7.2.4 Discussion

The fast extraction runs had a preacidified organic phase, and therefore extraction simply involved anion exchange between aqueous uranyl complexes and extractant-acid complexes in the organic phase. The "slow" extraction runs required that sulfuric acid first be taken up by the extractant molecules before the aqueous uranium could be extracted. Slow extraction runs involved loading the extractant to a much higher degree than the fast extraction runs (86 vs 20%). There were differences between drop sizes for the different sets of runs. Due to the larger drop sizes, the higher degree of uranium loading in the organic phase, and a more involved extraction process one would expect the "slow" extraction runs to have a lower stage efficiency, E , than the fast extraction runs. This was the case, as illustrated in Figure 7.4.

The rapidity of the extraction and stripping processes were well illustrated by the results. This presented problems of obtaining good data from which the mechanisms of extraction could be evaluated. Ryon and Lowrie (65) found that efficiencies were high even at residence times of only 5 seconds (For extraction at impellor speeds above 300 rpm).

The two mass transfer models for uranium transfer

gave similar predictions of the stage efficiency, E. With both models it is the drop size that largely determines E. The drop size in turn is strongly influenced by the impeller speed and the presence of solids. The diffusional model was the simpler of the two models. It was also a more flexible approach to analysing mass transfer, being able to easily incorporate residence time distributions. A comparison of experimental results and the simple models of mass transfer does not clearly indicate whether the stage efficiencies are appreciably affected by factors such as the interfacial reactions, adsorption and desorption of surfactants, or the depletion of extractant.

7.3 CONCLUSION

The phase sampling technique that was developed for this project was useful for determining the analysis of each phase in the highly agitated mixer. The filter papers were easily changed when dirty or torn, and allowed samples to be withdrawn over the course of a run in quantities sufficient for analytical purposes. Mass transfer efficiencies for the mixer were found to be greater than 85% for all of the runs. High stage efficiencies were thus obtained over the range of conditions used in this project.



8. SETTLER DISPERSION BAND HEIGHT AND PHASE ENTRAINMENT

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8. SETTLER DISPERSION BAND HEIGHT AND PHASE ENTRAINMENT

8.0 OBJECTIVES

As described in Section 1 of this report, the objective of this section was:

To observe the behaviour of the dispersion band height and phase entrainment in the settler during the course of the runs.

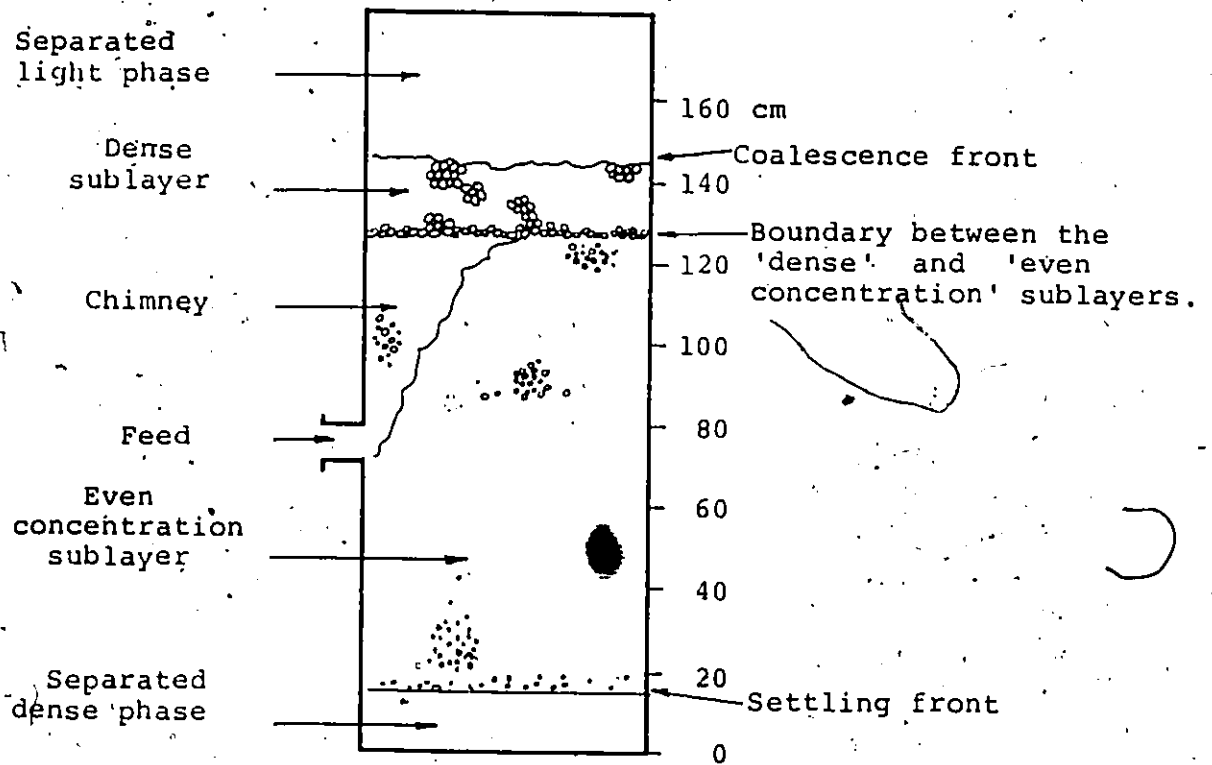
While intense agitation is used in the mixer to yield small drop sizes and good mixing, conditions in the settler are calm in order to allow drop coalescence and complete phase separation. Large amounts of expensive organic extractant are often contained within the settlers of a solvent extractant process, representing an important capital cost in addition to the cost of the large settler equipment itself. Losses of extractant through phase entrainment can be an important operating cost to a solvent extractant circuit. It is therefore important to know how the settling area requirements are affected by operating conditions of the mixer/settler. Data and calculations for this section are given in Appendix 8.

8.1 LITERATURE SURVEY

8.1.1 Introduction- The Settler and its Operation

The purpose of the settler is to allow the dispersed phase droplets to coalesce, thereby separating the organic and aqueous phases. In its simplest form the settler is merely a chamber, but special internal coalescing aids are sometimes used. Industrial operation usually requires that the dispersion form an even band within the settler, maximizing its capacity. In this project a simple box-like settler was used to obtain dispersions of uniform thickness. An article concerning the performance of such settlers written by Barnea and Mizrahi (5) was the basis on which the present work is analysed. A second paper by the same authors also describes aspects of settler operation and design (Barnea and Mizrahi (4)).

Figure 8.1 illustrates the processes occurring within a settler as described by Barnea for an oil in water dispersion. The upper surface of the dispersion band is where the dispersed oil drops coalesce with the separated oil phase. It is called the coalescence front. The lower face of the dispersion band, or settling front, is where the aqueous phase leaves behind smaller drops of oil and becomes part of the clear, separated aqueous phase. The dispersion band itself may be divided into three horizontal sublayers according to the local volume fraction of the dispersed phase, ϕ_d .



(less dense phase dispersed)

Figure 8.1 STRUCTURE OF THE SETTLER DISPERSION BAND
(BARNEA AND MIZRAHI (5))

Within the "stratified fluidized bed" sublayer adjacent to the settling front the local dispersed phase volume fraction, ϕ_d , decreases to zero as the interface is approached. Here the smallest drops in the band tend to be carried away with the continuous phase, but their settling velocity (back into the dispersion band) increases dramatically because of the decreasing ϕ_d as they separate from the band. (See the discussion about hindered settling velocities below for a full description.) This sublayer is only a few drop diameters in thickness.

The "even concentration" sublayer has an approximately uniform dispersed phase fraction, ϕ_d . Small droplets from the feed dispersion are carried into this layer by the continuous phase. Drops in this sublayer are in a fluidized state, free to move around and collide with neighboring drops. They coalesce with other drops in the sublayer until they are sufficiently large to settle against the "current" of continuous phase that flows towards the settling front. This sublayer therefore serves as a holdup volume that adjusts to feed conditions (i.e. drop sizes being fed to the settler and total flowrate) to allow small drops to grow to the point where they join other large drops in the third zone, the dense sublayer. According to Barnea the even concentration sublayer accounts for about 80% of the dispersion band.

The "dense" sublayer consists of closely packed drops separated by thin films of continuous phase. The drops are not free to move around, and will in general be deformed by the tight packing. Interdroplet coalescences occur as the films drain. The drops advance towards the coalescing front as coalescences occur between drops at the front and the separated dispersed phase. The dispersed phase fraction increases within the dense sublayer as the coalescence front is approached. This sublayer makes up about 10-20% of the dispersion band.

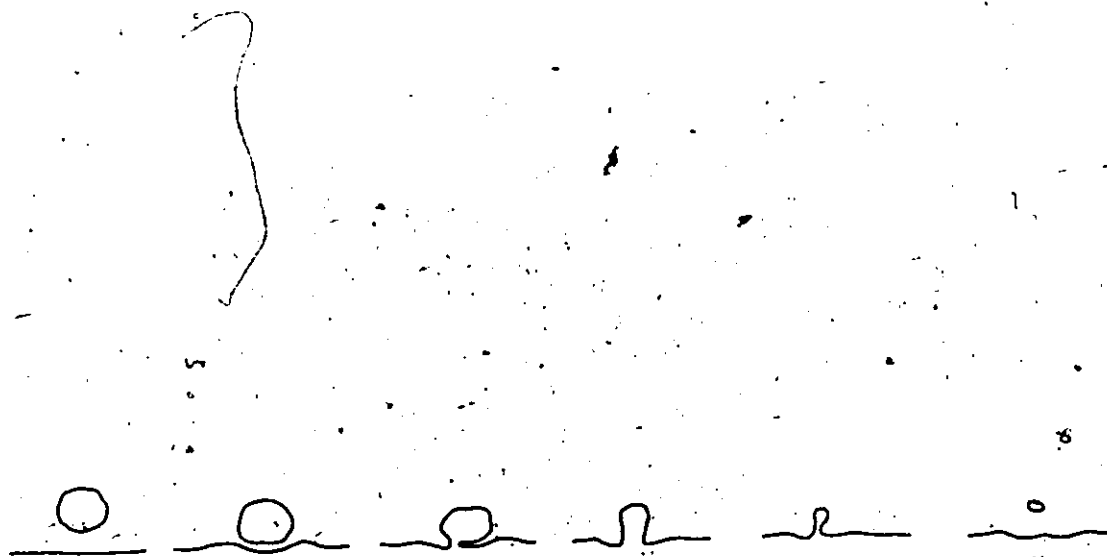
The feed dispersion enters the dispersion band at mid height, and according to Barnea it flows towards the coalescing front. Larger drops immediately join the dense sublayer, while smaller drops tend to be carried with the continuous phase into the even concentration sublayer where they coalesce with other small drops as described above. Barnea referred to the entrance path of the dispersion feed as the chimney (see Figure 8.1). The separated light phase is removed by an overflow, the heavy phase is drawn from the bottom of the settler.

8.1.2 Drop Breakup in the Dispersion Band

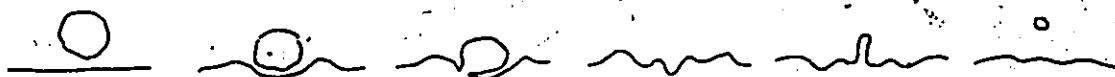
As is the case in the operation of the mixer, droplet coalescence and breakup are important processes affecting

the functioning of the settler. However, whereas drop breakup is the more rapid of the two processes in the mixer, coalescence predominates within the settler.

A description of drop breakup was given in Section 6 which was mainly concerned with highly turbulent flow. Conditions within the settler are necessarily calm, and for this case a possible cause of drop breakup is provided by, paradoxically, drop coalescence. As illustrated in Figure 8.2 the coalescence between a drop and a plane interface may produce small secondary drops. Whether this may occur as a result of coalescence between drops is not clear, and the point is an important one. For example, assume that very small dispersed phase drops are formed at the coalescing front (a drop-plane coalescence). In order that these small drops be entrained within the continuous phase, they must pass through the dense sublayer, the even concentration sublayer, and the stratified fluidized bed sublayer. It is likely that they will coalesce before doing that. However, assume now that small drops may be formed by interdrop coalescence within the even concentration or stratified fluidized bed sublayers. It is much more likely that small drops formed in those sublayers will be carried away by the continuous phase without coalescing with other drops.



'Necking' of a coalescing drop



Violent 'throwout' of a drop

Figure 8.2 THE FORMATION OF SECONDARY
DROPS DURING COALESCENCE
(from Jeffries and Davies (27p526))

8.1.3 Drop Coalescence in the Dispersion Band

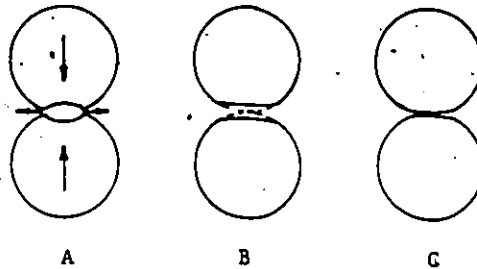
Drop coalescence may be considered to occur in three stages (Hanson (27p300)); approach or collision of drops, the draining of the intervening continuous phase film to a critical thickness for which film rupture may occur, and finally the rupture of the film and redistribution of drop contents so as to form a single drop. The film drainage step is recognized to be an important factor governing coalescence frequencies in drop dispersions, for even frequent collisions among drops may not lead to high coalescence rates if the duration of the contact times is too low to permit film drainage. Film rupture and redistribution of the drop contents are very rapid processes.

Smoluchowski (70) proposed a model for the frequency of coalescence of particles in a dilute dispersion that move about randomly according to Brownian motion;

$$\frac{dN}{dt} = -k_s N^2 \quad (8-1)$$

where N is the number of coalescences and k_s is a constant. Smoluchowski assumed coalescence upon contact (i.e. the collision rate is the rate determining step in a quiescent, dilute dispersion for which "bouncing" of particles is

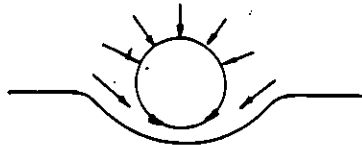
Inertial and viscous forces



Approach of a pair of drops. A, formation of a "dimple"; B, distortion without dimpling; C, formation of a flat lamella. (Kitchener & Mussel White (67)).

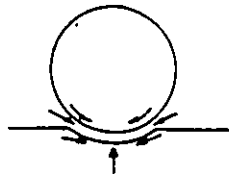


a. Diffusion out of a drop promoting film thinning and coalescence.



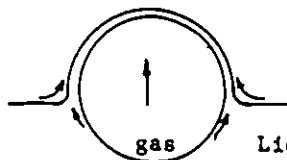
b. Diffusion into a drop reducing coalescence

Effect of mass transfer on coalescence for the case when the solute reduces the interfacial tension.



GIBB'S EFFECT

Depletion of surfactant due to film thinning.



MARANGONI EFFECT

an illustration of the formation of a foam

Liquid

gas

Lag between the creation of new interfaces and the adsorption of surfactant.

Figure 8.3 DYNAMIC FORCES AND COALESCENCE.

(Jeffries & Davies (27p539))

negligible.) Barnea (5) utilized the above relation for expressing the collision frequency in the somewhat concentrated dispersion of the even concentration sublayer of the settler dispersion band. In the case of the dense sublayer, as noted by Barnea, the drops are in continual contact and film drainage alone controls coalescence.

Upon approach to another drop or a flat interface, the surface of a drop will in general deform, either forming a flattened surface at the point of approach or even forming a "dimple" as illustrated in Figure 8.3. Several analysis of the rates of drainage of such films have been carried out for various systems. (see for example Hanson (27p513)). Numerous forces can affect the drainage of films, even to the extent of making an emulsion stable. This is discussed in more detail in the section "Surface Forces in Liquid Lamella".

The rupture of liquid films appears to be a random process that occurs when the film is sufficiently thin. Typical film thicknesses at rupture are from 50 to 500 Angstroms (cf Vrij (80p23), Hanson (27p535)). Once initiated, the rupture and formation of a new spherical drop occurs very rapidly.

8.1.4 Surface Forces in Liquid Lamella

As mentioned in the previous section, the forces present between two drops will have a great effect on the coalescence and even the stability of a dispersion. Kitchener and Musselwhite (see Sherman (67p77)) have reviewed this subject.

STATIC FORCES AFFECTING DROP COALESCENCE

Surface or interfacial forces may be categorized as being "static" forces which are independent of drop motion and "dynamic" forces which resist drop motion or fluid motion within the thin film between two drops. "Static" surface forces may also be classified as acting in the plane of the interface (surface tension and the associated surface pressures- which Derjaguin has called surface forces of the first kind), or perpendicular to the surface (surface forces of the second kind). The surface forces of the second kind may be either forces of attraction or of repulsion between drops.

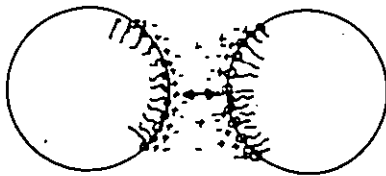
The interfacial tension is affected by surfactants present at the interface and by the nature of the phases adjacent to the interface. A close packing of surfactant molecules creates a surface pressure that tends to reduce the interfacial tension (Becher (8p21)). Likewise,

variations in the concentration of solutes close to the interface (in either phase) may also alter the interfacial tension. For example, the addition of strong electrolytes to pure water often has the effect of raising the interfacial tension, while the addition of surfactants to aqueous solutions can lower the interfacial tension (Becher (8p24)). Dynamic changes in the local values of interfacial tension are discussed in the "dynamic forces" section below.

The "static" forces acting perpendicular to an interface (surface forces of the second kind) can be classified as being attractive forces aiding coalescence or repulsive forces that tend to give stability to an emulsion.

The principal static attractive force acting between drops is the London Van Der Waals force that exists between similar molecules.

Repulsive forces may be electric or mechanical in nature. Surfactants or solids adsorbed at an interface may have a preferential charge, which then results in a charged layer at the interface and a diffuse countercharge that builds up in one or both phases. Thus, an electric double layer arises which is similar in nature for all drops in a dispersion, and as a result there is a mutual repulsion upon close approach of drops. This is illustrated in Figure 8.4. The electric double layer and associated repulsive forces



ELECTRIC DOUBLE LAYER
REPULSION



THICK, TOUGH POLYMER
FILMS



Oil droplets stabilized by a coating of mineral particles.
(quartz powder, rendered hydrophobic by dodecylamine hydrochloride).
(Kitchener & Mussel White(67)).

Figure 8.4 STATIC FORCES AFFECTING DROP COALESCENCE.

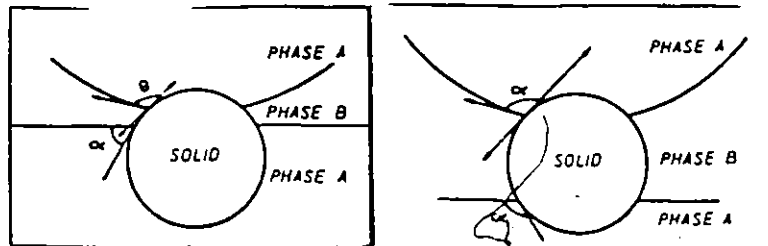
are related to the zeta potential, which is calculated from the velocity of a suspended particle under an applied electric field.

The presence of surfactants at an interface may also give rise to a strong interfacial film that mechanically resists close approach of drops, thus preventing coalescence as shown in Figure 8.4.

Mizrahi and Barnea (46) have proposed an interesting mechanism that predicts the effect of fine solid particles added to dispersions. A solid particle that is preferentially wetted by one of the phases, but only slightly so, will tend to collect at the interface, protruding some distance into each phase. The particles will easily contact the interfaces of adjacent drops. As illustrated in Figure 8.5, if the particles are slightly more wetted by the dispersed phase (the contact angle of the interface with the solid surface through the dispersed phase is less than 90°) then a particle between drops will lead to early film rupture and coalescence. Continuous phase wettability will retard coalescence.

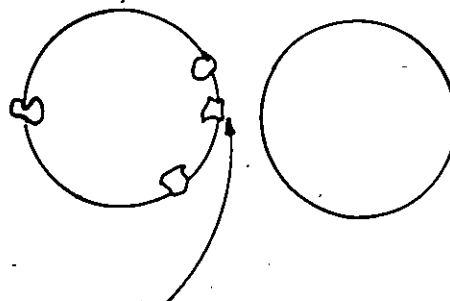
DYNAMIC FORCES AFFECTING DROP COALESCENCE

In a flowing dispersion such as the dispersion band of a settler, it is obvious that inertial and viscous



Schematic picture of the equilibrium acting on a drop in contact with a solid sphere reposing on a flat interface.

- 1-a Case a --The solid is preferentially wetted by the drop phase.
- 1-b Case b --The solid is preferentially wetted by the continuous phase. (Mizrahi & Barnea (46))



Protruding particle will easily contact the second drop.

Figure 8.5 DROP COALESCENCE IN THE PRESENCE OF FINE SOLIDS

stresses will influence the approach of drops. Thus, the rate of drainage of the film between drops will depend on the viscosity of the continuous film, which may be quite different from the viscosity of the bulk phase due to the influence of the interface and any surfactants at the interface. The extent to which a drop may deform will be influenced by factors such as drop size, the bulk phase viscosities and the interfacial tension (Figure 8.3). Ease of deformation would presumably lead to large interdrop films and slow drainage.

Interfacial movements may also influence film drainage. An altered local value of the interfacial tension that affects the film between two drops will either tend to stretch or compress the local interface depending on whether the interfacial tension is reduced or increased. The moving interface drags adjacent fluid with it and hence the film is either thinned or thickened. Local variations in the interfacial tension may arise in several ways.

1. Depletion of Surfactant in Very Thin Films (Gibb's effect- Figure 8.3)- A film cannot be thinned indefinitely without leading to an eventual depletion of any continuous phase surfactant. Local depletion of surfactant will result in a high value of interfacial tension between drops, tending to increase the film thickness. This effect should not be important for very high surfactant concentrations.

2. Stretching or Compressing Surfactant Monolayers (Marangoni Effect- Figure 8.3)- Local stretching or compression of an interface may be faster than the adsorption/desorption of surfactants. In this case the local interfacial tension will differ from its equilibrium value.

3. Mass Transfer (Figure 8.3)- Mass transfer may affect local values of the interfacial tension, depending on whether the solutes or complexes have the effect of raising or lowering the interfacial tension.

These "dynamic" forces may therefore give an elasticity to interdrop films, allowing flat lamella to be formed and retarding normal thinning and thus coalescence as well.

8.1.5 Empirical Correlations of Coalescence Time

Glasser et al.(26) reviewed correlations for the mean coalescence time, as well as film drainage models. The relations are approximate, especially with respect to effects of surfactants (usually very clean systems are used in the studies). For example, the effect of drop size has been described as:

$$t_c \propto d^n \quad t_c = \text{coalescence time} \quad (8-2)$$

$d = \text{drop diameter}$

where the ~~exponent~~ n varies from -1 to 5 according to different work reviewed by Glasser. No attempt seems to have been made in the empirical correlations or in the film drainage models to account correctly for the surface forces of the second kind (neither zeta potentials, interfacial viscosities, nor the mechanical barrier of surfactants or solids are used in the correlations). Barnea (5p78) developed a model for the dispersion band height of the settler using the following simplified form of several empirical correlations for the coalescence time of a single drop on a flat interface:

$$t_c \propto \mu_c d^{1.5} \quad (8-5)$$



Barnea found that the overall coalescence rate in the settler was proportional to the volume of the dense sublayer.

$$Q_d = \int_0^H \phi_c dh \quad (8-6)$$

8.1.6 Hindered Settling

A single drop falling (or rising) through a fluid is acted on by gravitational, buoyant, and viscous and dynamic forces of resistance. The drop will reach a maximum velocity relative to the fluid, called its terminal velocity, at which point the forces balance. If, however, the drop is surrounded by other drops, their motions will have an effect on one another, and the relative velocity of the drops with respect to the fluid will be reduced, or hindered. Hindered settling is the situation that exists in the even concentration sublayer of the settler dispersion band, for which flow between the drops and the continuous phase appears to be largely countercurrent in nature with some circulation patterns superimposed. Barnea (5) reviewed literature correlations for the hindered settling of drops, and proposed a general correlation based on the drag coefficient for a single sphere, but using modified definitions of the continuous phase viscosity and drag coefficient;

$$v_{\phi}^2 = \frac{4d(\rho_d - \rho_c)g}{3\rho_c c_D(Re_{\phi})} \left[\frac{1-\phi}{1+\phi^{1/3}} \right] \quad (8-7)$$

$$Re_{\phi} = \rho v d / \mu_{\phi} \quad (8-8)$$

$$\mu_{\phi} = \mu_c \exp \left[\frac{5\phi}{3(1-\phi)} \right] \quad (8-9)$$

These relations were used to calculate the maximum entrainable drop size for the system used in this project (aqueous drops in an organic fluid). Results are shown in Figure 8.6. It is assumed that the Sauter mean diameter is an appropriate mean diameter for the correlations.

8.1.7 Settler Design Equations

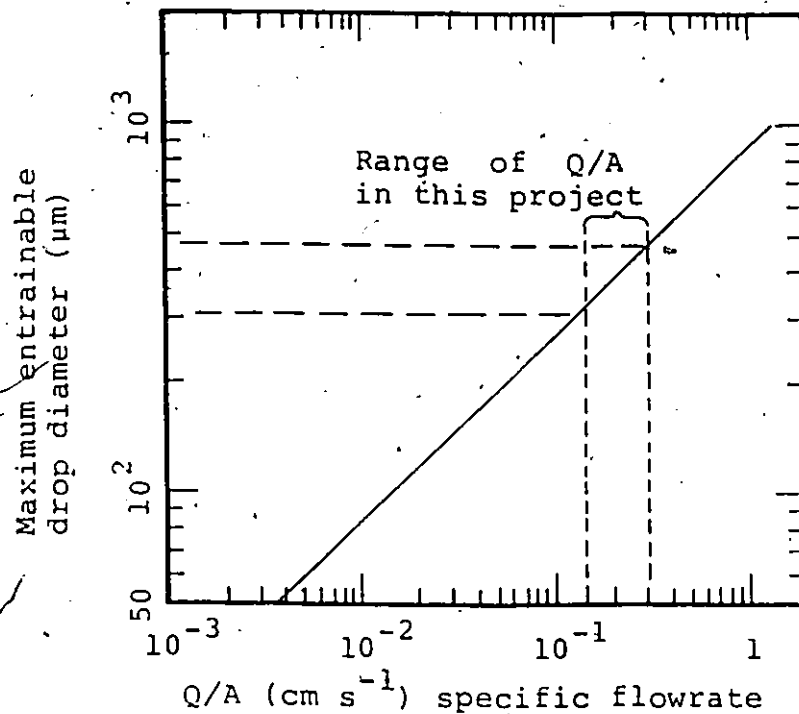
Ryon, Daley, and Lowrie (64) proposed a relation between the height of the dispersion band for a particular system and the specific throughput (volumetric flowrate of the dispersed phase per unit horizontal cross sectional area of the settler):

$$H = K(Q_d/A)^y \quad K, y \text{ constants} \quad (8-9)$$

Q_d = volumetric flowrate of the dispersed phase

A = horizontal(plan) area of the settler

Barnea derived a similar equation to that above from theoretical considerations:



Physical quantities used in the calculations

		aqueous	organic	dispersion
ϕ		-	-	0.04
ρ	g cm^{-3}	1.03	0.80	0.89
μ	$\text{g cm}^{-1} \text{s}^{-1}$	1.1×10^{-2}	1.65×10^{-2}	5.0×10^{-2}

Figure 8.6 HINDERED SETTLING CALCULATIONS

$$H = K(Q/A)^y \quad Q = \text{total flowrate} \quad (8-10)$$

(dispersed + continuous phases)

where the dispersed phase fraction in the feed is assumed to be approximately equal to that of the even concentration sublayer. The exponent 'y' should have a minimum value of 2.5 according to Barnea. This applies to the case where flow within the even concentration layer is creeping flow, and droplet growth is controlled by drop collision (The continuous phase film between drops thins rapidly, allowing most collisions to result in coalescence i.e. no drop "bouncing"). Barnea notes that plots of $\log H$ vs $\log Q/A$ have an upward curvature for small H , indicating that for small dispersion bands (such as in this project) y is not constant.

8.1.8 Micelle and Microemulsion Formation

As is evident from Figure 8.6, any very small drops, microemulsions, or micelles present in the feed dispersion or created in the dispersion band would normally be carried away with the continuous phase. Coalescence within the dispersion band tends to screen out small drops, but this may not be complete. Such phase entrainment can be very important to an industrial operation. Emulsion drops are generally considered (Becher (8p297)) to be greater than 0.1 μm in diameter. Microemulsions (or micellular

structures) are smaller than this, and will leave a solution clear as they are too small to interfere with light transmission.

8.2- EXPERIMENTAL WORK- SETTLER DISPERSION BAND HEIGHT AND PHASE ENTRAINMENT

8.2.1 Equipment and Procedures

The arrangement of the settler is shown in Figure 8.7. The dispersion was fed into the half height of the dispersion band via a rectangular slit. A mobile baffle allowed the variation of settling area for the different runs. The position of the dispersion band within the settler was controlled by adjusting the outflow level of the heavier phase (see illustration). The settler was thoroughly rinsed with warm water and wiped clean after each run in order to get rid of any accumulation of crud or film. Each run lasted 20 residence times based on the volume of the mixing vessel (870 cm^3). The settling volume varied with the positioning of the baffle from 455 cm^3 to 2700 cm^3 , meaning that the runs lasted from 6 to 38 settler residence times.

During the runs measurements were made of the dispersion band height, phase entrainment, uranium concentrations at the phase outlets from the settler, and of any crud formation. At the end of each run a series of measurements were made of the height of the mixer dispersion band (which formed shortly after the mixing and pumping were stopped) versus time. This was carried out to determine if there was a correlation between the mixer settling time and

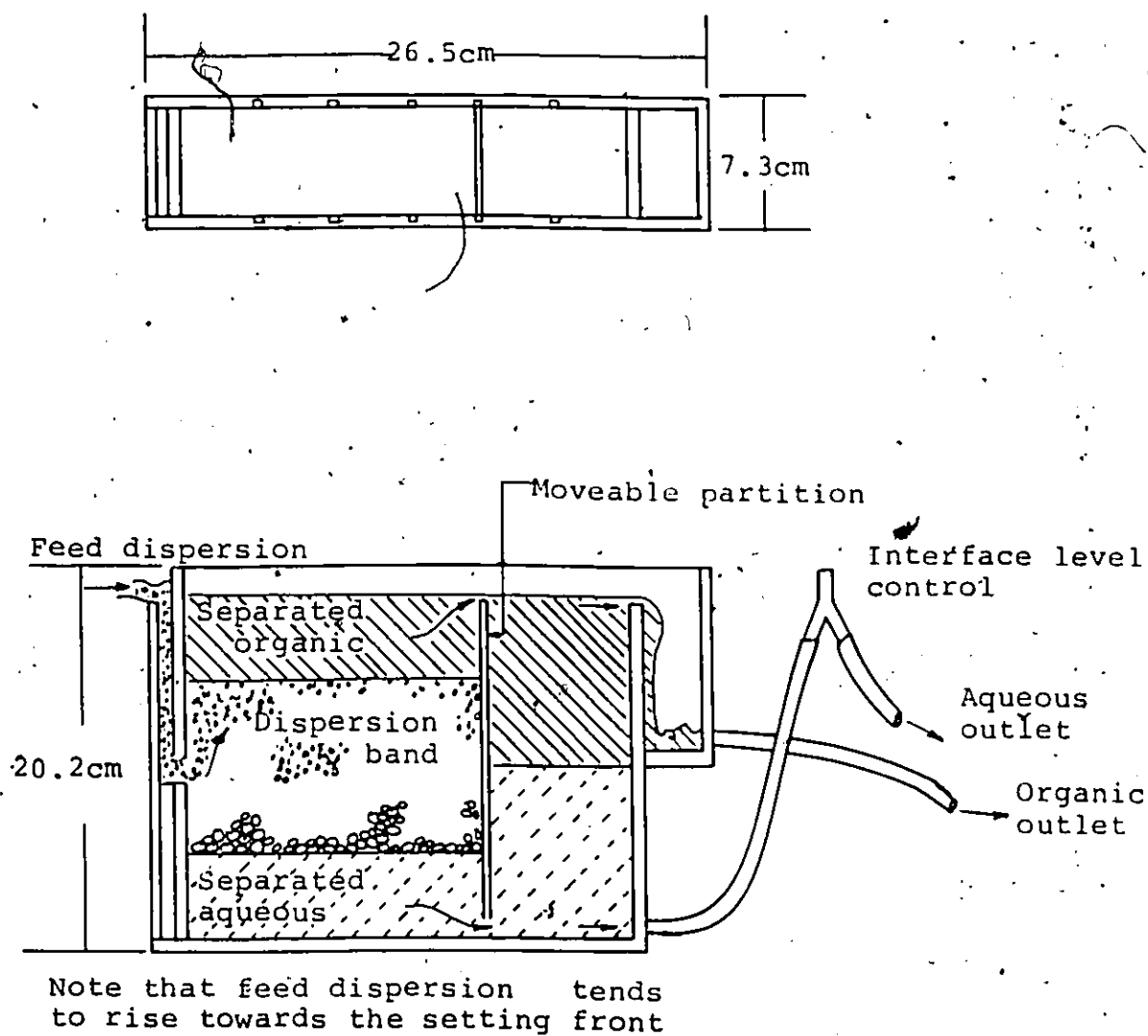


Figure 8.7 DETAILS - SETTLER ARRANGEMENT

the settler dispersion band height.

Phase entrainment measurements were made by taking samples from each phase and centrifuging them (acceleration = 380 g's) for 15 to 20 minutes. In most cases there was insufficient entrainment in either phase to be measured quantitatively by centrifugation, consequently qualitative observations were made of the phase cloudiness and the number of drops that separated out.

8.2.2 Data and Observations

This project involved only aqueous drops in an organic phase continuous dispersion. Because the organic phase was less dense it collected above the dispersion band. The settling front was therefore the upper face of the dispersion band and coalescence of the aqueous drops occurred at the lower face. The dispersion being fed into the settler was observed to form a chimney as described by Barnea. However, the chimney tended to rise to the settling front and not the coalescing front as described by Barnea. (see Figure 8.1) At low impellor speeds the settling front was well defined and regular, but at higher speeds it was more spread out and not well defined. There was a tendency for very small drops to swell up into the separated organic phase and slowly settle back to the dispersion band.

It appeared that the drop size in the dispersion band and at the coalescing front varied with mixer's impellor speed. No quantitative measurements of actual drop sizes in the dispersion band were made. Drops near to the settling front were much smaller than drops at the coalescing front. They were also less densely packed and more free to move around. Deformation of drops at the coalescing front was observed.

A surprising observation was the rapidity of coalescence for runs with crud at the interface. Even when appreciable portions of the coalescence front were apparently covered with crud, the settler dispersion band height was less than it would have been in the absence of solids or cruds.

The organic phase layer above the dispersion band was usually clouded. Heavy cloudiness of the organic phase was observed at moderate to high impellor speeds. The aqueous phase was only slightly clouded at moderate to high impellor speeds, particularly for stripping. At low impellor speeds the aqueous phase was very clear.

Several batch mixing tests were carried out in a beaker at an O/A ratio of 1:1. After a minute of moderate agitation the dispersion in the beaker was allowed to settle. An interesting observation was the "firing" of small

droplets into the separated continuous phase at the settling front. The droplets subsequently settled back to the dispersion band. This arose during tests for which the aqueous phase was continuous. It is not known how the drops were projected into the continuous phase. One possibility is that the violence of coalescence of large drops threw adjacent smaller drops. Another possibility is that the droplets were secondary droplets produced by the coalescence of larger drops. In either case, this type of drop behaviour at the settling front could give rise to phase entrainment in a continuous settler.

8.2.3 Calculations and Results

Run times were not sufficiently long to ensure that steady state values of the dispersion band height or crud formation were attained. There was, however, considerable difference in the dispersion band heights for the different runs. A "reduced" dispersion band height is defined below in order to compare results of the progression of dispersion band heights for different runs.

$$H_r(t) = H(t)/H_0 \quad \text{where } H_0 \text{ is the height at the end of the run} \quad (8-11)$$

Figures 8.8, 8.9, and 8.10 show the trend in the reduced dispersion band height with time for runs of 20, 10 and 6

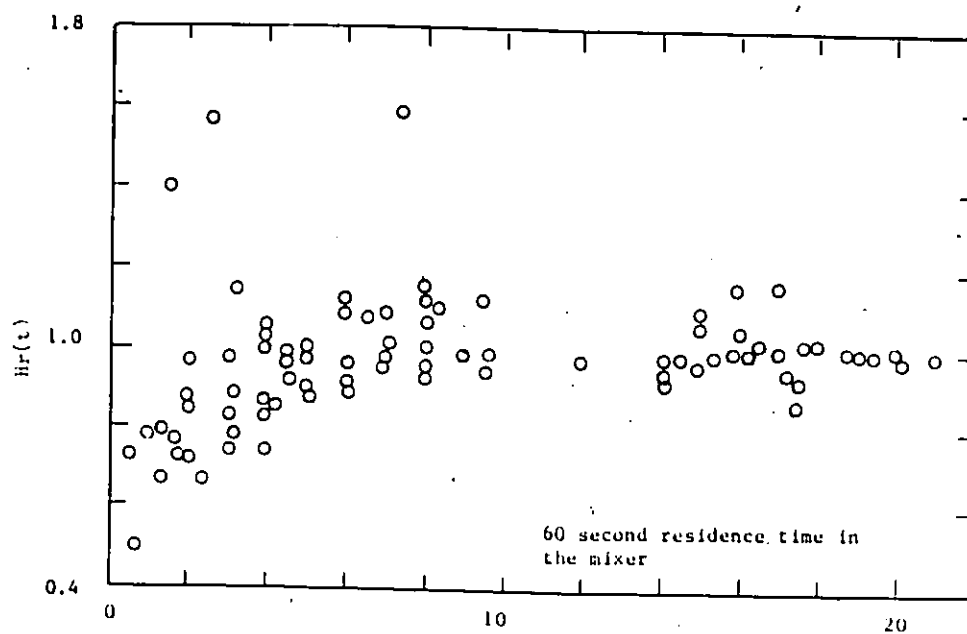


Figure 8.8 APPROACH OF THE DISPERSION BAND
TO ITS STEADY STATE VALUE - ALL SERIES

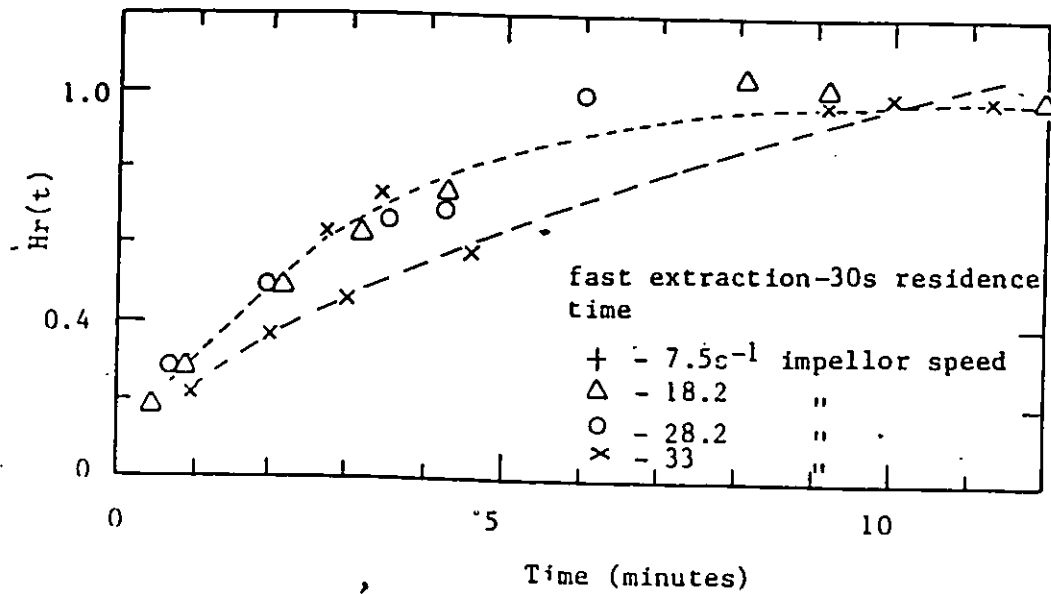


Figure 8.9 APPROACH OF THE DISPERSION BAND TO ITS STEADY STATE VALUE - EXTRACTION SERIES

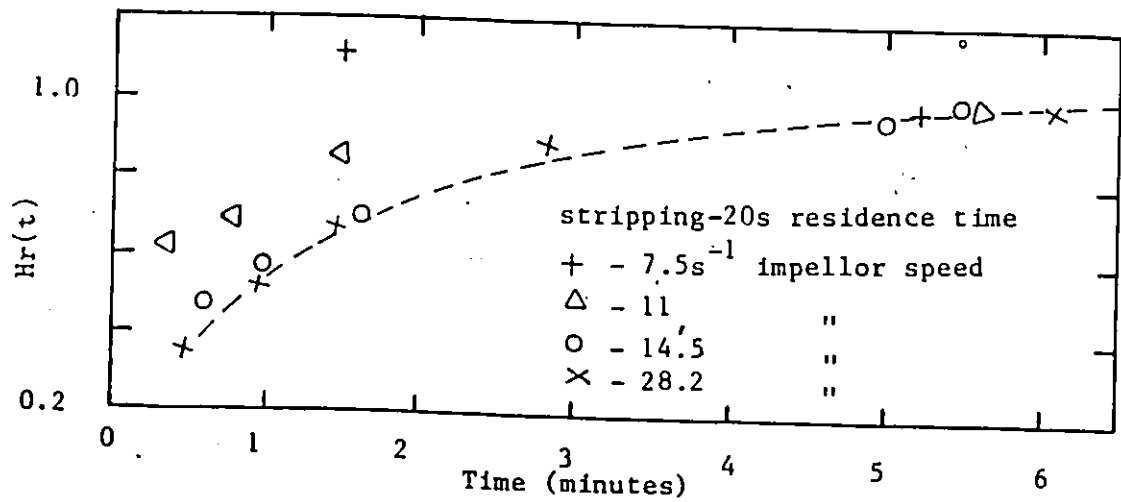


Figure 8.10 APPROACH OF THE DISPERSION BAND HEIGHT TO ITS STEADY STATE VALUE - STRIPPING SERIES

minutes duration (corresponding to residence times in the mixer of 60, 30 and 20 seconds). Zero slope in the graphs for an appreciable time would indicate that steady state had been attained, although the gradual accumulation of impurities or buildup of very small drops within the dispersion band could affect the height over longer periods of time. From the figure it appears that the dispersion band height remains essentially constant after 6 to 10 minutes. This means that run times of 10 to 20 minutes should give a reasonable base of comparison of the effects of different variables on the dispersion band height. The runs of 6 minutes duration were barely adequate.

Due to the different settler areas and specific throughputs employed in the experiments, the dispersion band heights have been normalized for comparison purposes, using the equation (8-10) as discussed in the literature survey:

$$H = K(Q/A)^y \quad (8-10)$$

The exponent y was calculated from data from three sets of runs involving two different settling areas. The value so obtained can only be considered to be approximate and useful for relative comparisons, as it may not be a constant for the various conditions (extraction/stripping, solids/no solids, loaded organic/barren organic) of the experiments.

Still, the value of 2.5 obtained for y seems reasonable in comparison to results of other workers (Ryon et al. (64), Barnea and Mizrahi (5)).

Normalized dispersion band heights at "steady state" are presented in Figures 8.11 and 8.12. Note that the lines joining the data points are not intended to imply a specific functional relationship, but were added to aid the reader to "connect the dots" visually. Heights for stripping and for extraction runs in the presence of solids are much less than those for extraction runs without solids. It is apparent that the stripping runs and extraction runs with solids were "sensitive" to the impellor speed in the sense that initial increases in the impellor speed have an important effect on the dispersion band height. However, there does not appear to be much effect above a certain impellor speed. The effect of the residence time may be studied by comparing runs for the same series (i.e. extraction, extraction with solids, or stripping) but of different residence times. For the fast extraction runs (no solids) it can be seen that the series of runs for a 60 second residence time gave narrower dispersion bands than the runs at 30 seconds residence times. In the case of stripping there is little difference between the results for residence times of 60 and 20 seconds.

Figure 8.12 presents results for extraction runs in

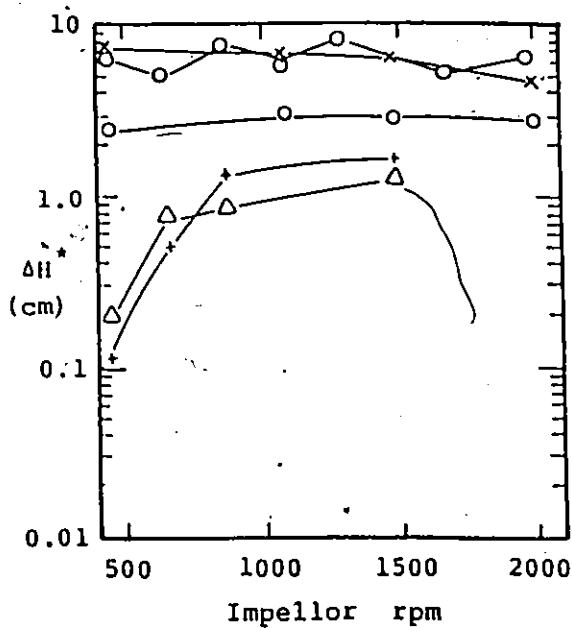


Figure 8.11 THE EFFECT OF IMPELLOR SPEED ON THE SETTLER DISPERSION

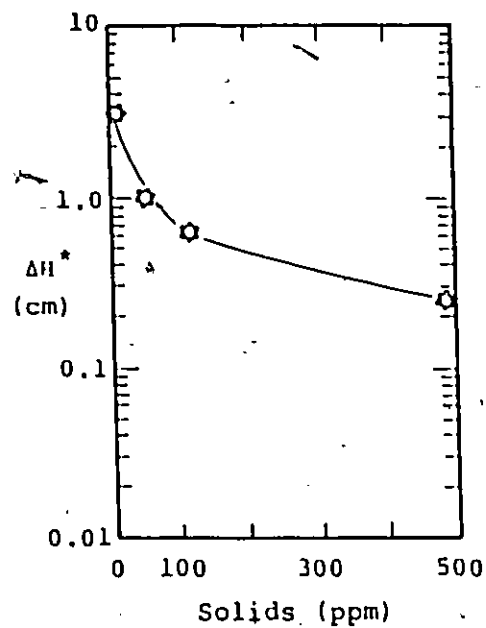
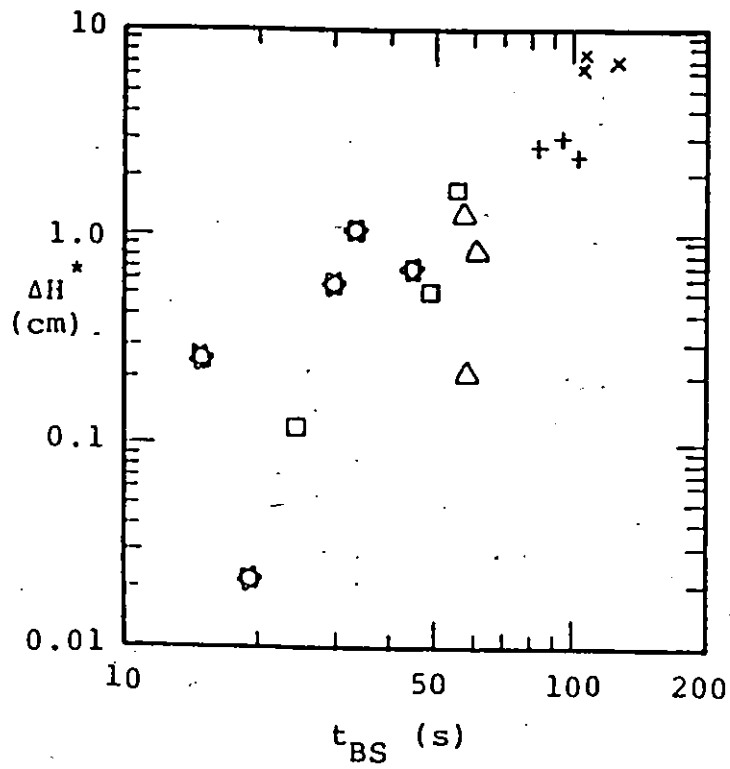


Figure 8.12 THE EFFECT OF THE SOLIDS ADDED ON THE SETTLER DISPERSION (@ 870 rpm).

Symbol table

Mixer residence time	60s	30s	20s
No extraction	O		
Fast extraction	+	x	
Slow extraction	⊗		
Stripping	Δ		□



Symbol table

Mixer residence time	60s	30s	20s
No extraction	O		
Fast extraction	+	x	
Slow extraction	⊗		
Stripping	Δ		□

Figure 8.13 CORRELATING THE NORMALIZED
DISPERSION BAND HEIGHT WITH THE BATCH
SETTLING TIME

which the impellor speed maintained constant but the solids content was varied.

A comparison of batch settling times for the mixer and the normalized dispersion band heights for the settler is presented in Figure 8.13. The batch separation time was taken from the instant the pumps and impellor are stopped to the first appearance of clear (without drops) sections at the interface. The two variables are not well correlated.

No numerical data are available for evaluating phase entrainment in the settler. However, it is interesting to review the calculations of hindered settling velocities of the extraction system as presented in Figure 8.6. There it may be seen that the specific flowrate (Q/A) within the settler was sufficiently high during these runs to entrain average drop sizes produced in the mixer at moderate to high impellor speeds. That this did not arise must be attributed to the rapidity of coalescence within the dispersion band and also within the channel leading from the mixer to the settler.

8.2.4 Discussions

Several limitations of the results for the dispersion band must be acknowledged which relate to the small size of the equipment. Barnea suggests that a minimum dispersion

band height of 20 cm is required to get results that may be classified as being applicable to a deep layer settler. He also states that the heights of industrial dispersions are more typically 40 to 100 cm. In this project the maximum attainable height was only 15 cm, and often heights of 2 cm or less were obtained. Wall effects for the small settler would be much more important than for a full sized settler. Run times of 20 minutes are much less than the several hours used by some other workers in similar work. In light of these discrepancies the data can not be recommended for scale up purposes.

A major discrepancy between the observations of this project and those reported by Barnea was the behaviour of the chimney formed by the dispersion fed into the settler. As reported in this project, the chimneys tended to drift towards the settling front and not towards the coalescence front. This indicates that the density of the feed dispersion was less than the density of the majority of the dispersion band. A possible explanation is that for the low specific throughputs in this project, the resulting dispersion band was largely made up of the dense sublayer and not of the even concentration sublayer as described by Barnea. This explanation requires that the lower specific throughput was not sufficient to entrain dispersion drops according to the hindered settling mechanism previously described. If this actually is the case in this project,

then the total dispersion height will not behave according to the same mechanisms as those of Ryon and Barnea:

$$H = K(Q/A)^y$$

but will instead be influenced by the relation for the dense sublayer:

$$Q_d = \int_0^H \phi_d dh$$

The dispersion bands showed a strong sensitivity to the lower impellor speeds for the stripping series and the slow extraction series. In the case of stripping it is known that precipitate forms to a limited extent, and therefore the observed fast coalescence and sensitivity of the two series could have been due to the presence of fine solids in the dispersion. Fine suspended solids are known to affect dispersions, especially if they have suitable surface properties (Figure 8.4).

The effect of the residence time in the mixer on the normalized dispersion band height is less clear. In the case of extraction without solids, a 30 second residence time resulted in a greater height than a 60 second residence time. For stripping there did not appear to be much

difference between results for 60 and 20 seconds residence time.

The fact that the presence of crud at the interface did not adversely affect the dispersion band height indicates that the structure of the crud is fairly loose or "porous" to the dispersed phase. This subject is discussed in more detail in the next section.

8.3 CONCLUSIONS

The impellor speed only affected the settler dispersion band heights of the slow extraction and stripping series (both of which contained solids). In these series the dispersion band height increased with increasing impellor speeds, but only at the lower range of impellor speeds. The dispersion band heights were reduced by the presence of solids. Qualitative observations indicated that phase entrainment and cloudiness increased with increasing impellor speeds, especially for the organic (continuous) phase.

9. CRUD

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9. CRUD

9.0 OBJECTIVES

As described in Section 1 of this report, the objectives of this section was:

To determine if crud or stable emulsions would form during the runs. A hypothesis of interest was whether one may reduce the formation of crud by reducing the impeller speed in the mixer while still maintaining acceptable rates of mass transfer.

Several causes of crud in industrial solvent extraction circuits are discussed in the literature survey of this section. Many impurities which commonly cause crud or emulsion formation in industrial circuits were not present in the simple solutions used in this project. The only crud promoting additive used was a solid residue from a uranium leach. Data and calculations for this section are given in Appendix 9.

9.1 LITERATURE SURVEY

9.1.1 Crud and its Effects on Industrial

Solvent Extraction Circuits

Crud is a heterogeneous phase that collects within the dispersion band of a settler. It is usually made up of three component phases; aqueous liquid, organic liquid, and solid particles. Industrially it is also known as grungies, mung, gunk, and sludge (Ritcey (57)). The crud encountered at Gulf Mineral's Rabbit Lake operations in Saskatchewan is described in detail by Young (83). In the extraction circuit crud is present as "...thick viscous brown mud layers at the organic aqueous interface..", while for stripping crud "...is a brown, gummy material with a porridge-like texture...". The extraction crud may congeal and form "valleys" in the settlers, while the stripping crud is more fluid and stratified, forming a layer at the coalescing front.

Studies by Ritcey (57), and Young (83) give analysis of the major elements present in crud solids from three uranium milling operations located in Canada and the United States. Table 9.1 is taken from Young (83) and Ritcey (58), and compares the composition of dissolved matter in the feed leach liquor with the crud composition. As is typically the case, the crud components closely resemble the feed material

Table 9.1 Rabbit Lake Crud Analysis

	Feed Solution* (g/l)	Extraction Crud (weight %)	Stripping Crud (weight %)
U	1.87	11.3	12.1
Mo	5×10^{-4}	0.11	0.72
Fe	1.84	5.4	8.0
Si	0.44	13.1	7.45
Al	2.11	3.96	0.077
Mg	9.89	2.49	4.49

* (pH=1.6)

Table 9.2 The Degree of Concentration of Selected Elements in the Crud

	Extraction Crud	Stripping ¹ Crud	Stripping ² Crud
U	2.7	3.2	1.8
Mo	60	440	-
Fe	1.3	2.1	1.7
Si	13	8.4	2.8
Al	0.85	0.02	1.6
Ca	-	-	0.15

degree of concentration = $\frac{\text{rel \% of element in crud}}{\text{rel \% in feed}}$

1. $(\text{NH}_4)_2\text{SO}_4$ stripping solution
2. Na_2CO_3 stripping solution

but the relative amounts of the components in the crud differ from that of in feed. A "crud concentration factor" was defined in Table 9.2 in order to compare the degree of concentration of different elements in the crud. Also shown in Table 9.2 are results of the crud analysis for a stripping circuit using Na_2CO_3 instead of $\text{NH}_3\text{-(NH}_4)_2\text{SO}_4$. With this circuit the pH control is less critical and less uranium precipitates during stripping. Silica especially seems to be concentrated in the crud. Uranium, molybdenum, vanadium, and probably other metals that are extracted and concentrated by the organic phase are concentrated in the crud when pH control problems lead to precipitation in the stripping stages.

Carino (14) described crud as being perhaps the most common operating problem in solvent extraction circuits using amines. There is an important loss of settling area associated with the presence of cruds, leading to higher fluid velocities and consequent phase entrainment, uranium losses, solvent losses, and operational upsets in other parts of the plant. When severe, crud is easily carried from one part of the mixer settler circuit throughout the whole circuit, leading to an operational shutdown.

9.1.2 Factors Affecting Crud Formation

Ritcey (57), Young (83), and Mizrahi and Barnea (46)

describe factors that affect crud formation which are summarized below.

A very important factor influencing crud formation is the presence of solids. With pump-mix settlers using amines, fines in the feed must be kept below about 30 ppm to avoid crud problems. Solids may originate from several sources:

- solid fines in the feed leach liquor;
- precipitation due to:
 - supersaturated levels of impurities
(eg. zirconium in TBP systems- Ritcey(62));
 - pH change from extraction to stripping,
which may precipitate extracted metals such
as uranium, or compounds entrained with
aqueous drops in the organic phase;
- biological activity such as the growth of
bacteria and fungi;
- carryover of crud from one stage to the next; and
- dust and dirt from the immediate environment.

Organic surfactants have been suspected of aggravating crud problems in a number of cases. (Ritcey (57)). The surfactants may originate from organics present in the mill feed water (such as humic acids in the spring runoff), or breakdown of the organic phase, including the diluent, phase modifier, or extractant.

It is possible that special interfacial films are formed by the condensation of organics at the interface (and perhaps involving the extractant itself) as described in Figure 8.4. In addition, surfactants may alter the nature of solid surfaces, thus altering their role in crud formation.

Ryon and Lowrie's (65) investigation of an amine system indicated that silica in excess of 0.7 to 1.0 g/L in the feed caused emulsion problems. Ritcey (58) has described the effect of certain solutes on crud formation. Out of the group Fe, Al, Si, Ca, and Mg, the two elements iron and silica were found to be particularly important.

As with the mixer and settler operation in general, the phase continuity may have an important effect on crud formation. Ryon and Lowrie (loc. cit.) recommended organic continuous operation to minimize emulsion formation as feedwaters for industrial operations often contain agents that stabilize oil in water emulsions.

Extreme crud formation may be associated with operational upsets such as "...pump failure, launder plug up, or loss of organic flow for example..."(Young(loc.cit)).

9.1.3 Cruds Analyzed as Stable Emulsions

From the preceding descriptions of crud and the factors influencing its presence, it seems reasonable to analyse it in terms of stable emulsions. The subject of emulsions is reviewed by Becher (8) and Sherman (67). Emulsions are important in many industrial processes (paints, biological systems, petroleum refining, butter production, etc), and this has led to very extensive research on the subject.

STABILITY OF EMULSIONS

Dynamic and static forces affecting the coalescence of emulsions were discussed in Section 8 with respect to settler operation. However, it is necessary to elaborate on the mechanisms that lend a long term stability to emulsions.

Barnea and Mizrahi (46) have proposed a mechanism for the stabilization of emulsions by fine solid particles. Referring to Figure 8.4 in Section 7, solid particles that are slightly wetted by the continuous phase will tend to hinder the approach of drops, retarding or even preventing coalescence. The wettability of solid particles over moderate periods of time is influenced by the recent history of the particle. For example, solid particles that are initially immersed in water may have a hydrophilic nature

even though they would have a slight hydrophobic nature at equilibrium when in contact with oil and water. Ryon and Lowrie (65) found that the effect of particles on an emulsion depended on whether they were wet or dry prior to contacting the emulsion.



The DLVO theory, named after two independent groups of researchers who proposed it (Derjaguin and Landau (22) and Verwey and Overbeek (79)) shows how emulsions may be permanently stabilized when the only surface forces considered are the London van der Waals force of attraction and electric double layer repulsion. Drop movement is assumed to occur by Brownian motion. The theory predicts an energy of interaction curve as illustrated in Figure 9.1, which exhibits a secondary minimum. This minimum may be compared to the kinetic energy of motion of the drops in order to evaluate the emulsion stability, or indicate rates of flocculation. (This is somewhat reminiscent of molecular potential energy curves.) For "typical" lyophobic (solvent fearing) colloids, calculations indicate that the secondary minimum would be significant for spheres of $10\ \mu\text{m}$ radius and insignificant for spheres $0.1\ \mu\text{m}$ in radius (Kitchener and Musselwhite (see Sherman (67p105))).

Mechanical barriers formed by dense interfacial films of surfactants are described by Becher (8p97) and Sherman (67p80). Surfactant films have the effect of altering the



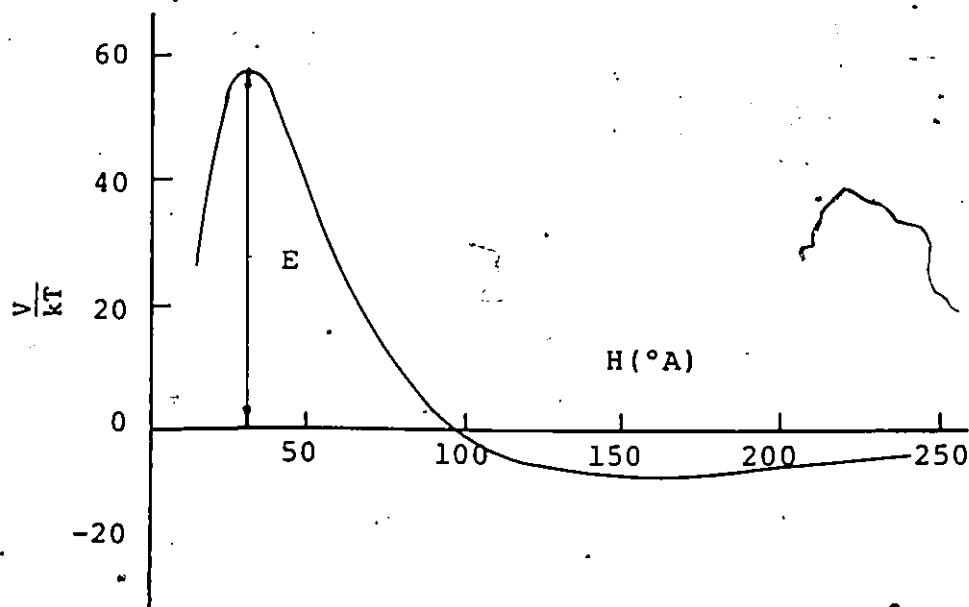
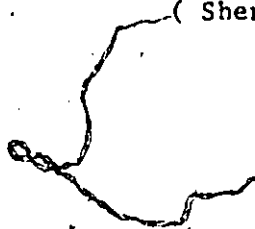


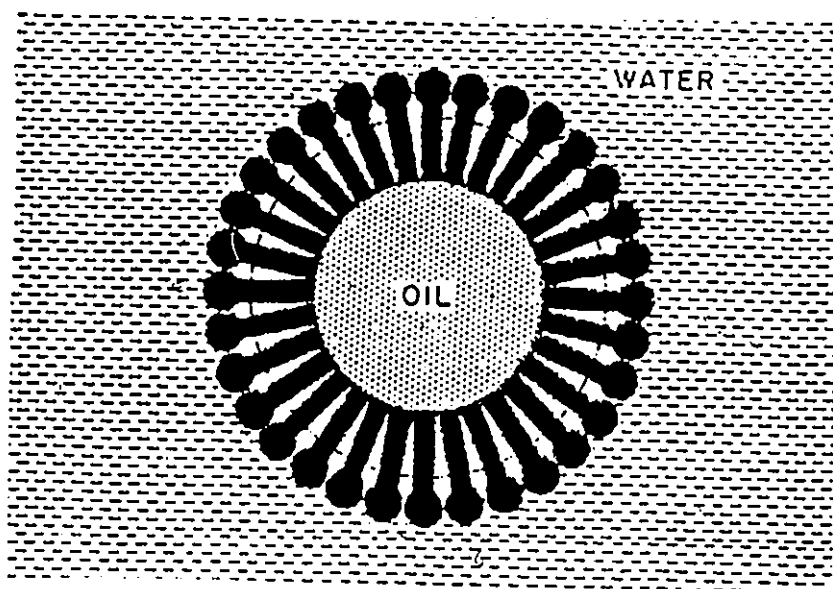
Figure 9.1 CALCULATED INTERACTION ENERGY CURVE FOR PARAFFIN OIL DROPLETS STABILIZED BY BOVINE SERUM ALBUMIN.
 Droplet radius = 1.24μ . 0.01 M KCl , $\zeta = 20\text{mV}$, $\Lambda = 1.27 \times 10^{-13}$
 (after Srivastava, S.N. and Haydon, D.A. (1964). Proc. Fourth Int. Congress on Surfactivity, Brussels).

(Sherman (67 pl04).

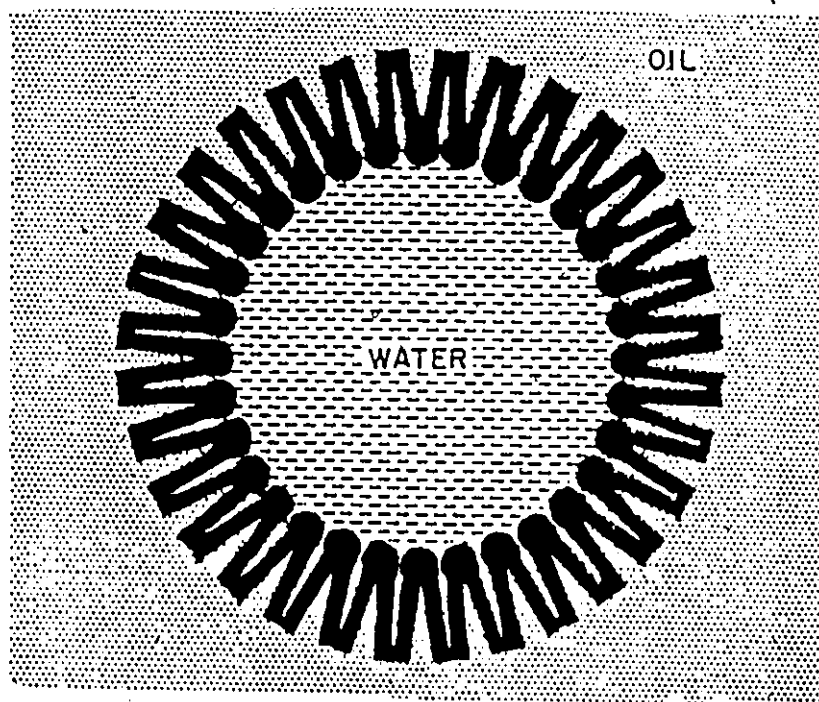


interfacial tension and viscosity, which have been correlated with emulsion stability. However, these properties are symptoms of stability and not its cause, which is more closely related to the properties of the densely packed interfacial film. Langmuir and Harkins (see Becher (8p97)) suggested that monomolecular films of oriented surfactants could stabilize emulsions (rather than the earlier theory of a thick multimolecular adsorbed surfactant film), and suggested how "oriented wedges" (Figure 9.2) could explain the phase continuity of such emulsions. Soaps of monovalent metals would be expected to produce O/W emulsions, while bivalent metals would promote W/O emulsions. Mixed emulsifier films formed by complexes of surfactants may give more stable emulsions than simple surfactants alone (Figure 9.3 from Becher). Other workers have related the stability of emulsions to the physical properties of the interfacial films- shear modulus of elasticity, shear viscosity (or dilational elasticity and viscosity). (Kitchener (67p77)).

The phase continuity of emulsions has been correlated in terms of the HLB system (Hydrophile/Lipophile Balance) of the surfactant. The method of phase mixing also influences phase continuity.

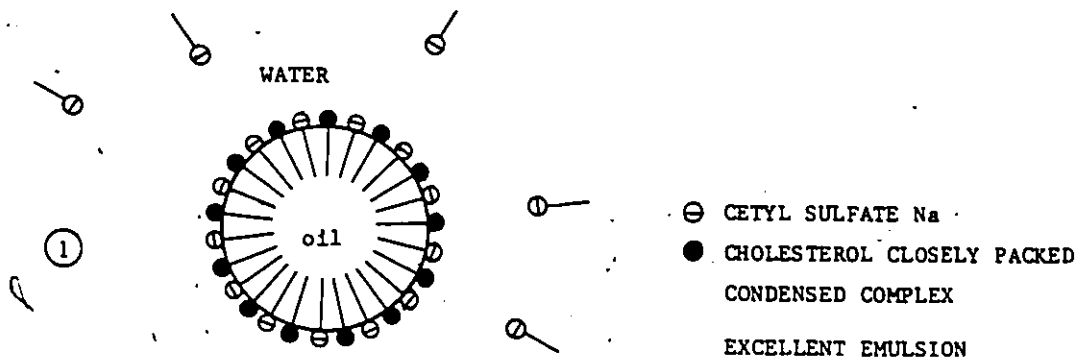


Stabilization of an O/W emulsion by the soap of a monovalent metal.

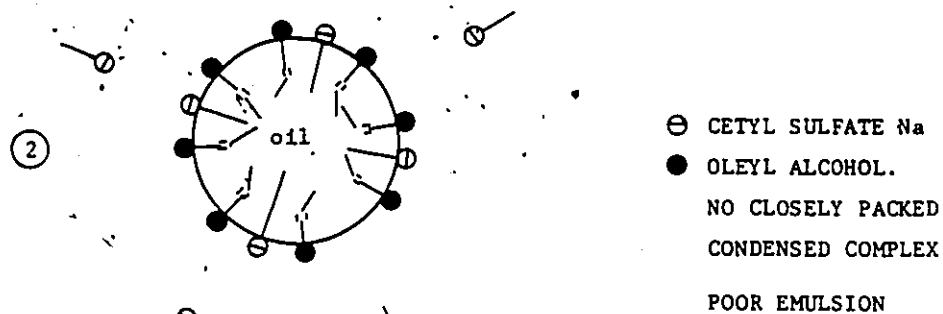


Stabilization of a W/O emulsion by the soap of a bivalent metal.

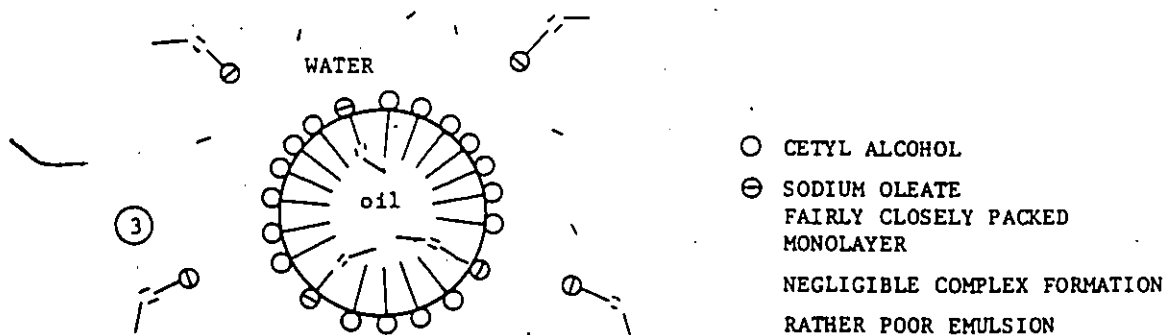
Figure 9.2 PHASE CONTINUITY AND "ORIENTED WEDGE" SURFACTANT FILMS
(Becher (8p98))



Sodium cetyl sulfate and cholesterol from a closely-packed condensed complex, giving a good emulsion.



Sodium Sulphate and oleyl alcohol from a poorly packed complex (because of the double bond in the alcohol), giving a poor emulsion.



Cetyl alcohol and sodium oleate from a fairly close-packed complex monolayer hence form a fair emulsion.

Figure 9.3 COMPLEX FORMATION AT THE OIL-WATER INTERFACE IN EMULSIONS, ACCORDING TO SCHULMAN AND COCKBAIN. Becher (8 p-108).

9.1.4 An Overview of Demulsification

Becher (8p369) lists several general techniques for demulsification. For water-in-oil emulsions (and in particular for the petroleum industry), settling may be sufficient to separate the phases. Heating the emulsion (at atmospheric or high pressures), distillation, exposing the emulsion to an electric field, using emulsifying agents to counteract the emulsion (eg. ferrous sulfate), centrifugation, and filtration through a dispersed phase wetted material are also employed to break water-in-oil emulsions.

Oil-in-water emulsions are commonly broken by acid cracking, centrifugal separation, and aeration or froth flotation.

Ritcey's paper (57) reviews industrial experience with crud treatment in hydrometallurgical liquid-liquid extraction circuits. In order to prevent crud formation, there must be good clarification of the feed streams to remove suspended solids, it is important to select the proper organic phase components (extractant, diluent, and modifier), and excessive agitation should be avoided. Techniques used to recover the organic phase from a crud include settling and skimming, filtering, acidification/deacidification, and agitation.

9.2 EXPERIMENTAL WORK- CRUD

9.2.1 Equipment and Procedures

Residue that had been produced in a sulfuric acid leach of Rabbit Lake ore was added to the aqueous feed of the slow extraction series in order to produce crud. The residue had been flocculated with 0.3 lb/ton Percol 351. A rough screen analysis of the solids is presented in Table 9.3. The analysis is only approximate as particle agglomerates formed during dry screening.

The only required modification to the single stage mixer-settler runs was the use of a well stirred feed tank (20 liters capacity). Industrial operation strives to maintain solids at levels less than 30 ppm (mg/L) in the aqueous feed, therefore larger doses were used in the laboratory runs.

9.2.2 Data and Observations

As indicated in Table 9.4, all runs having solids present in the leach produced crud that collected at the coalescing front. The amount of crud obtained in the runs (judging by visual appearances) was affected by the amount of solids introduced with the aqueous phase and by the

Table 9.3 Screen Analysis of Solids Added to the Leach

Tyler mesh	1100	+200	+325	-325
weight %	21%	56%	21%	2%
d minimum (clear opening)	147	74	44	44

(This is a rough result that overestimates particle size as the screening process of "dry" particles produced agglomeration.)

Table 9.4 Observed Crud Formation in the Settler

Solids in feed (ppm)	0	50	100	500	100	100
Impeller speed (rev/s)	14.5	14.5	14.5	14.5	7.5	25
Thickness of crud (mm)	0	1.2	1.2	F	F	3
% of interface covered (approximate estimate)	0	5-10	30-40	100	20	60

F - fingers of crude extended into the aqueous

impellor speed.

The crud formed brown films of syrup-like consistency, which sometimes bunched up into masses of crud. "Fingers" of crud sometimes extended into the aqueous phase. There was a tendency for the crud to collect at the corners of the mixing vessel. If a fragment of crud broke away from the interface it would sink slowly through the aqueous phase. Larger grains of "sand" fell as clean, individual particles to the bottom of the settler. As mentioned in the last chapter, even extensive crud at the interface did not hinder coalescence of the dispersion. From Table 9.3 and Figure 6.8 it is seen that much of the solid material consisted of particles smaller than typical drop sizes produced in the mixer (50-800 μm).

Although an extensive crud phase was not produced in the series of runs for which solids were not added (no-extraction, fast-extraction, stripping), several observations are relevant to the matter at hand.

Uranium precipitates that formed during stripping behaved in a manner similar to the cruds produced with residue. The precipitates collected at the coalescing front, had a fluffy yellow appearance, and did not retard coalescence.

When the organic and aqueous phases were left in contact a whitish film tended to form or collect at the interface. This was noticed especially during interfacial tension measurements, when films formed within minutes of initially contacting the phases (the films were syphoned off before taking measurements). During extraction runs in the absence of added solids, thin grey films sometimes collected at the corners of the setter.

A simple test was performed to determine if the solid particles were preferentially wetted by either phase. The particles were first wetted in the leach phase (to simulate their initial wetting in the process), after which the organic phase was spread over them. The organic phase neither beaded on the mud, nor did it rapidly displace the interstitial water.

During the cleaning process for the organic phase (section 3) at one point the organic phase was contacted with tapwater in a plastic 45 gallon drum. Mixing produced a moderately stable oil-in-water emulsion (with 120 L of organic and 60 L of water) that had to be left overnight to separate in comparison with separation times of only 2 to 5 minutes normally. The cause of the stable emulsion is unknown. It may have something to do with electric double layer repulsion (DLVO theory).

9.2.3 Discussion

Because a microscopic analysis of the crud was not done, nor were tests of crud formation carried out with different types of solids (graphites, silicas, plastics etc), the experimental results allow little to be said about the crud except that crud of a certain type was formed during the short run times used in these experiments. However, it is interesting to diagnose the results in the light of theories of emulsion stability, and to consider how those theories might apply to this system.

The crucial factor influencing crud formation seems to be the presence of solids, whether they are formed by precipitation (uranium or entrained impurities in the stripping section), are simply suspended in the feed leach liquor, or fall into the system as dust or dirt. The fine solids that were intentionally introduced were smaller than the drops in the settler dispersion band, and were therefore of the right size to promote the formation of emulsions.

Let us assume that the solids were slightly hydrophilic, and fairly small in relation to drops in the dispersion band. According to Mizrahi and Barnea's (46) model, we would expect the solids to accelerate coalescence in the dispersion band, leading to reduced dispersion band heights. On the other hand, the solids would tend to

stabilize any organic drops that formed, acting as a barrier preventing their close approach. Additionally, a very fine matrix of continuous aqueous film/ organic drops/ and fine solids would have a density between that of the aqueous and organic phases, provided the solids concentration was not too great. The crud would therefore float somewhere in the dispersion band. Mizrahi and Barnea's model therefore may provide a plausible explanation of the experimentally observed behaviour of the crud. Figure 9.4 illustrates the proposed structure of crud.

If the preceding model of the crud is accepted, questions arise as to how and where the crud is formed. Very small drops are produced in the mixer. However, the assumption that crud is formed in the mixer and is carried into the settler assumes that somehow a high concentration of solid particles must collect around a small oil drop in the mixer, which seems unlikely. At the coalescing front the concentration of solids is relatively high thus providing an ideal environment for crud formation of the proposed type. A suitable mechanism for the production of oil drops in the dense sublayer is provided by the phase inversion process illustrated by Figure 9.5.

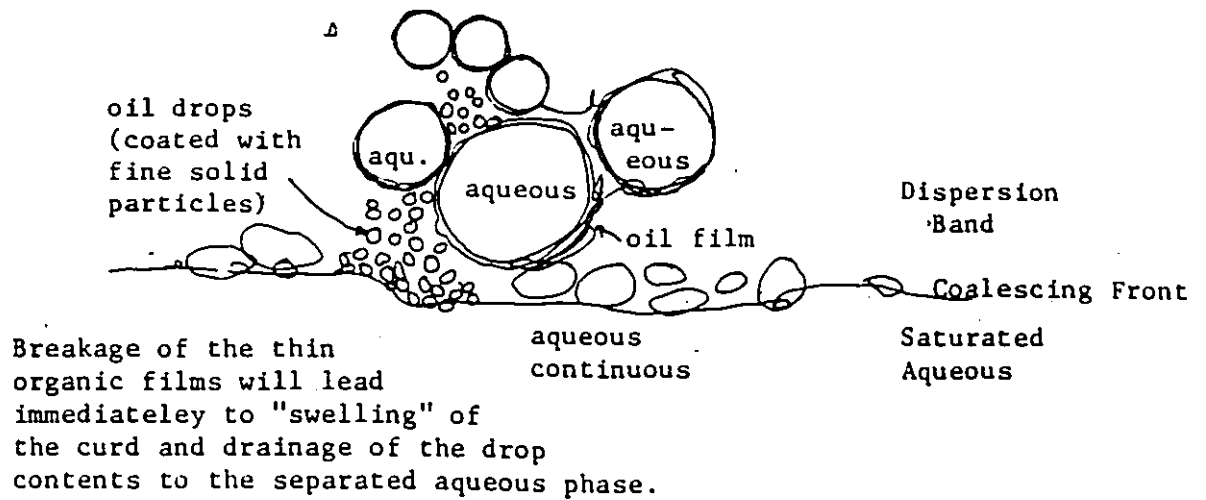


Figure 9.4 POSSIBLE STRUCTURE OF CRUD

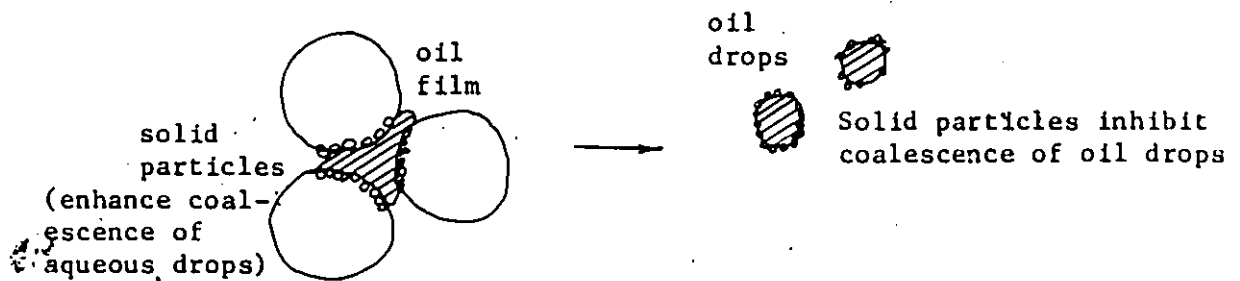
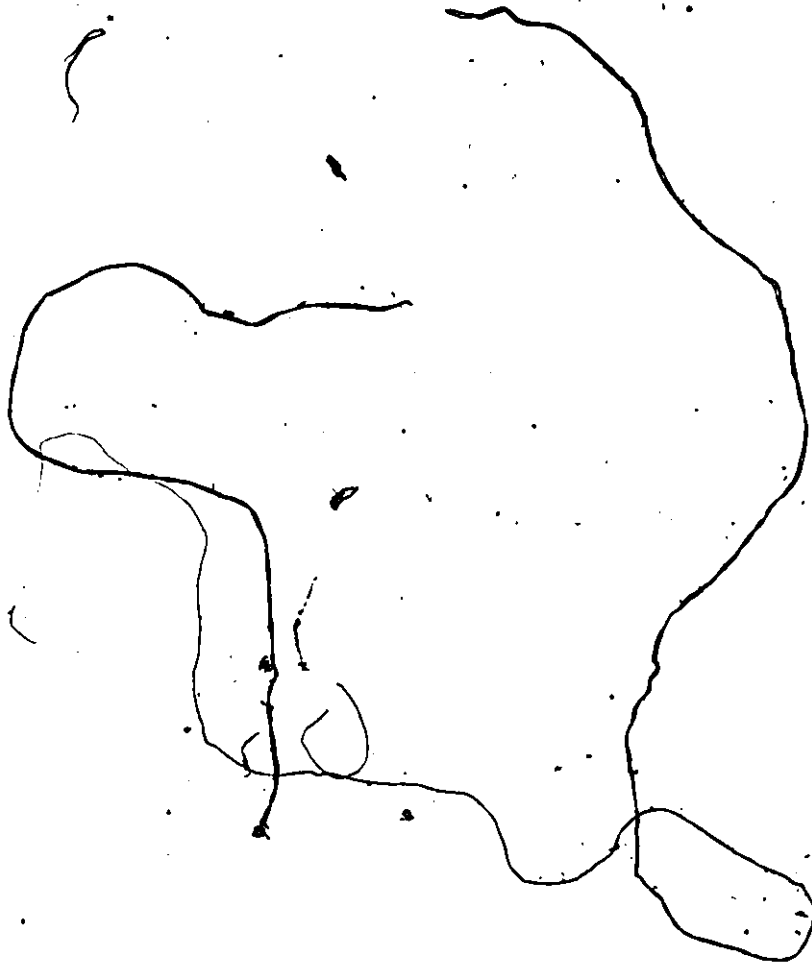


Figure 9.5 PHASE INVERSION MECHANISM OF CRUD FORMATION

9.3 CONCLUSIONS

Crud only formed in the settler when solids were present. Preliminary results suggested that higher impellor speeds promote crud formation.. However, further work is required to confirm this and to determine the onset of crud formation, the mechanisms of crud formation, the structure of crud, and its effects on settler performance, especially for long operating times.



REFERENCES

The following symbols have a special significance in the bibliography;

v volume of a journal
 n number of a journal
 p page number
 q a list of page numbers in this report that quote the reference

-
- 1 Arai, K. Konno, M. Matunaga, Y. Saito, S.
 Effect of dispersed-phase viscosity on the maximum stable drop size for breakup in turbulent flow
 J. Chem. Eng. Japan v10 n4 p325 1977 (q 109)

 - 2 Baird, M.H.I. Nirdosh, I.
 Surface and interfacial tension measurements by drainage methods
 Can. J. Chem. Eng. v59 n3 p369 1981 (q 75)

 - 3 Bajpai, R.K. Ramkrishna, D. Prokop, A.
 A coalescence redispersion model for drop size distributions in an agitated vessel
 Chem. Eng. Sci. v31 p913 1976 (q 119 120 121)

 - 4 Barnea, E. Mizrahi, J.
 Liquid-liquid contacting- art or science?

 Part I - Characteristics of liquid-liquid systems
 Hydrometallurgy v5 p15 1979 (q 165)

 Part II - Design methods for mixer-settlers
 Hydrometallurgy v5 p127 1980 (q 165)

 - 5 Barnea, E. Mizrahi, J.
 Separation mechanism of liquid-liquid dispersions in a deep layer gravity settler
 Trans. Inst. Chem. Eng. v53 p61 1975

 Part I- The structure of the dispersion band
 p61 (q 31 165)

 Part II- Flow patterns of the dispersed and continuous phases within the dispersion band
 (q 166)

 Part III- Hindered settling and drop-to-drop coalescence in the dispersion band
 (q 173 182 276)

 Part IV- Continuous settler characteristics
 (q 181 195)

- 6 Batchelor, G.K.
The theory of homogeneous turbulence
University Press, Cambridge 1953 (q 93)
- 7 Bates, R.L. Fondy, P.L. Corpstein, R.R.
An examination of some geometric parameters of
impeller power
I&EC Process Des. Dev. v2 n4 p311 1963 (q 92 101)
- 8 Becher, P.
Emulsions: theory and practice 2nd edition
Reinhold Publishing New York 1965
(q 97 174 175 185 209 212 213 214 215 276)
- 9 Bikerman, J.J.
Physical surfaces
Academic Press New York 1970 p13 (q 73)
- 10 Bird, R.B. Stewart, W.E. Lightfoot, E.N.
Transport Phenomena
John Wiley & Sons New York 1960 (q 143 332)
- 11 Bouyatiotis, B.A. Thornton, J.A.
Part I- Drop size and holdup measurements
in a seven inch diameter baffled vessel
Inst. Chem. Eng. Symp. Ser. 26 Inst. Chem. Eng. 1967
(q 101 102 123)
- 12 Brown, D.E. Pitt, K.
Drop size distribution of stirred non-coalescing
liquid-liquid system
Chem. Eng. Sci. v27 p577 1972 (q 19 136)
- 13 Calderbank, P.H.
Part I: The Interfacial Area in Gas-Liquid
Contacting with Mechanical Agitation
Trans. Inst. Chem. Eng. v36 p439 1958 (q 126)
- 14 Carino, A.B.
Uranium recovery at the Rabbit Lake operation
of Gulf Minerals Canada Ltd
Proceedings of the 8th CIM Conference on Hydrometallurgy
Montreal August 1978 (q 2 62 63 206)
- 15 Cayius, J.L. Schecter, R.S. Wade, W.H.
The measurement of interfacial tension via the
spinning drop technique
Adsorption at Interfaces, Symposium Series
Volume 8 American Chemical Society 1975 (q 75)
- 16 Coleman, C.F. Brown, K.B. Moore, J.G. Crouse, D.J.
Solvent extraction with alkyl amines
Ind. Eng. Chem. v50 n12 p1756 1958 (q 43 46 62 63)

- 17 Coualaloglou, C.A. Tavlarides, L.L.
Drop size distributions and coalescence frequencies of
liquid-liquid dispersions
AIChE J. v22 n2 p289 1976 (q 122)
- 18 Crank, J.
The mathematics of diffusion
Clarendon Press Oxford p90 1956 (q 147 148 310 312)
- 19 Crockford, H.D. Simmons, N.L.
The activity coefficients of sulfuric
acid in aqueous solutions of ammonium sulfate at 25°C
J. Am. Chem. Soc. v56 p1437 1934 (q 52)
- 20 Curl, R.L.
Dispersed phase mixing: I Theory and effects
in simple reactors
AIChE J. v9 n2 p175 1963 (q 145)
- 21 Davies, J.T. Rideal, E.K.
Interfacial phenomena
Academic Press New York 1961 (q 73)
- 22 Derjaguin, B.V. Landau, L.
Acta Phys. Chem. URSS v14 p633 1941
or J. Expt. Theor. Physics v15 p663 1945 (q 210)
- 23 Doulah, M.S.
An effect of holdup on drop sizes in liquid-liquid
dispersions
Ind. Eng. Chem. Fundam. v14 n2 p137 1975 (q 116)
- 24 Flynn, A.W. Treybal, R.E.
Liquid-liquid extraction in continuous flow
agitated extractors
AIChE J. v1 n3 p324 1955 (q 145 238)
- 25 Giles, J.W. Hanson, C. Marsland, J.G.
Drop size distributions in agitated liquid-liquid
systems with simultaneous interfacial mass transfer and
chemical reaction
Solvent Extr., Proc. Int. Solvent Extr. Conf., 1971
v1 p94 (q 116)
- 26 Glasser, D. Arnold, D.B. Bryson, A.W. Vieler, A.M.S.
Aspects of mixer-settler design
Miner. Sci. Eng. v8 n1 p23 1976 (q 149 339)

- 27 Hanson, C. editor
Recent advances in liquid-liquid extraction
Pergamon Press Oxford 1971 (q 149 171 173)
- Jeffries, C.V. Davies, G.A.
Chap 14- Coalescence of liquid droplets and
liquid dispersions (q 170 172)
- 28 Harriot, P.
Mass transfer to particles Part I-
Suspended in agitated tanks
AIChE J. v8 n1 p93 1962 (q 149 325)
- 29 Hinze, J.O.
Fundamentals of the hydrodynamic mechanism of
splitting in dispersion processes
AIChE J. v1 n3 p289 1955 (q 116 295)
- 30 Hinze, J.O.
Turbulence 2nd edition
McGraw-Hill, New York 1975 (q 93 94 110)
- 31 Holmes, D.B. Vancken, R.M. Dekker, J.A.
Fluid flow in turbine stirred baffled tanks- I
Chem. Eng. Sci. v19 p201 1964 (q 91)
- 31a Horner, D. Mailen, J. Thiel, S. Scott, T.
Interphase transfer kinetics of uranium using the drop
method, Lewis cell, and Kenics mixer
Ind. Eng. Chem. Fundam. v19 n1 p103 1980 (q 145)
- 32 Hornbeck, R.W.
Numerical Methods
Quantum Publishers Inc., New York, 1975 p16 (q 243)
- 33 Howarth, W.J.
Measurement of coalescence frequency in an agitated
tank
AIChE J. v13 n5 p1009 1967 (q 127)
- 34 Howell, W.N. Golding, J.A. Ritcey, G.M.
The submerged sphere analogy of isotropic turbulence
Unpublished - available from J.A. Golding
University of Ottawa (q 97)
- 35 Howell, W.N. Golding, J.A. Ritcey, G.M.
The vibrating drop model for drop breakup in isotropic
turbulence
Unpublished - available from J.A. Golding
University of Ottawa (q 93)

- 36 Howell, W.N. Golding, J.A. Ritcey, G.M.
Continuous phase mass transfer coefficients in
isotropic turbulence
Unpublished - available from J.A. Golding
University of Ottawa (q.127)
- 37 Hsia, M.A. Tavlarides, L.L.
A simulation model for homogeneous dispersions
in stirred tanks
Chem. Eng. J. v20 p225 1980 (q 124 136)
- 38 Kolarik, Z. Pipkin, N.
Drop size distribution in stirred tanks using
the uranyl nitrate/tributyl phosphate extraction system
Hydrometallurgy v9 n3 p371 1983
(q 19 116 123 131 136)
- 39 Kolmogoroff, A.N.
The local structure of turbulence in incompressible
viscous fluid for very large Reynold's numbers
C. R. Acad. Sci. URSS v30 p301 1941 (q 93 95)
- 40 Levenspiel, O.
Chemical reaction engineering 2nd edition
John Wiley & sons New York 1972 p260 (q 143)
- 41 London Chemical Society
Stability constants of metal ion complexes
Metcalf & Cooper London 1964 p232 (q 52 238)
- 42 Madden, A.J. Damerell, G.L.
Coalescence frequencies in agitated liquid-liquid
systems
AIChE J. v18 n2 p233 1962 (q 127)
- 43 McCabe, W.L. Smith, J.C.
Unit Operations of Chemical Engineering
McGraw-Hill New York 3rd ed 1976 (q 90 276)
- 44 Merritt, R.C.
The extractive metallurgy of uranium
Colorado School of Mines Research Institute 1971 (q 2)
- 45 Miller, R.S. Ralph, J.L. Curl, R.L. Towell, G.D.
Dispersed phase mixing:
II Measurements in organic dispersed systems
AIChE J. v9 n2 p196 1963 (q 127 145)
- 46 Mizrahi, J. Barnea, E.
The Effects of Solid Additives on the formation and
separation of emulsions
Brit. Chem. Eng. v15 n4 p497 1970 (q 177 178 206 209)

- 47 Mlynsek, Y. Resnick, W.
Drop sizes in an agitated liquid-liquid system
AIChE J. v18 n1 p122 1972 (q 116 126 131)
- 48 Mok, Y.I. Treybal, R.E.
Continuous phase mass transfer coefficients for
liquid extraction in agitated vessels: II
AIChE J. v17 n4 p916 1971 (q 122 123 149)
- 49 Mugele, R.A. Evans, H.D.
Droplet size distributions in sprays
Ind. Eng. Chem. v43 n6 p1317 1951 (q 120 121)
- 50 Murdoch, R. Pratt, H.R.
Liquid-liquid extraction Part VIII- The extraction
of uranyl nitrate in a wetted wall column
Trans. Inst. Chem. Eng. v31 p307 1953 (q 145)
- 51 Engineering Data Book 9th edition
Natural Gas Processors Suppliers Association
Tulsa 1972 pages 16-10 and 16-38 (q 270)
- 52 Nagata, S.
Mixing- Principles and Applications
John Wiley & Sons New York 1975 p156 (q 90 276)
- 53 Nienow, A.W. Miles, D.
Impeller power numbers in closed vessels
Ind. Eng. Chem. Process Des. Dev. v10 n1 p41 1971
(q 101)
- 54 Park, J.Y. Blair, L.M.
The effect of coalescence on drop size distribution
in an agitated liquid-liquid dispersion
Chem. Eng. Sci. v30 p1057 1975 (q 125)
- 55 Perry, R.H. Chilton, C.H. editors
Chemical engineer's handbook 5th edition
McGraw Hill New York 1963 (q 149 268 269 316 320)
- 56 Randall, M. Langford, C.T.
The activity coefficients of sulfuric acid in
aqueous solutions with sodium sulfate at 25°C
J. Am. Chem. Soc. v49 p1445 1927 (q 52 238)
- 57 Ritcey, G.M.
Crud in solvent extraction processing- a review of
causes and treatment
Hydrometallurgy v5 p97 1980 (q 204 206 207 215)
- 58 Ritcey, G.M. Wong, E.W.
Influence of cations on crud formation in uranium
circuits
CANMET report (to be published in Hydrometallurgy)
(q 44 208)

- 59 Ritcey, G.M. Ashbrook, A.W.
Solvent extraction principals and applications
to process metallurgy Part I
Elsevier Publ. Co. Amsterdam 1984 (q 2)
- 60 Ritcey, G.M. Ashbrook, A.W.
Solvent extraction principals and applications
to process metallurgy Part II
Elsevier Publ. Co. Amsterdam 1979 (q 2)
- 61 Roger, W. Trice, V.G. Rushton, J.H.
Effect of fluid motion on interfacial area of
dispersions
Chem. Eng. Prog. v52 n12 p515 1956 (q 116 123)
- 62 Ross, L. Verhoff, F.H. Curl, R.L.
Droplet breakage and coalescence processes
in an agitated dispersion
2- Measurement and interpretation of mixing experiments
Ind. Eng. Chem. Fundam. v17 p101 1978 (q 123 124 136)
- 63 Rushton, J.H. Costich, E.W. Everett, H.J.
Power characteristics of mixing impellers
Chem. Eng. Prog. v46 n9 p395 1950 (q 90)
- 64 Ryon, A.D. Daley, F.L. Lowrie, R.S.
Scale up of mixer settlers
Chem. Eng. Prog. v55 n10 p71 1959 (q 183 195 187)
- 65 Ryon, A.D. Lowrie, R.S.
Batch and continuous extraction of uranium from aqueous
sulfate solutions into kerosene and amines, stripping
with aqueous sodium carbonate: baffled vessels, turbine
agitated
Oak Ridge National Laboratory USAEC ORNL-3381 1960
(q 7 29 161 208 210)
- 66 Schindler, H.D. Treybal, R.E.
Continuous phase mass transfer coefficients
for liquid extraction in agitated vessels
AIChE J. v14 n5 p791 1968 (q 127)
- 67 Sherman, P. editor
Emulsion science
Academic Press London 1968 (q 97 209 210 211)

Gopal, E.S.

Chapter Principles of emulsion formation
(q 109 110)

Kitchener, J.A. Musselwhite

Chapter Theory of the stability of emulsions
(q 172 174 176 212)

- 68 Shinnar, R. Church, J.M.
Statistical theories of turbulence in predicting
particle size in agitated dispersions
Ind. Eng. Chem. v52 n3 p253 1960 (q 93 96 101 112)
- 69 Shinnar, R.
On the behaviour of liquid dispersions in mixing
vessels
J. Fluid Mech. v10 p259 1961 (q 24 93 114 115 116 126)
- 70 Smoluchowski, M. Von
Mathematical theory of the kinetics of the
coagulation of colloidal solutions
Z. Phys. Chem. v92 p129 1917 (q 171)
- 71 Snell, F.D. Ettre, L.S. editors
Encyclopedia of industrial chemical analysis
Interscience Publishers, New York, v19 p251 1974
(q 157)
- 72 Spielman, L.A. Levenspiel, O.
A Monte-Carlo treatment for reacting and coalescing
dispersed phase systems
Chem. Eng. Sci. v20 p247 1965 (q 145)
- 73 Sprow, F.B.
Drop size distributions in strongly coalescing
agitated liquid-liquid system
AIChE J. v13 n5 p995 1967 (q 126)
- 74 Swartz, N. Bezemer, C.
Kolloidzeitschrift v146 p139 1956
(refer to Sprow- reference 77)
- 75 Tavlarides, L.L. Stamatoudis, M.
The analysis of interphase reactions and mass
transfer in liquid-liquid dispersions
Adv. Chem. Eng. v11 p199 1981
(q 93 116 118 119 144 145)
- 76 Taylor, G.I.
Statistical theory of turbulence
Proc. R. Soc. London v151a p421 1935 (q 93)
- 77 Van Heuven, J.W. Beek, W.J.
Power input, drop size, and minimum stirrer
speed for liquid-liquid dispersions in stirred vessels
Solvent Extr., Proc. Int. Solvent Extr. Conf., 1971
(q 116)
- 78 Vermeulen, T. Williams, G.M. Langlois, G.E.
Interfacial Area in Liquid-Liquid and Gas-Liquid
Agitation
Chem. Eng. Prog. v51 n2 p85-F 1955 (q 98 116 276)

- 79 Verwey, E.J. Overbeek, J.T.
Theory of the stability of lyophobic colloids
Elsevier Publishing Co New York pl28 1948 (q 210)
- 80 Vrij, A.
Possible mechanism for the spontaneous rupture of thin,
free liquid films
Colloid stability in aqueous and non-aqueous media
Discussions of the Faraday Society v42 p23 1966 (q 173)
- 81 Waldpole, R.E. Myers, R.H.
Probability and statistics for scientists and engineers
Macmillan Co., New York, 1972 p67
- 82 Wirth, H.E.
Activity coefficients in sulfuric acid and
sulfuric acid- sodium sulfate mixtures
Electrochimica Acta vl6 pl345 1971 (q 52 238)
- 83 Young, W.
Crud in Gulf Mineral's Rabbit Lake solvent extraction
circuit
Gulf Minerals Canada Ltd 1979 (q 44 204 206)
- +

Appendix A.2

Mixer Settler Runs

The table on the following page summarizes the residence times and impellor speeds for the various runs of the project.

Table A.2.1 - Run Sequences, Impellor Speeds,
Mixer Residence Times, and
Nomenclature for the Different Series of Runs

SERIES									
	no extraction		fast extraction		slow extraction			stripping	
symbol	ENNA		ENNA 1&2		EMSS and EMSA			SMNAB 1&2	
run	T	N	T	N	T	N	solids	T	N
1	60	24.8	60	33.3	60	14.5	0	60	11
2	"	21.7	"	24.8	"	14.5	100	"	14.5
3	"	34.3	"	7.5	"	14.5	50	"	24.8
4	"	30.3	"	18.2	"	14.5	500	"	7.5
5	"	18.2	30	33.3	"	7.5	100	20	14.5
6	"	33.3	"	24.8	"	24.8	100	"	7.5
7	"	11	"	7.5				"	11
8	"	28.2	"	18.2				"	24.8
9	"	32.8							
10	"	14.5							
11	"	7.5							

T = mixer residence time (s)

N = impellor speed (s'')

solids = solids addition (ppm)

Appendix A.3 - Chemical Equilibrium

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A.3.0 INTRODUCTION

This appendix supplies supporting data and calculations for Section 3 in the main body of the report, which is concerned with phase preparation and chemical equilibrium. Tables A.3.1 and A.3.2 summarize the chemical equilibrium data for the distribution of uranium between the aqueous and the organic phases for extraction and stripping respectively. The remainder of this appendix deals with the calculation of chemical equilibrium between aqueous ionic species using literature values for the equilibrium constants.

Table A.3.1 - Chemical Equilibrium Data for Extraction (25°C)

O/A ratio	0.25	0.50	1.0	1.5	2.0	3.0	4.0	5.0	8.0	10
Equilibrium pH	1.65	1.64	1.64	1.63	1.63	1.64	1.66	1.66	1.66	1.66
[U] aqueous (g/L)	2.00	1.11	0.10	0.041	0.032	0.0077	0.0050	0.0028	0.0014	0.0032
[U] organic (g/L)	3.48	3.4	2.6	1.6	1.3	0.92	0.75	0.57	0.39	0.32

Table A.3.2 - Chemical Equilibrium Data for Stripping (25°C)

O/A ratio	0.25	0.50	1.00	1.5	3.0	5.0	10	15	20	40
Equilibrium pH	4.21	4.14	4.03	4.40	4.27	4.16	3.97	3.92	4.05	4.05
[U] aqueous (g/L)	0.72	1.6	2.7	4.6	9.7	12	18	34	40	40
[U] organic (g/L)	0.42	0.53	0.71	0.78	0.53	0.81	1.16	1.16	1.04	1.04

A.3.1 AQUEOUS PHASE EQUILIBRIUM CALCULATIONS

A.3.1.1 Chemical Equilibrium

The problem is to find the equilibrium endpoint of a solution of chemicals. Equilibrium constants were obtained from the literature that are intended to be used with the concentrations (not the activities) of reaction species. (see Crockford and Simmons (24), London Chemical Society (47), Randall and Langford (61), Wirth (85)). In the case of the hydrogen ion, the hydrogen ion activity was measured potentiometrically (pH meter). In order to convert the activity (a_{H^+}) to a concentration, a constant hydrogen ion activity coefficient (f_{H^+}) was assumed:

$$\log f_{H^+} = -0.1 = \log \left[\frac{a_{H^+}}{[H^+]} \right] \quad \text{or} \quad [H^+] = 10^{-(pH+0.1)}$$

A.3.1.2 Problem Formulation

1. Independent Variables - Independent chemical species were selected as a "basis" to calculate the concentrations of all other chemical species. Because physically there is a unique solution to the equilibrium problem (or at least there is assumed to be a unique solution) the number of independent species concentrations will equal the number of independent mass balances. The selected basis for extraction and

stripping are listed below:

leach equilibrium	strip equilibrium
$[\text{SO}_4^{2-}]$	$[\text{SO}_4^{2-}]$
$[\text{NaSO}_4^-]$	$[\text{HSO}_4^-]$
$[\text{UO}_2(\text{SO}_4)_3^{4-}]$	$[\text{NH}_4\text{SO}_4^-]$
	$[\text{H}_2\text{O}]$

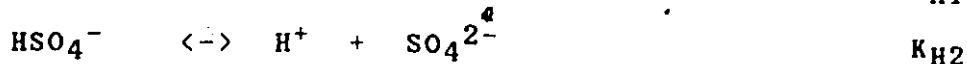
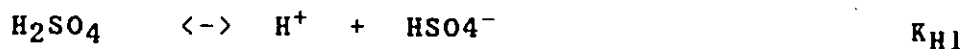
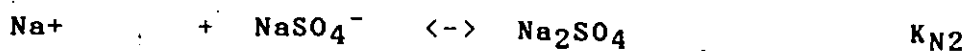
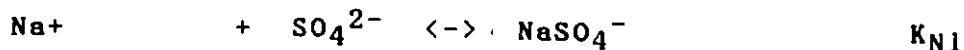
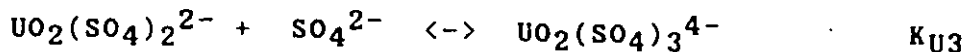
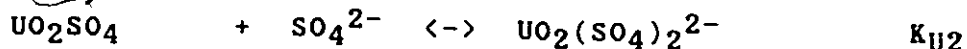
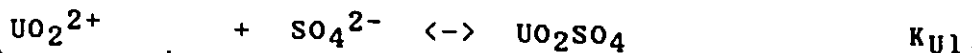
With one more degree of freedom, the solution of the chemical equilibrium conditions in the aqueous phase for stripping is more difficult than for extraction. Two approaches were actually tried for the solution of the stripping equilibrium. The first and more complete solution utilised the basis as shown above, resulting in the program in section A.3.2 of this appendix. A simpler problem resulted from assuming that all the NH_4OH disappears when added to an acidic solution, and that changes in the concentration of water could be ignored, thereby making the analysis for the case of stripping the same as for extraction except for the change from sodium to ammonium ions.

2. Equilibrium Equations

The assumed reactions for the aqueous ionic species are listed below along with estimates of their equilibrium constants. Equilibrium constants are of the form:

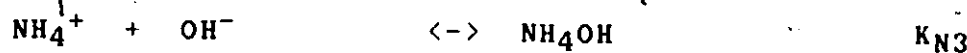
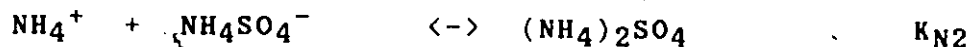
$$K = \frac{\prod [\text{products}]^{P_i}}{\prod [\text{reactants}]^{R_i}} \quad P_i, R_i - \text{stoichiometric coefficients}$$

Leach Equilibrium

Equilibrium
Constant

Strip Equilibrium

K_{U1} , K_{U2} , K_{U3} - are the same as for the leach equilibrium



K_{H1} , K_{H2} - are the same as for the leach equilibrium



3. Mass Balances - In the calculation routine, the values of the independent variables are initially guessed. The other chemical species are calculated according to the equilibrium equations. Mass balances are rearranged to recalculate the independent variables. It is implicitly assumed that phase volume changes are negligible and can be ignored in the mass balance equations. The differences between the initial and recalculated values of the independent variables are used to give an "error" term. Numerous criteria were then applied to

select a new set of values that would reduce the error term.

At a solution point the error term tends to zero.

Leach mass balances

$$\epsilon_{SO42-} = ([UO_2SO_4]_o + [Na_2SO_4]_o + [H^+]/2 - [HSO_4^-]/2 \\ - 2*[UO_2(SO_4)_2^{2-}] - 3*[UO_2(SO_4)_3^{4-}]) - [SO_4^{2-}]$$

$$\epsilon_{NaSO4-} = (2*[Na_2SO_4]_o - [Na^+] - 2*[Na_2SO_4]) - [NaSO_4^-]$$

$$\epsilon_{UO_2(SO_4)_3^{4-}} = ([UO_2SO_4]_o - [UO_2^{2+}] - [UO_2SO_4] - [UO_2(SO_4)_2^{2-}] \\ - [UO_2(SO_4)_3^{4-}])$$

Stripping mass balances

$$\epsilon_{SO42-} = ([(NH_4)_2SO_4]_o + [H_2SO_4]_o + [UO_2SO_4] - [HSO_4^-] \\ - [H_2SO_4] - [NH_4SO_4^-] - [(NH_4)_2SO_4] - [UO_2SO_4] \\ - 2*[UO_2(SO_4)_2^{2-}] - 3*[UO_2(SO_4)_3^{4-}]) - [SO_4^{2-}]$$

$$\epsilon_{NH4SO4} = (2*[(NH_4)_2SO_4]_o - [H_2O]_o - [NH_4^+] - 2*[(NH_4)_2SO_4] \\ + [OH^-] + [H_2O]) - [NH_4SO_4^-]$$

$$\epsilon_{UO2SO4} = ([UO_2(SO_4)_3]_o - [UO_2^{2+}] - [UO_2(SO_4)_2^{2-}] \\ - [UO_2(SO_4)_3^{4-}]) - [UO_2SO_4]$$

$$\epsilon_{H2O} = ([H_2O]_o + 2*[H_2SO_4]_o - [HSO_4^-] - 2*[H_2SO_4] - [H^+]) \\ - [H_2O]$$

A.3.1.3 Method of Calculations

1. Flowchart

Shortcut routines were used to calculate good initial guesses of the independent variables.

Objective function - square root of the sum of the squared error terms

Partial derivatives - were calculated from three point central differences for each independent variable.

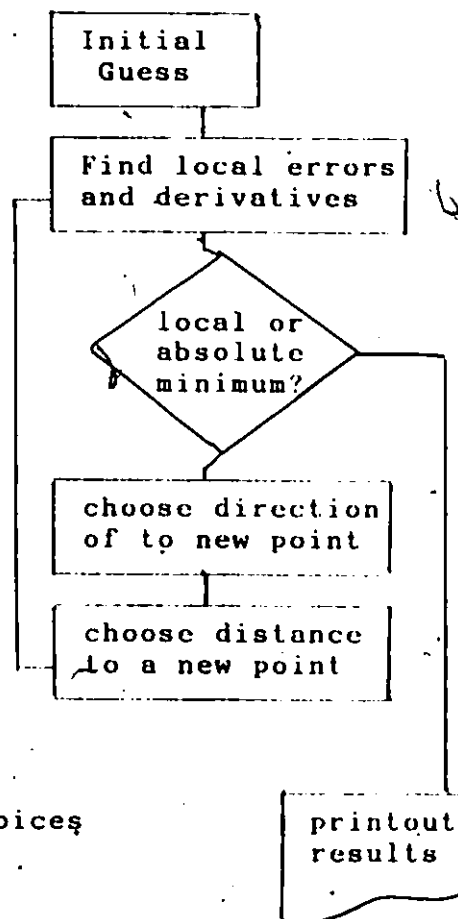
Convergence criteria -

- 1) absolute minimum - objective function less than a maximum permissible error
- 2) local minimum - gradient less than a certain value.

Direction of next search - two choices

- 1) gradient - follow the gradient (backwards)
- 2) maxer - minimize the maximum component error (due to the special form of the error terms)

Step size decision - explained on the next page



2. Distance to the new point - Having chosen the direction of search for a new point, it must be decided how far one should go in the specified direction. For this decision first, second, and third directional derivatives are calculated at the old point using a 4 point forward

difference formula. The four points are along the direction of search, spaced apart by a distance h equal to about 0.1% of the magnitudes of the independent variables.

Taking the gradient search for example and:

ϵ = objective function (rms of sum of squared individual errors)

$\vec{s}$ = unit vector in direction of search

$\vec{r}$ = vector to the new point (desired value, colinear with $\vec{s}$)

$|\vec{s}|$ = magnitude of the vector to the new point

h = distance between the 4 points

Therefore the direction of search is defined by:

$$\vec{s} = \frac{-\vec{\nabla}\epsilon}{|\vec{\nabla}\epsilon|}$$

Denoting the values of the objective function at the 4 points in the direction of search as $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$ and its value at the old point as ϵ_0 ; (from Hornbeck (32)) the first, second, and third derivatives of the objective function are given by:

$$\epsilon'(0) = (-11*\epsilon_0 + 18*\epsilon_1 - 9*\epsilon_2 + 2*\epsilon_3) / 6*h$$

$$\epsilon''(0) = (2*\epsilon_0 - 5*\epsilon_1 + 4*\epsilon_2 - \epsilon_3) / h^2$$

$$\epsilon'''(0) = (-5*\epsilon_0 + 18*\epsilon_1 - 24*\epsilon_2 + 14*\epsilon_3 - 3*\epsilon_4) / 2*h^3$$

Various criteria were then applied, each of which predicts a maximum permissible step size, s_{max} . The minimum of the maximum step sizes was taken as $|\vec{s}|$.

A) Relative maximum step size - An overall maximum step size was imposed, varying from 5% to 50% of the magnitude of the variables, depending on the particular problem being solved.

B) Descent criterion- The new point should have a lower error than the present point.

$$\text{i.e. } \epsilon'(s) \leq 0$$

Assuming a simple parabolic form of the path, the maximum step size will be where the path begins to curve upwards.

$$\epsilon'(s) = \epsilon'(0) + s*\epsilon''(0) + s^2*\epsilon'''(0)$$

$$\epsilon'(s) = 0$$

$$s_{\text{descent}} = \frac{-\epsilon''(0) \pm \sqrt{\epsilon''(0)^2 - 4*\epsilon'''(0)*\epsilon'(0)}}{2*\epsilon'''(0)}$$

Take the smallest positive value of s_{descent} .

C) Acceleration criterion- The maximum relative change of the gradient is limited.

$$\left| \frac{\epsilon'(s)}{\epsilon'(0)} \right| \leq \Delta\epsilon'_{\text{max}}$$

$$\text{use } \epsilon'(s) = \epsilon'(0) + s*\epsilon''(0) + s^2*\epsilon'''(0)$$

$$\frac{\epsilon'(s)}{\epsilon'(0)} = 1 + s*\frac{\epsilon''(0)}{\epsilon'(0)} + s^2*\frac{\epsilon'''(0)}{\epsilon'(0)}$$

$$\text{so } s_{\text{accel}} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \text{where } \begin{aligned} a &= \epsilon'''(0) / \epsilon'(0) \\ b &= \epsilon''(0) / \epsilon'(0) \\ c &= 1 - \Delta\epsilon'_{\text{max}} \end{aligned}$$

Take the smallest positive value of s_{accel} :

D) Steepness criterion - The overall relative change of the objective function is limited.

$$\Delta\epsilon_{\text{min}} \leq \frac{\epsilon(s)}{\epsilon(0)} \leq \Delta\epsilon_{\text{max}} \quad \text{in the program } \Delta\epsilon_{\text{max}} = 1/\Delta\epsilon_{\text{min}}$$

$$\text{use } \epsilon(s) = \epsilon(0) + s*\epsilon'(0) + s^2*\epsilon''(0) + s^3*\epsilon'''(0)$$

$$\frac{\epsilon(s)}{\epsilon(0)} = 1 + s*\frac{\epsilon'(0)}{\epsilon(0)} + s^2*\frac{\epsilon''(0)}{\epsilon(0)} + s^3*\frac{\epsilon'''(0)}{\epsilon(0)}$$

An iterative approach was used to determine the maximum step size according to the steepness criterion.

E) Range of values criterion - A range of permissible values is assigned to each independent variable. This criterion warns of new points that lie outside of the permissible (or expected) range.

Having calculated the distance $s_{\max}$ to the new point, the corresponding changes in each of the individual variables is;

$$\Delta x_1 = \vec{s} \cdot \vec{\delta}_1 \quad \begin{array}{l} \vec{s} = \text{vector to new point} \\ \vec{\delta}_1 = \text{unit vector of the independent variable} \end{array}$$

$$= \frac{s}{|\vec{\nabla} \epsilon|} * \left(\frac{-\partial \epsilon}{\partial x_1} \right) \quad \frac{\partial \epsilon}{\partial x_1} = \text{partial derivative of the objective function}$$

x_1 = one of the independent variables

A.3.1.4 Nomenclature for the Computer Programs

The programs for calculating aqueous phase equilibria are included at the end of this appendix. A listing of the program variables and their meaning is included on the following three pages. Due to a lack of complete documentation, the use of unstructured programming style in a cramped (16 K) memory space, two character variable names, and the modest length of the programs there may be some difficulty in understanding all of what is written. Nevertheless, the explanations of the procedures along with these variable listings should allow someone to follow the programs with a little effort.

Search Constants and Variables

Step Size Criteria Constants

C1	=	ϵ	convergence at a local minimum
C3	=	$\Delta\epsilon'_{\max}$	acceleration
C4	=	$\Delta\epsilon_{\max}$	steepness
C5	=		relative maximum step size
C6	=	ϵ	convergence at the absolute solution
C9	=		safety factor

Range of Permissible Values Criteria

X8(I)	=	minimum permissible value of basis i
X9(I)	=	maximum permissible value of basis i

Step size variables and constants

S0	=	$s_{\max}$	
S2	=	s_{descent}	
S3	=	s_{accel}	
S4	=	s_{steep}	
S5	=	s_{step}	
S6(I)	=	$s_i(\text{step})$	
S9	=	dx	small relative increment in independent variables for calculation of derivatives

Equilibrium Constants

K1 = K_{U1}	K4 = K_{N1}	K7 = K_{H1}
K2 = K_{U2}	K5 = K_{N2}	K8 = K_{H2}
K3 = K_{U3}	K6 = K_{N3}	K9 = K_W

Nomenclature for the Computer Programs (continued)-----
Independent Variables and Functions

Independent Variables

N = # of independent variables
 $X1(I) = x_i$ old point
 $X2(I) = x_i$ used to calculate ϵ (subroutine)
 $X7(I) = (x_{imax} - x_{imin})$
 $X5(I) = \Delta x_i$ from old to new point
 $X8(I) = x_i \text{ min}$
 $X9(I) = x_i \text{ max}$
 $X6(I) = \Delta x_i$ equivalent to S9 for a given variable.

Functions

$F(I) = \epsilon_i$ for a given independent variable
 $E1 = \sqrt{2}\epsilon_i^2$ error at the new point
 $E(0) =$ error at the old point
 $E(1) \dots E(4)$ values of ϵ about the old point in the direction of search

Partial Derivatives

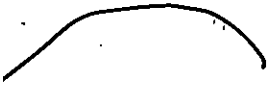
$P1(I) = d\epsilon/dx_i$
 $P2(I) = d^2\epsilon/dx_i^2$

Directional Derivatives (in the direction of the next point)

$D1 = \epsilon'(0)$
 $D2 = \epsilon''(0)$
 $D3 = \epsilon'''(0)$
 $D5(I) = dx_i/ds$

Special Variables

$P = \epsilon'^2 + 2\epsilon''\epsilon\Delta\epsilon_{\max}$





Nomenclature for the Computer Programs (continued)

Chemical Species Concentrations

		Extraction	Stripping
Sulfate	A0	$[\text{SO}_4^{2-}]$	same as leach
	A	$[\text{SO}_4]_{\text{Total}}$	"

Background Ion

N0	$[\text{Na}^+]$	$[\text{NH}_4^+]$
N1	$[\text{NaSO}_4^-]$	$[\text{NH}_4\text{SO}_4^-]$
N2	$[\text{Na}_2\text{SO}_4]$	$[(\text{NH}_4)_2\text{SO}_4]$
N9	$[(\text{Na}_2\text{SO}_4)]$	$[(\text{NH}_4)_2\text{SO}_4]$

Hydrogen Ion

H0	$[\text{H}^+]$	same as leach
H1	$[\text{HSO}_4^-]$	"
H2	$[\text{H}_2\text{SO}_4]$	"
H9	$[\text{H}_2\text{SO}_4]$	"

Uranyl	U0	$[\text{UO}_2^{2+}]$	same as leach
	U1	$[\text{UO}_2\text{SO}_4]$	"
	U2	$[\text{UO}_2(\text{SO}_4)_2^-]$	"
	U3	$[\text{UO}_2(\text{SO}_4)_4^-]$	"
	U9	$[\text{UO}_2\text{SO}_4]$	"

Hydroxide Ion

O1	$[\text{NH}_4\text{OH}]$
O3	$[\text{H}_2\text{O}]$
O7	$[\text{H}_2\text{O}]_o$
O9	$[\text{NH}_4\text{OH}]_o$

Polynomial Matrix

(graphing subrouting in the more complicated strip program)

W(M)

Best Point Found so far in the Stripping Program

W0	E(0)min	error at the point	
W1	A0	sulfate species	concentration
W2	N1	ammonium ion	"
W3	U1	uranyl sulfate complex	"
W4	O3	water	"

A.3.2 AQUEOUS STRIP PHASE EQUILIBRIUM

During stripping, sulfuric acid is released by the organic phase into the strip solution. Ammonium hydroxide is added to the solution to neutralize excess acid and thereby to maintain the pH at 4.0. Two approaches were used to analyse strip equilibrium.

1) Simple approximation - The total acid and ammonium hydroxide added to the solution were ignored. Instead the pH of a solution of uranyl nitrate and ammonium sulfate was calculated for varying amounts of sulfuric acid added to the solution. This approach allowed the application of the same program that was used for the aqueous leach phase, with minor modifications.

2) Involved approach - The total acid and ammonium hydroxide were taken into account. A modified but similar program was used for this case. Although this approach is "more rigorous" and more readily applicable to more complex equilibrium calculations, there were considerable problems with convergence to an accurate solution. Some of the results are plotted in Figure A.3.1. The inaccuracy of the results is evident in that the curves are irregular and their vertical sections predict more than one pH for the same ammonium hydroxide addition. It is also clearly seen how precise the NH_4OH additions must be in order to get the desired equilibrium pH.

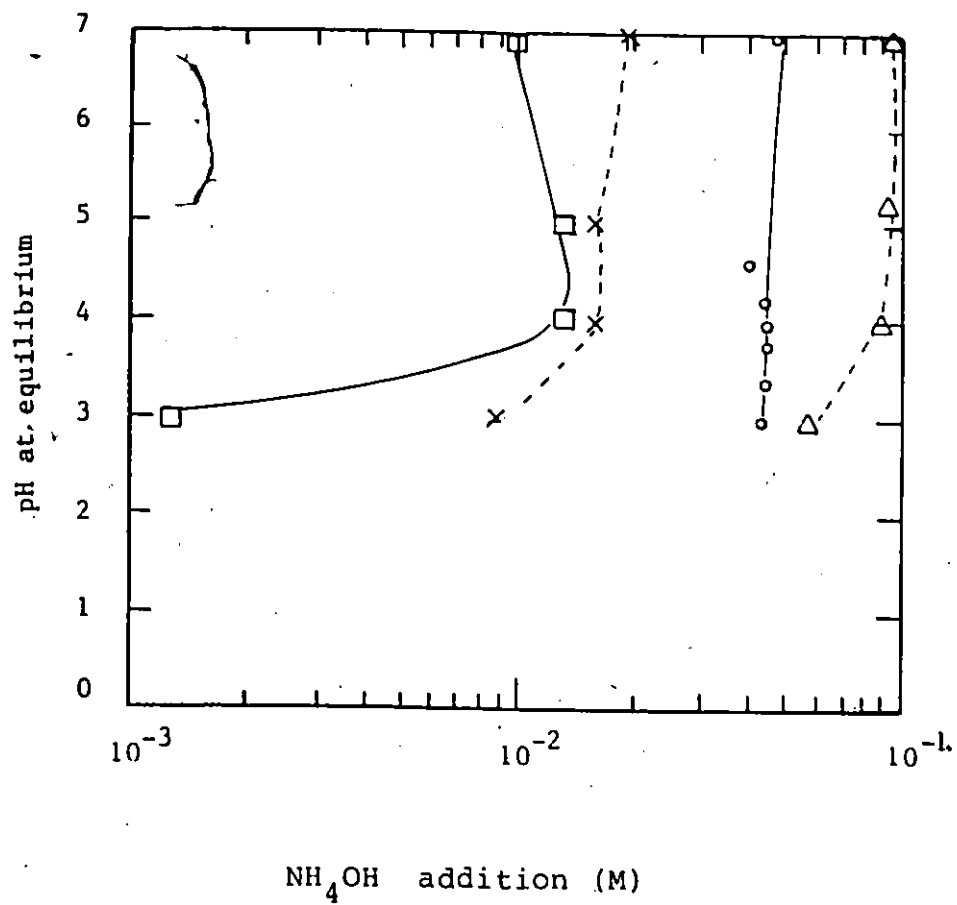


Figure A.3.1 pH ADJUSTMENT FOR THE STRIPPING
SOLUTION - INVOLVED APPROACH
TO THE CALCULATIONS

Listing A.3.1 Aqueous Leach Equilibrium Program

```

10 CLS :POKE-16553,255
30 'CHEMICAL CONSTANTS
40 DATA 64.5,4.92,15.8,3.16,0.01,0.164,0.0359,0
50 READ K1,K2,K3,K4,K5,K6,K7,K8,K9
60 'SEARCH CONSTANTS
65 C1=1E-4 :C3=10 :C4=50 :C5=500 :C6=0.01 :C8=2
70 C9=1.0 :S9=0.001 :K=3 :L1B="Y" :L2B="MAXER" :PH=3.2 :L3B="N"
75 'PRINTOUT OF CONSTANTS
77 IF L3B="Y" :GOSUB 3000
130 'DESIRED EQUILIBRIUM
131 J=0 :PH=PH+0.2 :N9=1E-5 :U9=1E-5
170 'PRINTOUT OF DESIRED EQUILIBRIUM
172 IF L1B="Y" :GOSUB 4100
190 'CONSTANTS OF CALCULATION
192 H0=10((-PH+0.1))
200 'CALCULATE THE INITIAL GUESS & PRINTOUT
205 GOSUB 8000 :IF L1B="Y" GOSUB 4150
210 'VARIABLE RANGES
215 FOR I=1 TO K :X8(I)=X1(I)/5 :X9(I)=X1(I)*5 :NEXT I
230 FOR I=1 TO K :X2(I)=X1(I) :NEXT I
233 GOSUB 2000
236 E(0)=E1 :FOR I=1 TO K :F1(I)=F(I) :NEXT I
238 'RESET THE CRITERIA
240 S0=C5 :S2=C5 :S3=C5 :S4=C5 :D1=0 :D2=0 :J=J+1
241 IF J=50 GOTO 900
245 IF L1B="Y" :PRINT :PRINT J
250 'CALCULATE E ALONG ALL AXIS ABOVE & BELOW OLD POINT
255 FOR I=1 TO K
260 FOR L=1 TO K :X2(L)=X1(L) :NEXT L
265 X6(I)=S9*X1(I) :X2(I)=X1(I)-S9*X6(I) :GOSUB 2000
270 E(1)=E1 :X2(I)=X1(I)+S9*X7(I) :GOSUB 2000
275 E(2)=E1
280 'FIRST AND SECOND PARTIAL DIFFERENTIALS
285 P1(I)=(E(2)-E(1))/2 :P2(I)=(E(2)-2*E(0)+E(1))
290 NEXT I
300 'DIRECTIONAL DERIVATIVES ESTIMATED FROM PARTIAL DERIVATIVES
305 FOR I=1 TO K :D1=D1+P1(I)*P1(I) :NEXT I
310 D1=SQR(D1)
315 FOR I=1 TO K :D5(I)=P1(I)/D1 :D2=D2+P2(I)*D5(I)*D5(I) :NEXT I
330 'PRINTOUT OF PARTIAL DERIVATIVES
340 IF L1B="Y" :GOSUB 4200
350 'DIRECTION OF THE NEXT STEP
360 'STEPPING ALONG THE GRADIENT
363 IF L2B="MAXER" GOTO 370
365 FOR I=1 TO K :X6(I)=X6(I)*(-D5(I)) :NEXT I
370 'STEPPING IN THE DIRECTION OF MAXIMUM ERROR
373 IF L2B="GRADIENT" GOTO 400
375 FOR I=1 TO K :IF D5(I)=0 THEN D5(I)=1
377 X6(I)=X6(I)*(-D5(I)/ABS(D5(I)))*SQR(F1(I)*F1(I)/E(0)/E(0))
380 NEXT I

```

Listing A.3.1 (continued)

```

400 'CALCULATE E, DE/DS, D2E/DS2 ALONG THE STEP DIRECTION
420 FOR I=1 TO 4 :FOR L=1 TO K :X2(L)=X1(L)+I*X4(L) :NEXT L
430 GOSUB 2000 :E(I)=E1 :NEXT I
440 D1=(-11#E(0)+18#E(1)-9#E(2)+2#E(3))/6
450 D2=2#E(0)-5#E(1)+4#E(2)-E(3)
460 D3=(-5#E(0)+18#E(1)-24#E(2)+14#E(3)-3#E(4))/2 :IF D3=0 THEN D3=1E-6
470 'PRINT OUT OF DIRECTIONAL DERIVATIVES
480 IF L18="Y" :GOSUB 4300
500 'FILTERING THROUGH THE STEP LENGTH CRITERIA
505 'CONVERGENCE CRITERIA
510 IF ABS(D1)<=C1 GOTO 900
515 IF E(0)<C6 GOTO 900
520 'DESCENT CRITERIA
525 P=D2#D2-4#D3#D1 :IF P<0 THEN 540
530 P=SQR(P)
535 T2=(-D2-P)/(2#D3) :IF T2<0 THEN 545
540 IF T2<S2 THEN S2=T2
545 T2=(-D2+P)/(2#D3) :IF T2<0 THEN 555
550 IF T2<S2 THEN S2=T2
555 IF S2<S0 THEN S0=S2
560 'ACCELERATION CRITERIA
565 A=D3/D1 :B=D2/D1 :V3=1-C3
570 P=B#B-4#A#V3 :IF P<0 THEN 630
575 P=SQR(P) :T3=(-B+P)/(2#A) :IF T3<0 THEN 585
580 IF T3<S3 THEN S3=T3
585 T3=(-B-P)/(2#A) :IF T3<0 THEN 625
590 IF T3<S3 THEN S3=T3
625 IF S3<S0 THEN S0=S3
630 'STEEPNESS CRITERIA
635 A1=D1/E(0) :A2=D2/(E(0)#2) :A3=D3/(E(0)#6) :GOTO 645
640 S4=S4/C8
645 R1=1+A1#S4+A2#S4#S4+A3#S4[3
650 IF R1<1/C4 THEN 640
655 IF R1>C4 THEN 640
660 IF S4<S0 THEN S0=S4
665 'MAXIMUM STEP SIZE CRITERIA- LIMITED BY C5
680 'PRINTOUT OF RESULTS OF STEP SIZE
685 IF L18="Y" :GOSUB 4400
700 'NEW POINT
710 FOR I=1 TO K :X1(I)=X1(I)+S0#X4(I)
720 IF X1(I)<X8(I) THEN PRINT USING "VARIABLE ## OUT OF RANGE (LOW)" I :X1(I)=X8(I)
730 IF X1(I)>X9(I) THEN PRINT USING "VARIABLE ## OUT OF RANGE (HIGH)" I :X1(I)=X9(I)
740 NEXT I
770 GOTO 230
900 'PRINTOUT OF FINAL RESULT
910 IF L18="Y" :GOSUB 4500
1000 'CALCULATION OF ALL SPECIES COMPONENTS
1010 A0=X1(1) :N1=X1(2) :U3=X1(3)
1020 U2=U3/(K3#A0) :U1=U3/(K2#K3#A0#A0) :U0=U3/(K1#K2#K3#A0[3)
1030 N0=N1/(K4#A0) :NN2=K5#N1#N1/(K4#A0)
1040 H1=H0#A0/K8 :H2=H0#H0#A0/(K7#K8)
1070 IO=0.5*(4#A0+H0+H1+N0+N1+4#U0+4#U2+16#U3)
1100 'MASS BALANCES - INITIAL COMPONENTS
1110 H9=H0/2+H1/2+H2
1120 GOSUB 3600
1800 'NEXT EQUILIBRIUM
1810 GOTO 130
1999 END

```

Listing A.3.1 (continued)

```

2000 'FUNCTIONS AND ERROR AT A POINT
2005 'CHEMICAL EQUILIBRIA
2010 AO=X2(1) :N1=X2(2) :U3=X2(3)
2020 U2=U3/(K3*AO) :U1=U2/K2/AO :UO=U1/K1/AO
2030 NO=N1/(K4*AO) :N2=K5*N1*N1/(K4*AO)
2040 H1=HO*AO/K8 :H2=HO*H1/K7
2100 'MASS BALANCES & ERROR
2110 F(1)=(U9+N9+H0/2-H1/2-N1-N2-U1-2*U2-3*U3)-AO
2120 F(2)=(2*N9-NO-2*N2)-N1
2130 F(3)=(U9-UO-U1-U2)-U3
2200 E1=0
2210 FOR M=1 TO K :F(M)=F(M)/X2(M) :E1=E1+F(M)*F(M) :NEXT M
2220 E1=SQR(E1)
2300 RETURN
3000 'LPRINTOUT OF INPUT
3010 LPRINT "CHEM CONST" :K1;K2;K3;K4;K5;K6;K7;K8;K9
3030 LPRINT "SEARCH CONSTANTS" :C1;C3;C4;C5;C6;C8;C9;S9;K
3040 LPRINT
3095 RETURN
3100 'LPRINTOUT OF THE DESIRED EQUILIBRIUM
3105 LPRINT :LPRINT
3110 LPRINT "PH,N9,U9" :PH;N9;U9
3195 RETURN
3200 'LPRINTOUT OF PARTIAL DERIVATIVES AT THE POINT
3205 LPRINT :LPRINT
3210 LPRINT "X          DE/DX          D2E/DX2          REL.ERROR"
3220 FOR I=1 TO K :LPRINT X1(I),P1(I),P2(I),F1(I) :NEXT I
3230 LPRINT "RELATIVE ERROR=",E(0)
3240 LPRINT "DE/DS (EST)=",D1
3250 LPRINT "D2E/DS2 (EST)=",D2
3295 RETURN
3300 'LPRINTOUT OF DE/DS,D2E/DS2,D3E/DS3 -NUMERICAL METHODS
3310 LPRINT "DE/DS,D2E/DS2,D3E/DS3 (NUM)" :D1;D2;D3
3395 RETURN
3400 'LPRINTOUT OF THE STEP SIZE RESULTS
3410 LPRINT "S0,S2,S3,S4" :S0;S2;S3;S4
3495 RETURN
3500 'LPRINTOUT OF FINAL RESULTS
3510 LPRINT :LPRINT
3520 LPRINT "LOCAL MINIMUM ERROR FOUND, ITERATION N° :J"
3530 LPRINT "DE/DS,D2E/DS2,D3E/DS3" :D1;D2;D3
3540 LPRINT "RELATIVE ERROR = " :E(0)
3550 LPRINT "S04,NA2S04,UO2(S04)3" :X1(1);X1(2);X1(3)
3595 RETURN
3600 'LPRINTOUT OF EQUILIBRIUM SOLUTION
3610 LPRINT PH;N9;U9;IO;E(0);J
3695 RETURN
4000 'PRINTOUT OF INPUT
4010 PRINT "CHEM CONST" :K1;K2;K3;K4;K5;K6;K7;K8;K9
4030 PRINT "SEARCH CONSTANTS" :C1;C3;C4;C5;C6;C8;C9;S9;N
4095 RETURN
4100 'PRINTOUT OF THE DESIRED EQUILIBRIUM
4105 PRINT :PRINT
4110 PRINT "INITIAL POINT-PH,N9,U9" :PH;N9;U9
4145 RETURN
4150 'PRINTOUT OF INITIAL GUESS
4160 PRINT "INITIAL GUESS-AO,N1,U3" :X1(1);X1(2);X1(3)
4195 RETURN
4200 'PRINTOUT OF PARTIAL DERIVATIVES AT THE POINT
4210 PRINT "X          DE/DX          D2E/DX2          REL. ERROR"

```

Listing A.3.1 (continued)

```

4220 FOR I=1 TO K :PRINT X1(I),P1(I),P2(I),F1(I) :NEXT I
4230 PRINT "RELATIVE ERROR=",E(0)
4240 PRINT "DE/DS (EST)=",D1
4250 PRINT "D2E/DS2 (EST)=",D2
4295 RETURN
4300 'PRINTOUT OF DE/DS,D2E/DS2,D3E/DS3 -NUMERICAL METHODS
4310 PRINT "DE/DS,D2E/DS2,D3E/DS3 (NUM)"ID1ID2ID3
4395 RETURN
4400 'PRINTOUT OF THE STEP SIZE RESULTS
4410 PRINT "S0,S2,S3,S4"IS0IS2IS3IS4
4495 RETURN
4500 'PRINTOUT OF FINAL RESULTS
4510 PRINT :PRINT :PRINT
4520 PRINT "LOCAL MINIMUM ERROR FOUND, ITERATION N="IJ
4530 PRINT "DE/DS,D2E/DS2,D3E/DS3"ID1ID2ID3
4540 PRINT "RELATIVE ERROR="IE(0)
4550 PRINT "S04,NA2S04,U02(S04)3 "IX1(1)IX1(2)IX1(3)
4595 RETURN
4600 'PRINTOUT OF EQUILIBRIUM SOLUTION
4610 PRINT PHIH9IN9IU9II0IE(0)IJ
4695 RETURN
8000 'CALCULATION OF THE INITIAL GUESS
8010 Q0=H0/2+N9 :Q1=1+H0/2/K8+2*K4*N9
8020 X1(1)=Q0/Q1 :X1(2)=2*N9/(1+1/(K4*X1(1)))
8025 A0=X1(1) :Q3=1/K1/K2/K3/A0/A0/A0+1/K2/K3/A0/A0+1/K3/A0+1
8030 X1(3)=U9/Q3
8095 RETURN

```

Listing A.3.2 Aqueous Strip Equilibrium Program

```

10 CLS :POKE 16553,255
100 'CHEM CONSTANTS
110 K1=64.3 :K2=4.92 :K3=15.8
120 K4=3.16 :K5=0.01 :K6=1.0
130 K7=166 :K8=0.0359 :K9=1E-14
200 'SEARCH CONSTANTS
210 C1=5E-6 :C2=4E-3 :C3=10 :C4=50 :C5=500 :C6=2
220 C7=1 :K=4 :S8=0.15 :S9=0.01
230 Z1=1 :Z2=2 :N9=0.91 :H9=0.01 :U9=1E-5 :O7=55.12
290 ON Z1 GOSUB 5100,6100
300 'DESIRED EQUILIBRIUM
305 INPUT "EQUILIBRIUM PH":PH
310 N9=0.91
320 H0=10*(-PH+0.1)
395 INPUT "INPUT INITIAL GUESS (Y/N)":L58
396 IF L58="Y" GOTO 800
400 'CALCULATE THE INITIAL ESTIMATE OF THE SOLUTION & ERROR
410 G0=K4*K8*(1-(H9+N9)/H0) :G1=SGR(G0*G0-4*K4*K8*(H9+N9)/H0)
420 X1(1)=(-G0-G1)/2/K4 :AO=X1(1) :X1(2)=H9+N9-AO*(1+H0/K8)
430 G3=1+1/K1/AO+K2*K3*AO*AO
440 X1(3)=U9/G3 :X1(4)=O7
500 'FIND THE LOCAL MINIMUM
510 J=0 :FOR I=1 TO K :X2(I)=X1(I) :NEXT I
550 GOSUB 12000
600 'TEST OF ABSOLUTE CONVERGENCE
610 IF E(0)<C2 GOTO 2000
620 E(0)=W0 :AO=W1 :N1=W2 :U1=W3 :O3=W4
630 PRINT :PRINT :PRINT "BEST POINT":E(0):AO:N1:U1:O3
700 'SEARCH AROUND FOR ANOTHER PROMISING POINT
710 PRINT :PRINT "SEARCH AROUND FOR ANOTHER PROMISING POINT"
720 PRINT :PRINT TAB(10):"1- ABANDON LOCAL SEARCH-NEXT EQUILIBRIUM"
725 PRINT TAB(10):"2- SPECIFY THE POINT"
730 PRINT TAB(10):"3- DIRECTION OF REDUCED INDIVIDUAL ERRORS"
740 PRINT :INPUT "CHOICE":J1 :ON J1 GOSUB 2000,800,850
800 'INPUT OF A SPECIFIC POINT
810 INPUT "GIVE AO,N1,U1,O3":X1(1),X1(2),X1(3),X1(4) :GOTO 500
850 'DIRECTION OF REDUCED INDIVIDUAL ERRORS- 6TH ORDER FIT
855 INPUT "STEP SIZE (EP. 0.15 TO 0.001)":S8
860 FOR I=1 TO K :X4(I)=S8*X1(I)+F1(I)*ABS(F1(I))/E(0)/E(0) :NEXT I
870 FOR M=1 TO 7 :FOR I=1 TO K :X2(I)=X1(I)+(M-3)*X4(I) :NEXT I
880 GOSUB 7000 :E(M)=E1 :NEXT M
1000 'CURVE FIT
1010 GOSUB 15000
1100 'REDO STEP OFFS
1110 PRINT 0,"GRAPH O.K. (Y/N)" :INPUT L58
1120 IF L58="N" GOTO 700
1200 'CHOICE OF NEXT INITIAL POINT
1210 PRINT 0,"VALUE OF S TO NEXT INITIAL POINT" :INPUT J
1220 FOR I=1 TO K :X1(I)=X1(I)+J*X4(I) :NEXT I
1230 GOTO 500
2000 'CALCULATE OTHER VARIABLES
2010 GOSUB 10000

```

Listing A.3.2 (continued)

```

2100 ON Z1 GOSUB 5700,6700
3000 'DO FURTHER EQUILIBRIUM CALCULATIONS
3010 GOTO 300
3500 END
5100 'PRINTOUT OF INPUT
5110 LPRINT "CHEM CONST"K1K2K3K4K5K6K7K8K9
5120 LPRINT "SEARCH CONST"IC1IC2IC3IC4IC5IC6IC8IC9IS8IS9IK
5130 LPRINT "INITIAL SOLUTION"IN9IH9IU9IO7
5140 LPRINT
5195 RETURN
5700 'LPRINTOUT OF RESULTS
5710 LPRINT PHIO9IOIE(O)
5720 LPRINT TAB(5)IAOINIU1IO3
5795 RETURN
6000 'PRINTOUTS
6100 'PRINTOUTS OF CHEM & CONV CONSTANTS
6110 PRINT "CHEM CONST"K1K2K3K4K5K6K7K8K9
6120 PRINT "SEARCH CONST"IC1IC3IC4IC5IC6IC8IC9IS8IS9IK
6130 PRINT "INITIAL SOLUTION"IN9IH9IU9IO7
6195 RETURN
6300 'PRINTOUT OF INITIAL GUESS
6310 PRINT "INIT GUESS-AO,N1,U1,O7"IX1(1)IX1(2)IX1(3)IX1(4)
6395 RETURN
6400 'EACH ITERATION
6405 'POINT LOCATION AND DERIVATIVES
6407 PRINT JIX1(1),X1(2),X1(3),X1(4)
6410 PRINT "ERRORS"IE(O)IF1(1)IF1(2)IF1(3)IF1(4)
6420 PRINT "D1,D2,D3",D1,D2,D3
6445 RETURN
6450 'STEP SIZES
6460 PRINT "S0,S2,S3,S4"IS0IS2IS3IS4 :PRINT
6495 RETURN
6700 'PRINTOUT OF ALL VARIABLES
6710 PRINT PHIO9IOIE(O)
6720 PRINT TAB(5)IAOINIU1IO3
6795 RETURN
7000 'FUNCTIONS AND ERROR AT A POINT
7005 'CHEMICAL EQUILIBRIA
7010 AO=X2(1) :N1=X2(2) :U1=X2(3) :O3=X2(4)
7020 UO=U1/K1/AO :U2=K2*U1*AO :U3=K3*U2*AO
7030 NO=N1/K4/AO :N2=K5*N1*NO
7040 H1=HO*AO/K8 :H2=HO*H1/K7
7050 O2=K9/HO :O1=K4*NO*O2
7100 'MASS BALANCE & ERROR
7110 F(1)=(N9+H9+U9-H1-H2-N1-N2-U1-2*U2-3*U3)-AO
7120 F(2)=(2*N9-O7-NO-2*N2+O2+O3)-N1
7130 F(3)=(U9-UO-U2-U3)-U1
7140 F(4)=(O7+2*H9-HO-H1-2*H2-O3)+10
7200 E1=0
7210 FOR M1=1 TO K :F(M1)=F(M1)/X2(M1) :E1=E1+F(M1)*F(M1) :NEXT M1
7220 E1=SQRT(E1)
7300 RETURN
8000 'GRAPH POINTS AND FUNCTION
8100 'SET UP BORDERS & LABEL
8110 CLS
8120 FOR I=0 TO 5 :J1=962+10*I :PRINT J1,(I-2)I :NEXT I
8125 PRINT 1021," 4"
8130 FOR I=45 TO 5 STEP -10 :SET(5,I) :NEXT I
8140 PRINT 894,"-3" :PRINT 704,"-2" :PRINT 512,"-1"
8150 PRINT 320," 0" :PRINT 64,"+1"

```

Listing A.3.2 (continued)

```

8200 'PLOT DATA POINTS
8210 FOR I=3 TO 63 STEP 10 :I1=(I-3)/10+1 :Y=LOG(E(I1)) :IF Y>1.0 THEN Y=1.0
8220 IF Y<-3.0 THEN Y=-3.0
8230 Y=320-64*INT(10*Y/3)+I
8240 PRINT Y,"*":NEXT I
8300 'CALCULATE & PLOT POLYNOMIAL VALUES
8310 FOR I=6 TO 126 :X=-2+(I-6)/20
8320 Y=LOG(A(1,8)+A(2,8)*X+A(3,8)*X*X+A(4,8)*X[3+A(5,8)*X[4+A(6,8)*X[5+A(7,8)*X[
6)
8330 IF Y>1.0 THEN Y=1.0
8340 IF Y<-3.0 THEN Y=-3.0
8350 Y=13-INT(10*Y) :SET(I,Y) :NEXT I
8500 RETURN
10000 'CALCULATION OF ALL VARIABLES
10020 U0=U1/K1/A0 :U2=K2*U1*A0 :U3=K3*U2*A0
10030 N0=N1/K4/A0 :N2=K5*N1*N0
10040 H1=H0*A0/K6 :H2=H0*H1/K7
10050 O2=K9/H0 :O1=K6*N0*O2
10070 IO=0.5*(4*A0+H0+H1+N0+N1+4*U0+4*U2+16*U3+O2)
10100 'MASS BALANCES-INITIAL COMPOUNDS
10110 O9=N0+N1+2*N2+O1-2*N9
10500 RETURN
12000 'LOCAL MINIMUM
12100 'VARIABLE RANGES
12105 S9=0.01 :W0=1.00
12110 FOR I=1 TO K :X8(I)=X1(I)/5 :X9(I)=X1(I)*5 :NEXT I
12120 FOR I=1 TO K :X2(I)=X1(I) :NEXT I
12130 GOSUB 7000
12140 E(0)=E1 :FOR I=1 TO K :F1(I)=F(I) :NEXT I
12145 IF E(0)<W0 THEN W0=E(0) :W1=X1(1) :W2=X1(2) :W3=X1(3) :W4=X1(4)
12150 'RESET THE CRITERIA
12160 S0=C5 :S2=C5 :S3=C5 :S4=C5 :J=J+1
12170 IF J=50 GOTO 14500
12200 'DIRECTION OF THE NEXT STEP
12210 FOR I=1 TO K :X6(I)=S9*X1(I)*F1(I)/E(0)*ABS(F1(I))/E(0)
12220 NEXT I
12300 'CALCULATE E,DE/DS, D2E/DS2 ALONG THE STEP DIRECTION
12310 FOR I=1 TO 4 :FOR L=1 TO K :X2(L)=X1(L)+I*X6(L) :NEXT L
12320 GOSUB 7000
12330 E(I)=E1 :NEXT I
12340 D1=(-11*E(0)+18*E(1)-9*E(2)+2*E(3))/6
12350 D2=2*E(0)-5*E(1)+4*E(2)-E(3)
12360 D3=(-5*E(0)+18*E(1)-24*E(2)+14*E(3)-3*E(4))/2 :IF D3=0 THEN D3=1E-6
12400 'PRINTOUT OF DERIVATIVES
12410 ON Z2 GOSUB 5400,6400
12500 'FILTERING THROUGH THE STEP LENGTH CRITERIA
12510 'CONVERGENCE CRITERIA
12520 IF ABS(D1)<=C1 GOTO 14500
12530 IF E(0)<C2 GOTO 14500
12600 'DESCENT CRITERIA
12610 P=D2*D2-4*D3*D1 :IF P<0 THEN 12700
12620 P=ESR(P) :T2=(-D2-P)/(2*D3) :IF T2<0 THEN 12640
12630 IF T2<S2 THEN S2=T2
12640 T2=(-D2+P)/(2*D3) :IF T2<0 THEN 12660
12650 IF T2<S2 THEN S2=T2
12660 IF S2<S0 THEN S0=S2
12700 'ACCELERATION CRITERIA
12710 A=D3/D1 :S=D2/D1 :U3=1-C3
12720 P=S*S-4*A*U3 :IF P<0 THEN 12800
12730 P=ESR(P) :T3=(-S+P)/(2*A) :IF T3<0 THEN 12750

```

Listing A.3.2 (continued)

```

12740 IF T3<S3 THEN S3=T3
12750 T3=(-B-P)/(2*A) :IF T3<0 THEN 12770
12760 IF T3<S3 THEN S3=T3
12770 IF S3<S0 THEN S0=S3
12800 'STEEPNESS CRITERIA
12810 A1=D1/E(0) :A2=D2/(E(0)*2) :A3=D3/E(0)/6 :GOTO 12830
12820 S4=S4/C8
12830 R1=1+A1*S4+A2*S4*S4+A3*S4*(3
12840 IF R1<1/C4 THEN 12820
12850 IF R1>C4 THEN 12820
12860 IF S4<S0 THEN S0=S4
12900 'MAXIMUM STEP SIZE CRITERIA- MET BY C5
13000 'NEW POINT
13010 FOR I=1 TO K :X1(I)=X1(I)+S0*X6(I)
13020 IF X1(I)<XB(I) THEN PRINT USING "VARIABLE # OUT OF RANGE (LOW)"I :X1(I)=
XB(I)
13030 IF X1(I)>XB(I) THEN PRINT USING "VARIABLE # OUT OF RANGE (HIGH)"I :X1(I)=
XB(I)
13040 NEXT I :S9=S9*SQRT(S0) :IF S9>0.01 THEN S9=0.01
13045 IF E(0)<0.25 THEN S9=0.01
13060 IF E(0)<0.03 THEN S9=0.001
13070 IF E(0)<0.01 THEN S9=0.0005
14000 'PRINTOUT OF RESULTS OF THIS ITERATION
14100 ON Z2 GOSUB 5450,6450
14400 GOTO 12120
14500 RETURN
15000 'FIT A 6TH ORDER POLYNOMIAL TO THE DATA
15010 'COEFFICIENT MATRIX
15020 FOR M=1 TO 7 :W(M)=M-3
15030 FOR I=1 TO 7 :A(M,I)=W(M)*((I-1)) :NEXT I
15040 A(M,8)=E(M) :NEXT M
15100 'MATRIX REDUCTION- FINAL VALUES ARE A(M,8)
15110 FOR M=1 TO 7 :V=1/A(M,M) :PRINT M
15120 FOR I=1 TO 8 :A(M,I)=A(M,I)*V :NEXT I
15130 FOR I=1 TO 7 :IF I=M GOTO 15150
15140 V1=A(I,M) :FOR L=M TO 8 :A(I,L)=A(I,L)-A(M,L)*V1 :NEXT L
15150 NEXT I :NEXT M
16000 'GRAPHING OF FUNCTION
16010 GOSUB 8000
16500 RETURN

```

Appendix A.4 - Physical Properties

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A.4.0 INTRODUCTION

This appendix supplies supporting data and calculations for Section 4 in the main body of the report, which is concerned with the physical properties of the aqueous and organic phases. Experimental measurements of the density, viscosity, and interfacial tension are given in the first three subsections. Calculated estimates of the mass diffusivities of an aqueous and an organic uranyl species are then illustrated. Literature values for the physical properties of kerosene are included at the end of this section that provide a basis of comparison for the properties of the organic phase.

A.4.1 DENSITIESTable A.4.1 - Verification of the
Density Measurement Techniques

Distilled Water 21.9 to 23.5 °C

Hydrometer (60°F) (range 0.900-1.010)	0.9989, 0.9987, 0.9989
Volumetric Flasks	
50 ml.	0.9950, 0.9954
250 ml.	0.9963, 0.9967
Literature Value (22°C Perry(55))	0.9978

Table A.4.2 - Phase Densities

A. Preparatory Phases

Phase	Method (@ 22°C)	Readings
Aqueous Leach	Hydrom. (1.000-1.220)	1.033
Aqueous Strip	"	1.066, 1.065
Acidifier	"	1.029
pH Control	" (0.900-1.010)	0.9725, 0.9727
Acidified	" (0.800-0.910)	0.8040
Organic	Volumetric (50, 250ML)	0.8003, 0.8017
Free Amine	"	0.7996, 0.7977
Fully Loaded	Hydrom. (0.800-0.910)	0.8090, 0.8090

B. Equilibrated Phases

Circuit	O/A Ratio	Paqueous	Porganic
Extraction	0.25	1.023, 1.022	0.7996, 0.8000
	8.0	1.015, 1.018	0.796, 0.796
Stripping	0.25	1.055, 1.057	0.791, 0.790
	20.0	1.121, 1.125	0.797, 0.797

Done at about 25°C with 25 mL volumetric flasks
Room temperature @ end of tests = 27.3°C

A.4.2 VISCOSITIES

Table A.4.3 - Verification of the Brookfield Viscometer

Viscosity Standard	Speed (rpm)	Temp. (°C)	Readings	Factor	Viscosity (cP)
5 cP @25°C	60	27.5 I	47.2, 47.3	0.1	4.72
	30		23.45, 23.55	0.2	4.70
	12		9.8, 9.60	0.5	4.85
	6	? F	5.1, 4.8	1.0	4.95
	60	22.0 I	51.2, 51.0	0.1	5.1
	30	23.0 F	25.5	0.2	5.1
	60	27.8 I	88.50, 88.4, 88.4	0.1	8.84
	30		44.3, 44.4	0.2	8.87
10 cP @25°C	6	28.5 F	9.3, 9.0	1.0	9.15
	30	21.75 I	47.7	0.2	9.5
	60	22.9 F	95.2, 95.9	0.1	9.55
	60	21.9 I	10.7, 10.6	0.1	1.05
	30	22.4 F	5.4	0.2	1.08
	30	26.3 I	4.85	0.2	0.97
H ₂ O distilled	60	25.5 F	9.95, 10.5, 10.60	0.1	1.04

I = Initial temperature at the start of the test
 F = Final temperature

Table A.4.4 - Viscosities of the Phases

Phase	Speed (rpm.)	Temp. (°C)	Readings	Factor	Viscosity (cP)	Avg.
Acidified Organic	60	21.0 I	15.1, 16.4, 16.5	0.1	1.63	
	30	23.8 F	8.5, 8.5	0.2	1.70	1.65
	60	29.5 I	14.6, 14.6	0.1	1.46	
	30	26.7 F	7.4, 7.3	0.2	1.46	1.46
Fully Loaded	60	21.9 I	16.50, 16.4, 16.3	0.1	1.64	
	30	? F	8.8, 8.4, 7.1, 8.3	0.2	1.70	1.66
	60	28.0 I	15.4, 15.3, 15.1	0.1	1.53	
	30	25.2 F	7.9, 7.9, 7.9	0.2	1.58	1.55
Stripped Organic (PH=4.0)	60	21.0 I	16.0, 15.9, 15.9		1.59	
	30	21.9 F	8.0, 8.0		1.60	1.59
	60	27.7 I	14.8, 14.6, 14.8		1.47	
	30	27.3 F	7.6, 7.1, 7.3, 7.		1.44	1.46
Aqueous Leach	60	22.5 I	11.1, 11.0, 11.0		1.10	
	30	23.0 F	5.6, 5.6, 5.5		1.11	1.10
	60	30.3 I	9.6, 9.7, 9.7		0.97	
	30	29.8 F	4.9, 5.0, 4.7, 5.1		0.99	0.98
Aqueous Strip (Barren)	60	21.3 I	12.1, 12.3, 12.4, 12.3		1.24	
	30	22.2 F	6.0, 6.2, 6.0		1.21	1.23
	60	28.0 I	11.2, 11.3, 11.3		1.13	
	30	27.9 F	5.8, 5.7, 5.9		1.15	1.15
Acidifer Solution	60	21.1 I	11.2, 11.1, 11.4		1.12	
	30	21.4 F	5.5, 5.8, 5.6		1.13	1.12
	60	28.0 I	9.75, 9.6, 10.0, 9.7		0.98	
	30	28.2 F	5.0, 4.8, 5.0		0.99	0.98
Fully Loaded Strip (aqueous)	60	21.4 I	13.4, 13.4, 13.5		1.34	
	30	22.0 F	6.5, 6.7, 6.6		1.32	1.33
	60	30.2 I	11.6, 11.5, 11.6		1.16	
	30	30.6 F	5.6, 6.0, 6.2, 6.0		1.19	1.17

I = Initial temperature at the start of the test
F = Final temperature

A.4.3 INTERFACIAL TENSIONS

The following three tables contain measurements of the interfacial tension for standard phases and the phases used in this project. The De Nuoy ring tensiometer was first calibrated with special weights, then a series of readings were taken of two equilibrated phases in contact. The reading from the instrument (labelled P in the tables) must be corrected for the density differences of the phases ($\rho_1 - \rho_u$). This is done by reading from a chart from the equipment manufacturer a correction factor F that is given as a function of the reading P divided by the density difference between the phases ($\rho_1 - \rho_u$). The factor F times the reading P gives the absolute value for interfacial or surface tension, σ .

The ratio of the diameter of the De Nuoy ring to the diameter of the platinum iridium wire that it was made from was 53.8. In the case of extraction, three times out of four the interfacial tension that was measured in going from the light phase to the heavy phase was 0.4 dynes/cm greater than that measured from the heavy phase to the light phase. In the case of stripping, no consistent difference was noted between the values obtained by approaching the interface either from above or below. However, in both cases there were very large differences in measurements for the surface tension as approached from above or below the surface.

Table A.4.5 - Verification of the De Nuoy Ring Tensiometer

Lower Fluid	Upper Fluid	Temp °C	Density (g/cm ³) Lower Upper	Readings - Apparent Interfacial Tension	Average P	P/ (σ - σ)	Correction Factor	Interfacial Tension (dynes/cm) Expt. Lit.	Error %
Distilled Water	Air	23.2	0.9975	0.0012	75.0, 71.0, 72.3, 76.2, 76.2, 60.2, 75.7, 75.4	75.6	75.9	0.937	70.8 71.9 -1.5%
H ₂ O (Sat'd CCl ₄)	Air	23	1.00	0.0012	73.4, 60.5, 72.8	73.1	73.4	0.937	68.5
H ₂ O (Sat'd Heptane)	Air	20	1.00	0.0012	(65.3, 64.5, 65.1)+	65.0	65.2	0.924	60.1
CCl ₄	Air	24.0	1.588	0.0012	31.8, 31.9, 31.8	31.8	20.1	0.870	27.7
CCl ₄ (Sat'd H ₂ O)	Air	21.2	1.588	0.0012	31.85, 31.60, 31.8	31.8	"	"	"
CCl ₄	Water	23	1.59	1.00	35.3, 37.1, 39.8 39.65, 37.4	37.9	64.1	0.928	35.2 45.0 -22%
Water	Heptane	20	1.00	0.680	44.5, 44.2, 44.85 (42.1, 41.7, 42.0)+	44.5	139.1	0.989	44.0 50.4 -13%
Heptane (Sat'd H ₂ O)	Air	20	0.680	0.0012	23.1, 22.8, 23.0, 22.9 22.9, 22.5, 22.8, 22.7 34.5	22.8	33.6	0.890	20.3 20.3 0%
Tap Water	Air				75.1				70.3

* - Surface or interface broke due to jarring the instrument. The data was therefore not included in calculating the average P.

sat'd - indicates that the primary phase has been saturated with the indicated component.

Expt. - experimental results

Lit. - literature values

Table A.4.6 - Interfacial Tensions for Extraction
(dynes/cm @ 22°C)

O/A Ratio	0.25	0.50	1.00	1.50	2	4	8	10
Aqueous Surface								
P readings	59.0, 59.0	57.4, 57.0 (56.85, 57.2) (57.3)	55.0, 55.0 (54.3)	(58.4)	57.1, 57.9 (59.0)	60.4 (-)	(61.7)	64.5, 63.5 (56.5)
P average	59.0 (-)	57.2 (57.1)	55.0 (54.3)	- (58.4)	57.5 (59.0)	60.4 (-)	- (61.7)	64.0 (56.4)
P/($\sigma_1 - \sigma_2$)	57.2	55	53	57	58	59	60	62
f factor	0.916	0.915	0.912	0.918	0.916	0.920	0.922	0.922
f absolute	54.0 (-)	52.3 (52.2)	50.2 (49.5)	- (58.4)	52.7 (54.0)	55.6 (-)	- (56.0)	59.0 (52.0)
Interface								
P readings	13.8, 14.1, 14.3	13.7, 13.0, 13.7 13.2 (15.6, 16.0) 13.4 (15.8) 0	9.9 (14.4) (14.3, 13.7) 9.9 (14.1)	(12.5)	10.7, 11.0 (12.2)	10.3, 10.7 10.5 (-)	10.25 (12.5)	(11.75) 10.5 (11.75)
P average	14.1 (-)			- (12.5)	10.9 (12.2)	10.5 (-)	- (12.5)	
P/($\sigma_1 - \sigma_2$)	62	59	43	56	48	46	55	46
f factor	0.922	0.920	0.902	0.915	0.907	0.905	0.916	0.905
f absolute	13.0 (-)	12.3 (14.5)	8.9 (12.7)	- (11.4)	9.9 (11.1)	9.5 (-)	- (11.5)	9.5 (10.6)
Organic Surface								
P readings	28.4	28.9, 29.0 (28.5)	28.2, 28.5 (28.5)	(28.3; 28.1)	(28.4)	28.7, 28.7	(28.2)	28.45, 28.7, 27.9 (27.8)
P average	28.4	29.0 (28.5)	28.4 (28.5)	- (28.2)	- (28.4)	28.7 (-)	- (28.2)	28.4 (27.8)
P/($\sigma_1 - \sigma_2$)	35.3	35	35	35	35	35	35	35
f factor	0.891	0.891	0.891	0.891	0.891	0.891	0.891	0.891
f absolute	25.3 (-)	25.8 (25.4)	- 25.3 (25.4)	- (25.1)	- (25.3)	25.6 (-)	- (25.1)	25.3 (24.8)

Numbers in parentheses refer to a second set of solutions.
prepared independently of the first set of solutions.

Table A.4.7 - Interfacial Tensions for Stripping
(dynes/cm @ 25°C)

O/A Ratio	0.25	1.00	3.0	5.0	10.0	20
Aqueous Surface						
P readings	53.5, 53.1	55.1, 54.6	51.8	52.5, 52.0	51.9, 57.3	46.5, 48.5
P average	53.3	54.9	51.8	52.3	51.6	46.5
P/(σ - μ)	50	51.5	49	48	44	
F factor	0.909	0.910	0.908	0.909	0.909	0.905
γ absolute	48.4	50.0	47.1	47.5	46.9	42.1
Interface						
P readings	12.4, 11.9	12.3, 10.8	12.1, 12.8	8.7, 13.2, 8.7	12.5, 12.2	12.3, 12.3, 11.2
P average	12.2	11.6	12.5	10.2	12.3	11.9
P/(σ - μ)	47.0	45.0	48.6	40.0	48	46.3
F factor	0.908	0.906	0.909	0.898	0.909	0.906
γ absolute	11.1	10.5	11.4	9.3	11.2	10.8
Organic Surface						
P readings	28.5, 28.1	28.3, 28.6	28.2, 27.9	28.5, 28.5	28.4	-
P average	28.3	28.4	28.1	28.5	28.4	-
P/(σ - μ)	35	35	35	35	35	-
F factor	0.891	0.891	0.891	0.891	0.891	-
γ absolute	25.2	25.8	25.5	25.9	25.8	-

A.4.4 CALCULATED ESTIMATES OF THE MASS DIFFUSIVITIESA.4.4.1 Aqueous Phase Diffusivity

For electrolytes at infinite dilution
is for binary solutions):

This correlation

$$D_v^0 = 8.93 \times 10^{-10} T \left[\frac{1+l-}{\Omega} \right] \left| \frac{z+z-}{z+z-} \right| \text{ equation 3-34 Perry's}$$

	$UO_2(SO_4)_3^{4-}$	$UO_2(SO_4)_2^{2-}$
l+ cationic conductance (mho/equiv) $Na^+ NH_4^+$	60	60
l- anionic conductance	100	80
$\Omega = l+ + l-$ electrolyte condition at infinite dilution	160	140
T temperature Kelvin	298	298
z+ valence of the cation	1+	1+
z- valence of the anion	4	2

$$D_v^0 UO_2(SO_4)_3^{4-} = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \quad D_v^0 UO_2(SO_4)_2^{2-}$$

For concentrated electrolytes;

$$D_L = D_v^0 \left(1 + m \frac{\delta \ln \Gamma}{\delta m} \right) \frac{1}{c_B V_B} \left(\frac{\mu_B}{\mu} \right)$$

- m molality $\approx 2\text{g/l}$ $U \approx 2 \times 10^{-3}$ molal
 $\delta \ln \Gamma / \delta m \approx 0$ at higher concentrations
 c_B molar density of solvent (water)
 V_B partial molal volume of water $\approx 1/c_B$
 μ_B viscosity of water = 1 cP
 μ viscosity of the solution = 1.1 cP

$$D_L \approx D_v^0 \mu_B / \mu = 9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

D_v^0 and D_L are diffusivities (cm^2/s).

A.4.4.2 Organic Phase Diffusivity

The Wilke-Chang relation for diffusion in non-electrolytes is applicable to the diffusion uranyl/amine complexes in the organic phase (see Perry (55p3-234)).

$$\frac{D_{AB}\mu_B}{T} = 7.4 \times 10^{-8} \frac{(\phi M_B)^{0.5}}{V_A^{0.6}}$$

A - refers to solute
B - refers to solvent

For the free amine R_3N in kerosene:

μ_B	viscosity	1.65 cP
T	temperature	298 K
ϕ	association parameter	1.00 for kerosene (2.26 for H_2O)
M_B	molecular weight	140 g/L
V_A	molar volume of solute @ normal boiling point	573 $cm^3 gmol^{-1}$

In order to estimate the diffusivity for the uranyl/amine complexes, a general trend for the effect of molecular weight of solutes on their diffusivity in water was obtained from Table 17-10 of Perry (55p17-38). The data was roughly of the form:

$$D_{AB} = cM_A^a$$

c, a - constants
 $a \approx 0.30$

Using the above value for the exponent a:

$$D_A = 2.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ for } (R_3NH)_4UO_2(SO_4)_3$$

$$= 7.5 \times 10^{-7} \text{ for } (R_3NH)_2UO_2SO_4$$

A.4.5 LITERATURE VALUES FOR THE PHYSICAL PROPERTIES
OF KEROSENE

The following information is taken from the Natural Gas Processor's Association Manual (51).

	Viscosity @ 25°C
n-C ₁₀	0.88 cP
n-C ₁₁	1.1 cP
for a molecular weight of 146	1.3 cP

surface tension at 20°C $\approx$ 24 dynes/cm

Appendix A.5

Fluid Flow in the Mixer

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A.5.0 INTRODUCTION

This appendix supplies supporting data and calculations for Section 5 in the main body of the report, which is concerned with power and pumping in an agitated vessel. The information in this appendix is specifically related to flowrates and the apparent viscosity of the dispersion in the mixer.

A.5.1 FLOWRATES AND O/A RATIOS

The tables on the next two pages contain details about the flowrates and O/A ratios for the mixer/settler runs. The solution volumes were measured in order to provide an accurate figure for the phase flowrates, even though the peristaltic pumps are usually very steady and reliable as metering devices. The ratio of the organic to the aqueous flowrates is the feed O/A ratio. The ratio of the organic to the aqueous volumes in the mixer at the end of the run is the mixer O/A ratio, which may differ considerably from the feed O/A. Another way to express the mixer O/A ratio is in terms of the dispersed phase volume fraction, ϕ_d .

In the last three tables two measurements are given of the organic and the aqueous feed volumes. One estimate is based on the measured input volume, and the other is based on the measured output volume.

Table A.5.1 - Flowrates and O/A Ratios
No Extraction Series

Run #	Impeller Speed (rev/s)	Duration (s)	Organic Volume (L)	Aqueous Volume (L)	Residence Time (s)	Feed O/A (-)	Mixer O/A (-)	O/A Mixer Feed (-)	Aqueous Mixer (-)
1	24.8	1260	9.16	7.69	62.82	1.192	1.349	1.132	0.43
2	21.7	1290	8.97	6.83	68.59	1.313	-	-	-
3	34.3	1410	11.96	7.89	59.67	1.517	1.525	1.005	0.40
4	30.3	1230	10.95	6.96	57.70	1.573	1.623	1.032	0.38
5	18.2	1240	10.74	6.99	58.74	1.537	1.693	1.101	0.37
6	33.3	1260	11.69	7.16	56.15	1.632	1.807	1.107	0.36
7	11.0	1320	11.37	6.96	60.55	1.637	1.730	1.056	0.37
8	28.2	1290	11.82	7.24	56.87	1.633	1.767	1.082	0.36
9	32.8	1290	11.93	7.22	56.57	1.653	1.730	1.047	0.37
10	14.5	1296	12.33	7.38	55.25	1.670	1.730	1.036	0.37
11	7.5	1290	12.02	7.25	56.23	1.658	1.295	0.781	0.44
12	24.8	1356	10.01	6.38	69.52	1.568	1.405	0.896	0.42

Table A.5.2 - Flowrates and O/A Ratios
Fast Extraction Series

Run	Impeller Speed (rev/s)	Duration (s)	Organic Volume Input (L)	Organic Volume Output (L)	Aqueous Volume Input (L)	Aqueous Volume Output (L)	Residence Time (s)	O/A Ratio Feed (-)	O/A Ratio Mixer (-)	O/A Mixer Feed (-)	Aqueous Mixer (-)
1	33.3	1220	-	9.07	-	5.94	68.28	1.527	1.494	0.978	0.40
2	24.5	1255	10.0	9.3	7.0	6.19	68.03	1.502	1.590	1.059	0.390
3	7.5	1245	10.5	9.86	7.0	6.25	64.92	1.577	1.196	0.758	0.46
4	18.2	1235	10.0	9.95	7.0	6.33	63.75	1.573	1.767	1.123	0.36
5	33.3	630	11.0	10.74	7.0	6.98	29.86	1.538	1.623	1.058	0.38
6	24.8	690	11.0	11.37	7.5	7.41	30.85	1.534	1.494	0.974	0.40
7	7.5	685	12.0	11.39	8.0	7.59	30.32	1.500	1.295	0.863	0.44
8	18.2	795	14.0	13.05	8.0	8.09	31.60	1.613	1.525	0.945	0.40

Table A.5.3 - Flowrates and O/A Ratios
Slow Extraction Series

Run	Impeller Speed (rev/s)	Duration (s)	Organic Volume		Aqueous Volume		Residence Time (s)	O/A Ratio Feed (-)	O/A Ratio Mixer (-)	O/A Mixer		β Aqueous Mixer (-)
			Input (L)	Output (L)	Input (L)	Output (L)				O/A Feed (-)	(-)	
1	14.5	1275	9.0	10.25	6.5	6.24	64.91	1.642	1.525	0.929	0.929	0.40
2	14.5	1290	10.0	10.48	7.12	6.24	64.80	1.678	1.658	0.988	0.988	0.38
3	14.5	1305	10.5	10.81	7.21	6.48	63.43	1.669	1.590	0.953	0.953	0.39
4	14.5	1290	10.5	10.17	7.15	6.36	65.56	1.598	1.494	0.936	0.936	0.40
5	7.5	1275	9.5	10.10	6.94	6.35	65.07	1.590	0.836	0.526	0.526	0.54
6	24.8	1275	10.0	9.92	7.06	6.48	65.32	1.531	1.494	0.976	0.976	0.40

Table A.5.4 - Flowrates and O/A Ratios
Stripping Series

Run	Impeller Speed (rev/s)	Duration (s)	Organic Volume		Aqueous Volume		Residence Time (s)	O/A Ratio Feed (-)	O/A Ratio Mixer (-)	O/A Mixer		β Aqueous Mixer (-)
			Input (L)	Output (L)	Input (L)	Output (L)				O/A Feed (-)	O/A Mixer (-)	
1	11.0	1260	10.0	9.69	6.5	6.06	67.2	1.598	1.525	0.954		0.51
2	14.5	1290	10.0	9.57	7.0	6.39	66.04	1.751	1.845	1.054		0.35
3	24.8	1290	10.0	9.57	7.0	6.39	67.89	1.497	1.730	1.156		0.37
4	7.5	1305	8.5	10.37	8.5	6.29	65.80	1.650	1.061	0.643		0.49
5	14.5	435	12.0	10.79	7.5	6.82	20.75	1.582	1.730	1.094		0.37
6	7.5	440	10.5	10.4	8.0	6.66	21.67	1.561	0.980	0.628		0.51
7	11.0	375	11.0	10.48	7.4	6.53	18.52	1.606	1.405	0.877		0.42
8	24.8	450	12.0	10.58	7.0	6.78	21.77	1.560	1.525	0.978		0.40

A.5.2 THE APPARENT VISCOSITY OF A DISPERSION

Many correlations frequently require a knowledge of the apparent viscosity of a liquid-liquid dispersion, which is non-Newtonian in nature. Although the apparent viscosity is a function of several variables (see Becher (8), and Nagata (52)), a rigorous analysis was not attempted in this project. Predictions of the apparent viscosity for this project according to several simple correlations are listed below. The correlation of Vermeulen et al (78) was chosen for mixer power calculations, while Barnea and Mizrahi's (5) correlation was used for hindered settling. The predicted apparent viscosities at different O/A ratios for the conditions of the no-extraction runs are given in Table A.5.5 for the various correlations.

$$\text{Vermeulen et al (78)} \quad \mu_m = \frac{\mu_c}{(1-\phi)} * \left[1 + \frac{1.5 \mu_d \phi}{\mu_c + \mu_d} \right]$$

$$\text{Barnea and Mizrahi (5)} \quad \mu_m = \mu_c * \exp \left[\frac{5 * \phi}{3 * (1-\phi)} \right]$$

$$\text{Oliver-Ward (8)} \quad \mu_m = \frac{\mu_c}{1-K*\phi} \quad K \approx 2.5 \quad (\phi < 20\%)$$

$$\text{Sibree (8)} \quad \mu_m = \frac{\mu_c}{1 - (H\phi)^{1/3}} \quad H=1.3 \quad (\phi > 50\%)$$

$$\text{Taylor (8)} \quad \mu_m = \mu_c * \left[1 + 2.5 * \phi \left[\frac{\mu_d + 2/5 \mu_c}{\mu_d + \mu_c} \right] \right]$$

$$\text{McCabe and Smith (43)} \quad \mu_m = \mu_c * \exp(4.19 * \phi)$$

Table A.5.5 - Correlations of Apparent Viscosity
(in g/cm/s - applied to this project)

phase ratio	Laity Treybal	Barnea Mizrahi	Oliver Ward	Sibree	McCabe Smith	Becher (data) *
0.1	0.019	0.020	0.022	0.033	0.025	
0.2	0.023	0.025	0.033	0.046	0.038	0.047
0.3	0.028	0.034	0.066	0.061	0.058	0.050
0.4	0.034	0.050	-	0.084	0.088	0.086
0.5	0.043	0.087	-	0.123	0.134	0.135
0.7	0.078	0.806	-	0.533		0.512
0.8	0.122	(13.0)	-	(-1.2)		

* data from Becher (8)

Appendix A.6

Drop Distributions in the Mixer

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A.6.0 INTRODUCTION

This appendix supplies supporting data and calculations for Section 6 in the main body of the report, which is concerned with drop size distributions in an agitated vessel. Subappendices A.6.1 and A.6.2 summarize the data concerning drops in the mixer. Subappendix A.6.3 explains in more detail the common form utilised in this project for expressing drop size distributions, which allows comparison of empirical relations of widely different type. Critical Weber and Viscosity numbers are calculated in Subappendix A.6.4.

A.6.1 ANALYSIS OF DROP PHOTOGRAPHS AND SKETCHES

Several photographs and sketches of photographs of the mixer dispersion are shown on the next few pages. They were chosen to illustrate the range of quality obtained with the photographic techniques.

Photographs

Figure A.6.1 was obtained at a low impellor speed, and the camera focus, magnification, lighting, and shutter speed were well set. Figure A.6.2 is still reasonably good, but in Figure A.6.3 the drops are very small and some drops have stuck to the dispersion window (this can be determined by examining successive photographs).

Sketches

It was originally intended to circle about 200 drops on each sketch (taken from the film negative that was projected onto a graphics tablet). The example sketches show that this was rarely the case. Two common and very serious problems are illustrated by the sketches.

1) Drops that are circled in red appeared in two or more successive photographs of the same dispersion. They must therefore have been "stuck" on the dispersion window. These drops were not included in the drop size analysis, but any "stuck" drops not detected in this manner would have affected the calculated drop size distribution. As the "stuck" drops are large, this is a serious problem.

2) Some sketches only yielded 10 to 20 drop images. The rest of the drop population was presumably too small for the optical and lighting systems.

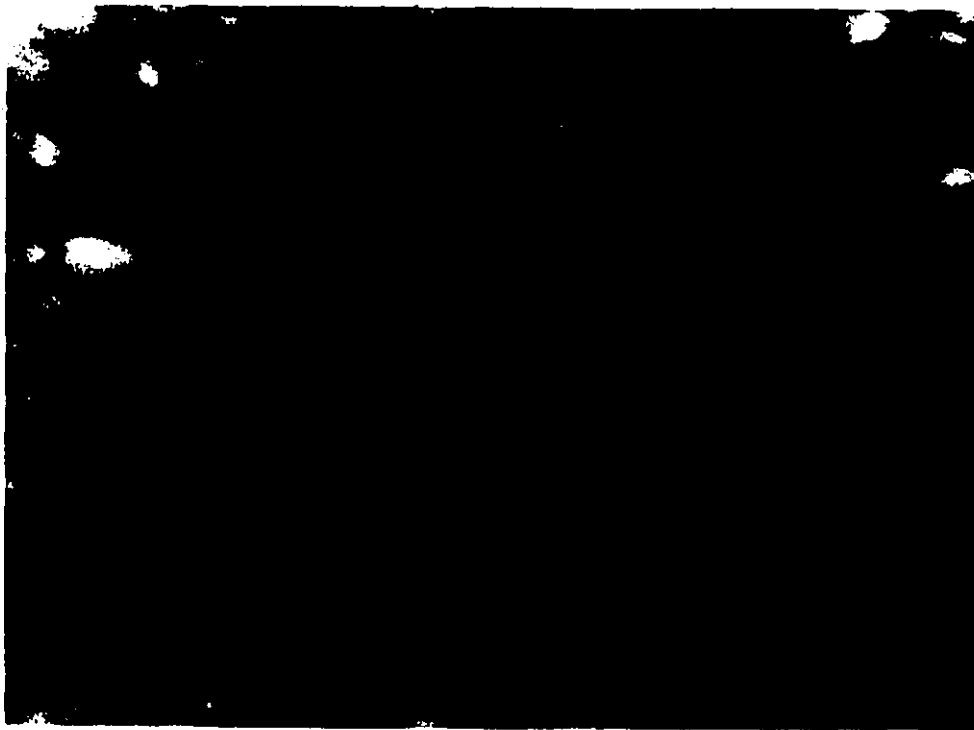


Figure A.6.1 A GOOD QUALITY DROP PHOTOGRAPH

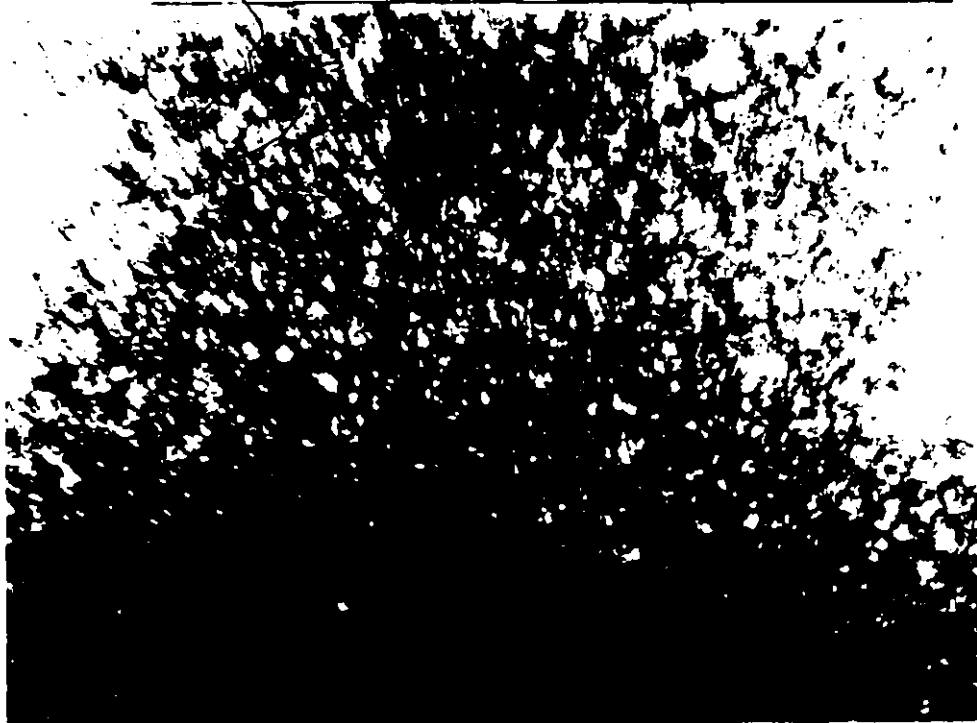
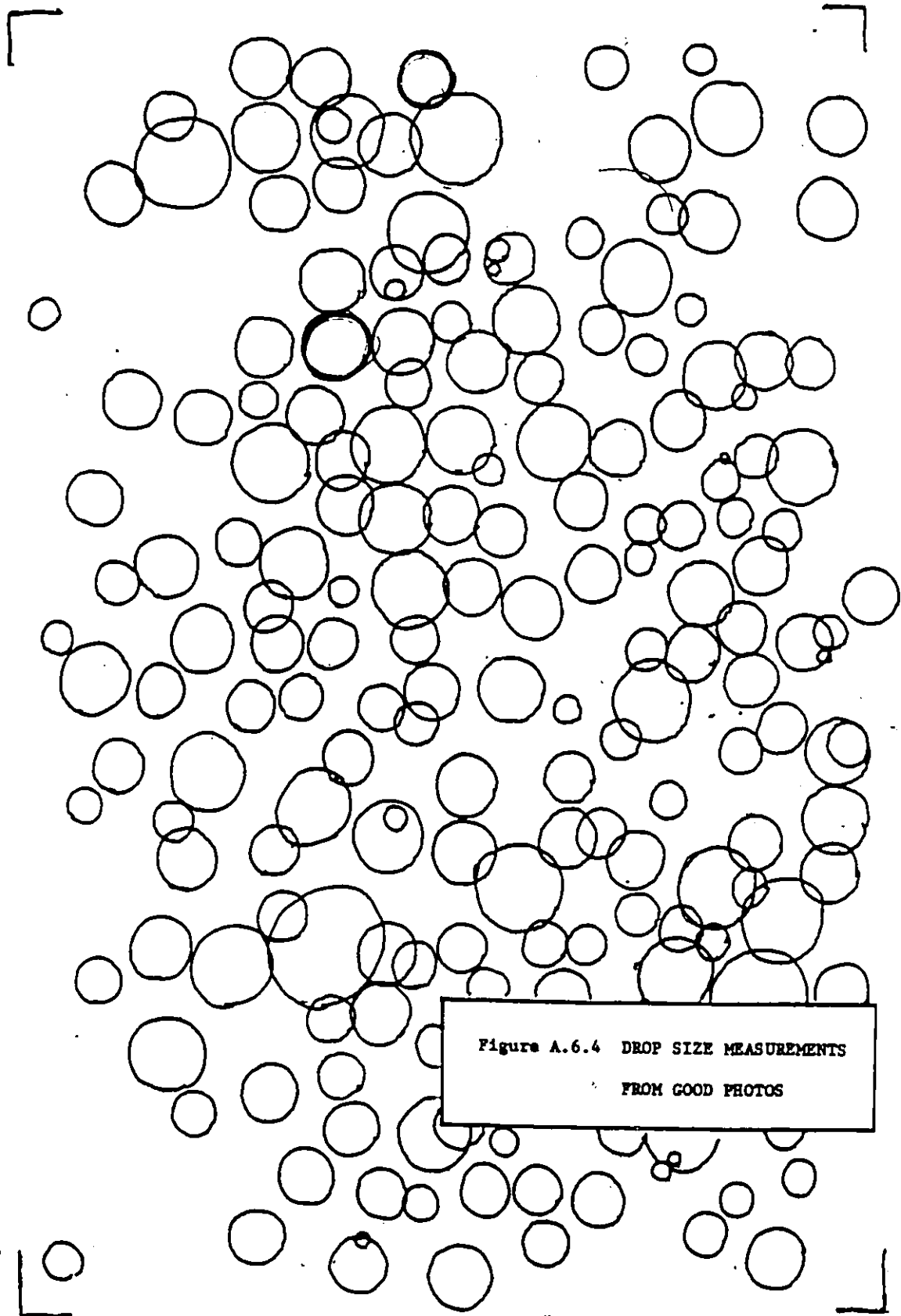


Figure A.6.2 A MEDIUM QUALITY DROP PHOTOGRAPH



Figure A.6.3 A POOR QUALITY DROP PHOTOGRAPH



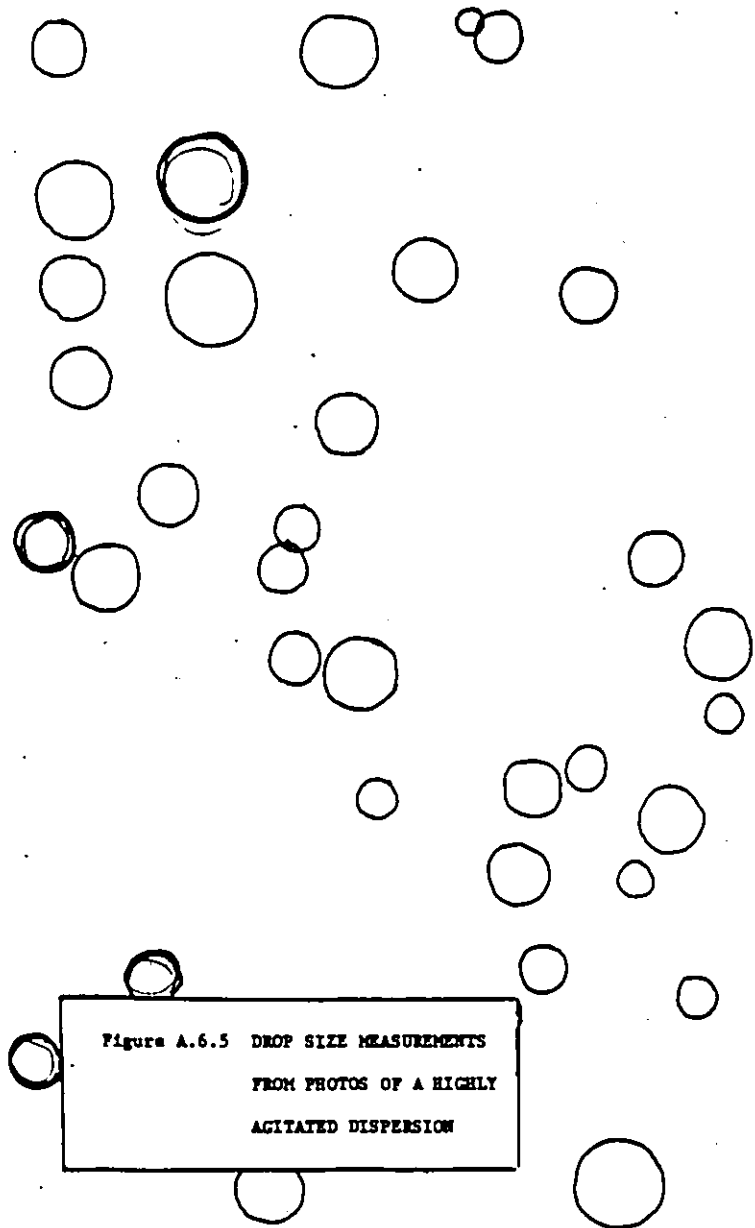
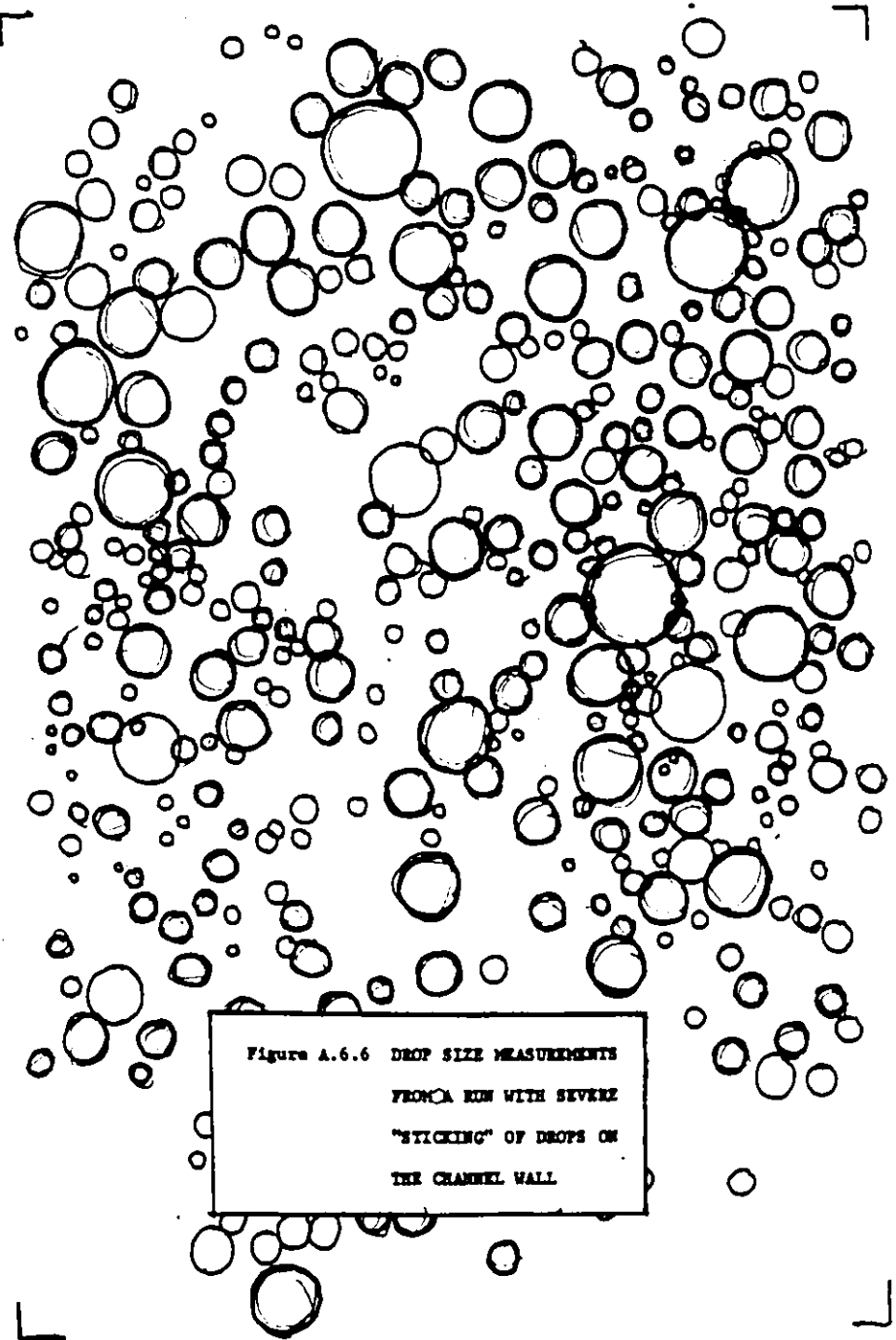


Figure A.6.5 DROP SIZE MEASUREMENTS
FROM PHOTOS OF A HIGHLY
AGITATED DISPERSION



A.6.2 RESULTS OF THE DROP PHOTOGRAPH ANALYSIS

The following tables summarize the analysis of the drop photographs. Although analysis were made of at least two photographs from each series of runs, not all of the runs were analysed because of many poor photographs that resulted when experimenting with the photographic technique. Explanations of particular items in Table A.6.1 are given below.

Photo Quality - The quality of the photographs is indicated by;

1) Overall quality - P=Poor F=Fair A=Average G=Good
VG=Very Good

2) Interpretation - Considerable interpretation was necessary to glean any information from some of the photographs. The rating refers to the fraction of the drop population that was hard to distinguish. (eg. All - no drops were clearly imaged.) Some interpretation was always required when drawing the drop boundaries.

3) Stuck - This fraction indicates the portion of all drop images that were found to have been stuck to the plexiglass wall. These drops were not included in the size distribution or the number count below.

4) Number - This is the number of drops that were measured in order to obtain the drop size distributions. Note that a minimum of 500 to 800 drops is usually required for a proper size distribution.

5) Time Taken - This indicates whether the drop photograph was taken half way through the run (1/2) or at the end of the run (end).

6) A_v - This number is the ^{surface} area per volume of dispersion.

Table A.6.1 - Drop Size Measurements

Run #	Implr. Speed (rev/s)	Power	Photo Quality			Time Taken	A. 10^4 (m^2/m^2)	d minimum (μm)	d maximum (μm)	d32. Average (μm)
			Overall	Interp.	Stock					
No Extraction Series										
1	24.8	12X	?	1/2	1/2	359	2.1	24	268	125
2	12X					114	2.9	33	133	88
3	30.3	12X		all	?	50	2.7	52	117	84
4	18.2	12X	G	1/4	1/4	348	1.6	23	339	140
5	11	25X	G	1/2, 3/4	0	274	1.7	18	247	132
6	14.5	25X	P	all	1/3	36	1.4	41	267	162
7	7.5	25X	VG	1/2, 1/4	1/5	159	0.9	31	412	282
Fast Extraction Series										
1	24.8	25X	F, A	all	1/2	101	2.0	12	206	118
2	7.5	12X	G, VG	1/2, none	0	306	0.9	27	640	319
3	18.2	12X	G, F	all	1/3	244	2.2	36	215	100
4				3/4	1/3	84	2.3	33	167	93
5	24.8	50X	F	all	1/2	50	3.5	12	99	68
6	7.5	25X		none	none	320	0.8	9	785	320
7	18.2	25X		1/2	3/4	187	2.4	20	250	98
Slow Extraction Series										
1	14.5	25X		1/2	5/6	142	2.0	14	274	119
2	14.5	25X	G, A	1/4	1/3	242	1.6	22	298	142
3	14.5	25X		3/8	2/3	192	2.2	16	276	106
4	14.5	25X	A	3/8	1/2	178	1.6	26	440	147
5	7.5	12X	VG, G	1/4	0	171	1.0	16	453	243
6	24.8	50X	F	none	0	328	0.4	21	1566	805
Stripping Series										
1	11	25X	G, F	1/2	0	88	2.1	22	200	113
2	14.5	25X	A, F	3/4	1/4	72	1.3	40	381	244
3	24.8	50X	P	all	1/5	18	1.7	61	272	156
4	7.5	12X	VG	none	0	390	0.6	18	188	133
5	14.5	25X		none	0	311	0.3	18	1181	504
6	7.5	12X		all	1/2	117	1.3	14	2362	861
7	11	12X		none	none	404	0.4	24	339	170
8	24.8	50X		1/2	2/3	424	0.6	25	1326	717
				3/4	3/4	25	1.9	17	766	410
									199	127

Power = nominal magnification of the microscope
Implr. = impeller

Table A.6.2 below compares drop sizes as measured half way through some of the runs to the drop size at the end of the runs.

Table A.6.2 - Comparison of Drop Sizes at Half Time and at the End of the Runs

Run	Impellor Speed (s ⁻¹)	Residence Time (s)	Half Time		End	
			d ₃₂ (μm)	S	d ₃₂ (μm)	S
NE-1	24.8	60	125	1.5	88	1.3
FE-4	18.2	60	100	1.3	93	1.3
SE-2	14.5	60	142	1.6	106	1.5
ST-4	7.5	60	504	2.5	861	2.7

Where: d₃₂ - Sauter Mean Diameter
 S - Variance of the Log Frequency vs.
 Diameter Distribution
 NE - No Extraction Series
 FE - Fast Extraction Series
 SE - Slow Extraction Series
 ST - Stripping Series

A.6.3 DROP SIZE DISTRIBUTIONS - EMPIRICAL FORMS

There are numerous mathematical expressions for the form of drop size distributions. In order to compare them, a standard form must be adopted. Let's define the probability density function f or some variable α with respect to another variable β :

$$f_{\alpha}(\beta) = \frac{1}{\alpha_T} \frac{d\alpha}{d\beta} \quad \text{where } \alpha_T = \int_{\text{whole population}} d\alpha$$

$$\text{and } \int_{\text{whole range of } \beta} f_{\alpha}(\beta) d\beta = 1$$

For this project, the chosen form is:

$$f_N(d') \quad \text{where } \begin{matrix} N = \text{number of drops} \\ d' = \log \text{ of drop diameter } d \end{matrix}$$

This form has several advantages:

- 1) For spherical drops - the same distribution curve may serve for several frequency distributions, necessitating only scaling factors.
- 2) The log format permits examination of the smaller drop sizes, and gives a better idea of the differences between the smallest and the largest drops. This was very important in the present study.

Actually, the frequency distribution $f_V(d')$ or $f_N(V')$ or almost any other form may be preferred for given applications.

Conversion to the chosen distribution form may be accomplished by the following formulae:

$$f_N(d') = f_N(d) * d$$

$$f_N(d') = \frac{D_T}{N_T d} f_d(d') = \frac{A_T}{2.3 \pi N_T d^2} f_A(d') = \frac{6 V_T}{2.3 \pi N_T d^3} f_V(d')$$

where:

d, A, V = diameter, area, and volume of a size range
 N_T, A_T, V_T = total number, area, and volume of a population of drops

For example:

$$f_V(d') = 2 * f_V(a') = 3 * f_V(v')$$

a', v' are logs of the drop area, volume

Several formulas from the literature for drop size distributions are listed below along with their modified expressions as $f_N(d')$. These formulas contain constants for mean drop volume etc. that were merely guessed when calculations were done. Although this affects their accuracy and consistency (the integral of the frequency distribution over its entire range no longer equals 1.00), the form of the distributions and hence a qualitative comparison are unchanged.

Bajpai and Ramkrishna (3)

$$f_N(V) = \frac{1}{V_m} \exp \left[\frac{-V}{V_m} \right]$$

$f_N(V)$ - number frequency distribution of drop volumes

V - drop volume

$$f_N(d') = \frac{3V}{V_m} \exp \left[\frac{-V}{V_m} \right]$$

$V_m = \frac{\pi \sum d_i^3}{6 N_T}$ mean drop volume

Mugele (55)

$$f_N(r) = \frac{16 r^2}{\pi r_v^3} \exp \left[- \left(\frac{4}{\sqrt{\pi}} \right)^{2/3} \frac{r^2}{r_v^2} \right]$$

r - drop radius
 r_v - volume mean drop radius

$$f_N(d') = \frac{32 d^3}{\pi d_v^3} \exp \left[- \left(\frac{4}{\sqrt{\pi}} \right)^{2/3} \frac{d^2}{d_v^2} \right]$$

standard form

Log Normal Distribution

$$f_N(d') = \frac{1}{\sqrt{2\pi}\sigma'} \exp \left[-\frac{1}{2} \left(\frac{d' - \mu'}{\sigma'} \right)^2 \right]$$

$d' = \log(d)$
 $\mu' = \log(\text{mean } d)$
 $\sigma' = \text{std. deviation of } \log(d)$

This expression is already in the standard form.

Four experimental drop distributions have also been put into the standard form in Table A.6.3 below.

Table A.6.3 - Experimental Drop Distributions Expressed in the Standard Form

d	no extr.-1		fast ext.-3		slow ext.-2		strip-4	
	H	$f_N(d')$	H	$f_N(d')$	H	$f_N(d')$	H	$f_N(d')$
18	-	-	-	-	-	-	0.07	0.03
24	0.19	0.079	-	-	0.35	0.22	0.19	0.08
31	0.42	0.174	0.19	0.09	0.26	0.15	1.20	0.50
40	1.70	0.706	0.43	0.21	0.76	0.47	2.08	0.86
51	2.47	1.03	0.38	0.186	1.21	0.75	3.86	1.60
66	5.32	2.21	0.87	0.42	2.57	1.58	2.65	1.10
84	6.69	2.77	0.93	0.45	3.50	2.15	2.15	0.89
110	2.71	1.13	1.12	0.65	2.88	1.71	1.49	0.62
140	1.10	0.46	0.86	0.42	1.65	1.02	1.43	0.59
180	0.70	0.29	2.13	1.04	1.20	0.74	0.94	0.39
230	0.55	0.23	3.80	1.85	0.43	0.26	0.98	0.41
300	0.08	0.033	4.82	2.34	0.08	-0.049	1.39	0.58
390	-	-	2.80	1.36	-	-	1.62	0.67
500	-	-	0.32	0.16	-	-	1.50	0.62
650	-	-	0.10	0.049	-	-	0.36	0.15
820	-	-	-	-	-	-	0.33	0.14
1100	-	-	-	-	-	-	-	-
1300	-	-	-	-	-	-	0.08	0.03

where d = drop diameter

d' = log of the drop diameter

H = a measure of the absolute # of drops

A.6.4 CRITICAL WEBER NUMBER AND VISCOSITY NUMBER

Hinze (29) suggested that three forces were important to drop break-up in a dispersion; the inertial forces on a drop, interfacial forces, and viscous forces within the drop. This was refined and related to a physical model by Arai et. al. (1). Three dimensionless groups may be formed by the three forces. Only two are independent. The chosen two are;

We - Weber number = inertial/interfacial stresses

Nvi - Viscosity number = inertial/viscous stresses

The formulas for these numbers are given in section 5.

Figure 6 in the paper of Arai et al (1) presented their experimental data and model correlation of the maximum stable drop size as a function of the viscosity number. Their correlation is specifically intended for high viscosity systems, but it is still interesting and informative to compare the results of this project with their work, keeping in mind that much higher dispersed phase volume fractions were employed in their work. Their data is translated from their format to a We-Nvi set of data in Table A.6.4. The data from this project (using the average drop diameter instead of the maximum stable drop size) is given in the same form in Table A.6.5. The critical Weber numbers for this project are all fairly low (in the range of 0.05 to 0.33), which compares well with the value of Arai et al. of 0.2 for low viscosity systems. There is considerable

scatter, in the values of the critical Weber number for this project, which is to be expected in light of the errors in the measurements of the mean drop sizes.

Table A.6.4 - Critical Weber Numbers

Nvi	$(1+f(Nvi))^{0.6}$	$1+f(Nvi)$	We _{critical}
1E-3	1	1	0.20
SE-3	11	1	0.20
1E-2	1	1	0.20
5E-2	1.2	1.35	0.27
0.1	1.4	1.75	0.35
0.5	2.6	4.91	0.98
1	3.8	9.24	1.8
5	8.5	35.4	7.1
10	10.1	47.1	9.4

Table A.6.5 - Conditions for Drop Breakup in this Project

Implr Speed (s ⁻¹)	d ₃₂ (μm)	We	Nvi	Implr Speed (s ⁻¹)	d ₃₂ (μm)	We	Nvi
No Extraction Series				Slow Extraction Series			
24.8	125	0.223	0.152	14.4	14.2	0.097	9E-3
18.2	140	0.152	0.0166	14.5	243	0.241	0.011
11	132	0.050	9E-4	7.5	805	0.48	8.5E-3
14.5	162	0.123	0.01	24.8	113	0.20	0.014
7.5	282	0.083	6E-3	14.5	119	0.074	8.7E-3
24.8	88	0.130	0.013	14.5	106	0.061	8.4E-3
30.3	84	0.179	0.0162	14.5	147	0.105	9.4E-3
Fast Extraction Series				Stripping Series			
24.8	118	0.212	0.015	11	244	0.14	8.4E-3
7.5	319	0.102	6.3E-3	14.5	156	0.115	9.6E-3
18.2	100	0.087	0.010	24.8	133	0.259	0.0155
24.8	68	0.085	0.012	7.5	504	0.218	7.3E-3
18.2	93	0.077	0.010	7.5	861	0.53	8.7E-3
7.5	320	0.102	6.3E-3	14.5	170	0.133	9.8E-3
18.3	98	0.084	0.010	7.5	717	0.39	8.2E-3
				11	410	0.33	0.010
				24.	127	0.239	0.0153

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A.7.0 INTRODUCTION

This appendix supplies supporting data and calculations for Section 7 in the main body of the report, which is concerned with mass transfer especially in the mixer. After presenting the data of uranium concentrations in the two phases, stage efficiencies for the mass transfer runs are then given. Two simple models are presented for predicting idealistic rates of mass transfer in the mixer under the conditions of this project. The last two subappendices deal with questions concerning the validity of the data from the point of view of phase sampling and the potential effect of high rates of mass transfer on the mass transfer coefficients.

A.7.1 MASS TRANSFER DATA

The comments below refer to the data in Tables A.7.1, A.7.2, and A.7.3 which are given in the next three pages.

Equilibrium Samples - Aqueous and organic samples were taken from the settler during the runs. In some cases, after analysing each phase for uranium content, they were then contacted together at an O/A ratio equal to the estimated "O/A feed" during the run and were again analysed for uranium. This gave an estimate of the equilibrium uranium concentrations for those runs. For some of the other runs, the equilibrium concentrations are estimated from chemical equilibrium distribution data from Section 3.

Sample Phase Entrainment - Phase samples often contained amounts of the unwanted phase. A rough estimate of the volume percent of the unwanted phase in the initial, unfiltered sample is given. Sometimes the entrainment was fairly minor, in which case the number of inches of unwanted phase is marked, which refers to the length of unwanted phase in a 3/8" sampling line.

Mass balance error - The error in the mass balance is calculated from the aqueous and organic concentrations of uranium at the end of the run and the initial amount of uranium present.

Calculated Initial [U] (g/L)

= [U]aqueous + O/Afeed * [U]organic for extraction
 = [U]aqueous : O/Afeed + [U]organic for stripping

Table A.7.1 - Uranium Concentrations (g/L)
Fast Extraction Series

60 Seconds Residence Time

Phase	Sample	N=	Uranium Concentration (g/L)			
			7.5	18.2	24.8	33.4
Organic	Feed		0	0	0	0
	Mixer		0.89	0.88	0.95	0.93
Aqueous	Mixer		0.086	0.027	0.013	0.005
	Feed		1.41	1.41	1.41	1.41
Conditions						
O/A feed			1.58	1.57	1.50	1.53
Entrainment	<organic		4" tube	?	?	12%
	<aqueous		4" tube	?	?	10%
Mass balance error			-5.7%	+0.7%	-2.1%	+1.4%

30 Seconds Residence Time

Phase	Sample	N=	Uranium Concentration (g/L)			
			7.5	18.2	24.8	33.3
Organic	Feed		0	0	0	0
	Mixer		0.82	0.80	0.93	0.91
	Settler		0.92	0.85	0.93	0.87
Aqueous	Settler		-	-	-	-
	Mixer		0.05	0.008	0.040	0.049
	Feed		1.41	1.41	1.41	1.41
Conditions						
O/A feed			1.50	1.61	1.53	1.54
Entrainment	<organic		?	cloudy	30-50%	1" tube
	<aqueous		20%	30%	1" tube	1" tube
Mass balance error			+9.2%	+7.8%	-3.5%	-2.8%



Table A.7.2 - Uranium Concentrations (g/L)
Slow Extraction Series

Variable Impellor Speed (100 ppm solids)

Phase	Sample	N=	Uranium Concentration (g/L)		
			7.5	14.5	24.8
Organic	Feed		0	0	0
	Mixer		2.87	2.76	3.00
	Settler		3.33	-	3.92
	Equilibrium		3.70	-	3.82
Aqueous	Equilibrium		0.29	-	0.29
	Settler		0.56	-	0.28
	Mixer		0.83	0.52	0.41
	Feed		4.85	4.85	4.85
Conditions					
pH settler			1.57	1.57	1.62
O/A feed			1.59	1.68	1.53
Entrainment	<organic		none	none	none
	<aqueous		"	"	"
Mass balance error			-11.1%	-6.2%	-3.1%

Variable Solids Content (14.5 s⁻¹ Impellor Speed)

Phase	Sample	Solids=	Uranium Concentration (g/L)			
			0 ppm	50	100	500
Organic	Feed		0	0	0	0
	Mixer		2.95	3.41/3.63	2.76	2.90
	Settler		3.04/3.61	2.69/3.54	-	-
	Equilibrium		3.29*	3.73*	-	-
Aqueous	Equilibrium		0.29*	0.24	0.29*	0.29*
	Settler		0.24/0.23	-	-	-
	Mixer		0.71	0.67	0.52	0.45
	Feed		4.85	4.85	4.85	4.85
Conditions						
pH settler			1.57	1.68	1.57	1.63
O/A feed			1.64	1.67	1.68	1.60
Entrainment	<organic		none	none	none	none
	<aqueous		"	"	"	"
Mass balance error			-14.4%	-38.7%	-6.2%	+4.9%

Table A.7.3 - Uranium Concentrations (g/L)
Stripping Series

60 Seconds Residence Time

Phase	Sample	N=	Uranium Concentration (g/L)			
			7.5	11	14.5	24.8
Organic	Feed		4.41	4.41	4.41	4.41
	Mixer		0.96	0.78	0.87	0.63
	Settler		0.86	1.16	0.89	0.56
	Equilibrium		1.23	0.83	1.16	0.93
Aqueous	Equilibrium		4.27	4.95	5.19	4.58
	Settler		4.54	4.63	5.15	5.10
	Mixer		4.05	4.60	4.63	5.25
	Feed		0	0	0	0
Conditions						
pH settler			4.79	4.51	3.92	4.02
O/A feed			1.65	1.60	1.75	1.50
Entrainment - organic			none	none	none	full tube
(samples) - aqueous			10-20%	10-20%	5-10%	40-50%
Mass balance errors			-23%	-17%	-19%	-6%
Precipitate - mixer			S	Y	N	N
- settler			S	?	?	N

20 Seconds Residence Time

Phase	Sample	N=	Uranium Concentration (g/L)			
			7.5	11	14.5	24.8
Organic	Feed		4.41	4.41	4.41	4.41
	Mixer		1.43	1.28	-	0.77
	Settler		1.27	-	-	0.78
	Equilibrium		-	-	-	-
Aqueous	Equilibrium		-	-	-	-
	Settler		1.69	-	-	5.33
	Mixer		4.73	3.79	3.88	4.35
	Feed		0	0	0	0
Conditions						
pH settler			5.64	5.10	4.61	4.11
O/A feed			1.56	1.60	1.58	1.56
Entrainment - organic			none	none	none	5%
- aqueous			60%	40%	10-20%	10-20%
Mass balance error			1%	-17%	-22%	-19%
Precipitate - mixer			N	S	M	N
- settler			Y	M	N	N

A.7.2 MURPHREE STAGE EFFICIENCIES FOR THE MIXER

The Murphree stage efficiency for the mixer is equal to the ratio of the uranium transferred from one phase to another at steady state to the amount that would have been transferred if equilibrium had been attained between the phases.

The efficiency may be calculated according to aqueous or organic analyses.

$$E_a = \frac{A_i - A_s}{A_i - A_e}$$

$$E_o = \frac{O_i - O_s}{O_i - O_e}$$

A	-	aqueous uranium concentration
O	-	organic "
i	-	initial (feed) concentration
s	-	steady state "
e	-	equilibrium "

Where sample phase entrainments (see Tables A.7.1 to A.7.3) exceeded 10%, the data was thrown out. "Reasonable" values for O_s , O_e , A_s , A_e were estimated from the data. Uncertainties in all the data make the calculations useful only for very generalized comparisons.

Table A.7.4 - Murphree Stage Efficiencies
Fast Extraction Series

Based on the Uranium Concentrations of the Mixer
@ Steady State

$$\begin{aligned} A_i &= 1.41 \text{ g/L} & A_e &= 0.004 \text{ g/L} \\ O_i &= 0 & O_e &= 0.94 \end{aligned}$$

Residence Time (s)	N	Uranium Concentrations and Stage Efficiencies			
		7.5	18.2	24.8	33.3
60	A_s	0.086	0.027	0.013	-
	E_a	0.939	0.981	0.99	-
	O_s	0.89	0.88	0.95	0.92
	E_o	0.94	0.936	1.01	0.978
30	A_s	0.05	-	0.04	0.049
	O_s	0.82	0.80	0.93	0.91
	E_o	0.91	0.89	-	1.01

N = impellor speed

A_s = aqueous phase concentration of uranium at steady state

O_s = organic " "

E = murphree stage efficiency of mass transfer

Table A.7.5 - Murphree Stage Efficiencies
Slow Extraction Series

Based on the Uranium Concentrations of the Mixer @ Steady State (60 seconds residence time)

$$\begin{aligned} A_i &= 4.85 \text{ g/L} & A_e &= 0.29 \text{ g/L} \\ O_i &= 0 & O_e &= 3.25 \end{aligned}$$

Uranium Concentrations and Stage Efficiencies
(solids 100 ppm)

N (rev/s ⁻¹)	7.5	14.5	24.8	(N = impellor speed)
A _s	0.83	0.52	0.41	
E _a	0.882	0.95	0.974	
O _s	2.87	2.76	3.0	
E _o	0.883	0.849	0.923	

Uranium Concentrations and Stage Efficiencies
(impellor speed 14.5 s⁻¹)

Solids (ppm)=	0	50	100	500
A _s	0.71	0.67	0.52	0.45
E _a	0.908	0.917	0.950	0.965
O _s	2.95	3.5	2.76	2.90
E _o	0.908	1.076	0.849	0.892

Table A.7.6 - Murphree Stage Efficiencies
Stripping Series

Based on the Uranium Concentrations in the Mixer
@ Steady State

$A_i = 0 \text{ g/l}$ $A_e = 4.2 \text{ g/l}$
 $O_i = 4.41$ $O_e = 1.04$

Residence
Time

Uranium Concentrations and
State Efficiencies

(s)	N	7.5	11	14.5	24.8 [®] (N=impellor speed)
60	A_s	4.05	4.60	4.63	-
	E_a	0.96	1.10	1.10	-
	O_s	0.96	0.78	0.87	-
	E_o	1.02	1.08	1.05	-
20	A_s	-	-	3.88	4.35
	E_a	-	-	0.924	1.04
	O_s	1.43	1.28	-	0.77
	E_o	0.884	0.929	-	1.08

A.7.3 MIXER PHASE SAMPLING
RESIDENCE TIME ON THE FILTER PAPER

The following calculation is an estimate of the "residence time" of a phase on the surface of the sampler filter paper during the process of sampling. Although only an estimate, it gives an idea of the possible extent that the phase sample differs from the bulk phase within the mixer.

Total sample volume - 50 mL
 time required - 5 min or 300 seconds

$$Q_{\text{sampling}} = 1.67 \times 10^{-1} \text{ cm}^3 \text{ s}^{-1}$$

Assuming a film of the sample phase x cm thick on the filter paper:

$$\begin{aligned} \theta_{\text{film}} &= \frac{Ax}{Q_{\text{sample}}} \\ &= 23 \text{ cm}^{-1} \text{ s} * x \end{aligned}$$

θ_{film} = residence time of
 the film on the paper
 A = area of the filter paper
 (3.8 cm²)
 Q_{sample} = sample flowrate

A reasonable estimate of the film thickness on the sampler filter paper would be the radius of the mean drop size, which varies from 50 to 250 micrometers. This estimate yields a film residence time θ of 0.12 to 0.6 seconds, which is small in comparison to the mixer residence times (from 20 to 60 seconds) and therefore should not have affected efficiency values.

Table A.7.7 below shows the drop sizes that were assumed in the simple mass transfer models that follow in the next two subappendices. The selected drop sizes were adopted from the measured drop sizes as given in Section 6, but a linear relation between the log of the drop diameter and the log of the impeller speed was assumed. In this manner, scatter is not introduced into the model calculations, but the values below should be recognized as approximations only.

Table A.7.7 - Assumed Drop Sizes for the Mass Transfer Model Calculations

N (s ⁻¹)	d ₃₂ (μm)	
	Fast Extr.	Slow Extraction
7.5	300	850
8	285	800
9	245	640
10	225	540
12	175	410
15	135	275
20	97	170
25	74	120

A.7.4 DIFFUSION MODEL FOR MASS TRANSFER**A.7.4.1 Summary of the Diffusional Model**

Molecular diffusion within the aqueous drops was assumed to control the transfer of uranium from the aqueous to the organic phase.

The Murphree stage efficiency is predicted by;

$$E_{MS} = \int \bar{q}(t) X(t) dt$$

where $\bar{q}(t) = \frac{\exp(-t/\tau)}{\tau}$ is the residence time distribution in the mixer

$X(t)$ => (from a solution by Crank (18))
is the degree of completion of mass transfer for a drop as a function of time

DATA Diffusivity of $UO_2(SO_4)_3$ in aqueous = $9E-6 \text{ cm}^2\text{s}^{-1}$
Mx= 100% (% of uranium transferred out of aqueous)

Table A.7.8 Predicted Mass Transfer Efficiencies
Diffusional Model

Impellor Speed Speed (s ⁻¹)	Fast Extract.		Slow Extract.	
	d ₃₂ (μm)	E (%)	d ₃₂ (μm)	E (%)
7.5	300	97.1%	850	83.1%
8	285	97.3	800	84.6
9	245	97.9	640	89.3
10	225	98.1	540	92.0
12	175	98.6	410	95.0
15	135	98.9	275	97.4
20	97	99.0	170	98.7
25	74	99.0	120	98.9

A.7.4.2 Assumptions - Diffusional Model

Important assumptions in this model are:

- There is a simple solvation of uranium. There are no heat effects or chemical reactions.
- The dispersed phase drops are quiescent.. Mass transfer occurs by molecular diffusion within the drops.
- The continuous phase immediately surrounding a drop remains with the drop while it is in the mixer. This "shell" of continuous phase is internally well mixed.
- There are no drop interactions (breakup/coalescence). The drops assume a constant, uniform size upon entering the mixer.
- There are no volume changes with extraction.
- The residence time distribution of drops within the mixer is that of a well mixed vessel:

$$\tilde{Q}(t) = \frac{\exp(-t/\tau)}{\tau}$$

where

- $\tilde{Q}(t)$ = probability that a drop will stay in the mixer for a time t
- t = time
- τ = mean residence time

A.7.4.3 Formulating the Diffusional Model

Because the drops and shells are identical and are modelled to behave independently, the degree of completion of mass transfer for each drop is only a function of its residence time in the mixer. Combining expressions for the degree of completion of mass transfer and for the residence time distribution, the Murphree stage efficiency is easily calculated.

Degree of completion of mass transfer for a drop

A solution to this problem is presented in graphical form by Crank (18).

$$X(t) = \frac{M_t}{M_\infty} = f \left[\frac{(Dt)^{1/2}}{(a)} , Mx \right]$$

where

M_t/M_∞ = mass transfer at time t divided by the total material that would be transferred at equilibrium

Mx = per cent of the original material (uranium) present that will change phases at equilibrium

D = mass diffusivity

a = drop radius

In the fast extraction runs nearly 100% of the uranium was extracted while for the slow extraction runs 95% was extracted.

Murphree efficiency

Combining the residence time and degree of completion expressions;

$$E_{MS} = \frac{\text{Amount of U transferred}}{\text{Amount transferable}} = \int \dot{q}(t) X(t) dt$$

This is numerically integrated in the program.

Listing A.7.1 A Program for the Diffusional Model
of Mass Transfer

```

3 ' "CRANK" COMPLETION OF MASS TRANSFER- CRANK & RES TIME
4 CLS :POKE 16353,255
10 DIM A6(30),B6(30),E6(30),F6(30),G6(30),H6(30)
20 DV=9E-6
30 'SET UP CUBIC SPLINE INTERP OF CONVERSION VS TIME
40 PRINT "SETTING UP CUBIC SPLINE" :GOSUB 6000
100 'INPUT OF DATA
110 INPUT "INPUT MEAN RESIDENCE TIME" TM
120 DT=TM/50 :TT=10*TM :MX=100
130 LPRINT "MEAN RES TIME (SEC)=" TM " INCR TIME =" DT " TOTAL T=" TT
135 LPRINT "DIFFUSIVITY=" DV " % COMPLETION @ EQUILIBRIUM=" MX
140 LPRINT "DIAMETER (UM)", "OVERALL CONV"
200 'START INTEGRATION- INITIAL P1 = 0
210 READ D :D=D*1E-4
220 P=0 :P1=0 :T=0
230 'INTEGRATE CONVERSION FOR INDIVIDUAL RES TIMES
240 T=T+DT :GOSUB 3000 :E2=E
270 J6=SQR(4*DV*T/D/D) :GOSUB 6400 :N2=L6
280 P2=E2*N2 :P=P+(P2+P1)*DT/2
290 P1=P2 :IF T>TT GOTO 1000
295 GOTO 230
1000 'PRINT OUT FOR A GIVEN DROP DIAMETER
1010 LPRINT D*1E4,P :GOTO 200
3000 'EVALUATION OF CONVERSION AT TIME T
3010 E=EXP(-T/TM)/TM
3020 RETURN
6000 'CUBIC SPLINE INTERPOLATION OF DATA
6010 DATA 14
6020 DATA 0,0,0,0.031,0.10,0,0.062,0.2,0,0.097,0.3,0
6030 DATA 0.132,0.4,0,0.173,0.5,0,0.218,0.6,0,0.27,0.7,0
6040 DATA 0.337,0.8,0,0.428,0.9,0,0.466,0.93,0
6050 DATA 0.55,0.97,0,0.609,0.99,0,0.667,1,0
6100 READ N6
6110 FOR L6=1 TO N6 :READ A6(L6),B6(L6),W6 :NEXT L6
6150 'COMPUTATION OF SLOPES
6160 X6=2 :GOSUB 6300
6170 E6(1)=2*C6*A6(1)+D6 :E6(2)=2*C6*A6(2)+D6
6180 FOR X6=3 TO N6-1 :GOSUB 6300
6190 E6(X6)=2*C6*A6(X6)+D6 :NEXT X6
6195 E6(N6)=2*C6*A6(N6)+D6
6200 'CUBIC SPLINE COEFFICIENTS
6210 FOR X6=1 TO N6-1
6220 F6(X6)=E6(X6)*(A6(X6+1)-A6(X6))
6230 G6(X6)=3*B6(X6+1)-E6(X6+1)*(A6(X6+1)-A6(X6))
6240 G6(X6)=G6(X6)-3*B6(X6)-2*F6(X6)
6250 H6(X6)=B6(X6+1)-B6(X6)-F6(X6)-G6(X6) :NEXT X6
6300 'COEFFICIENTS OF PARABOLA
6310 I6=(B6(X6-1)-B6(X6))/(A6(X6-1)-A6(X6))
6320 C6=I6-(B6(X6)-B6(X6+1))/(A6(X6)-A6(X6+1))
6330 C6=C6/(A6(X6-1)-A6(X6+1))
6340 D6=I6-C6*(A6(X6-1)+A6(X6))
6350 RETURN

```

Listing A.7.1 (continued)

```
6400 'CUBIC SPLINE INTERPOLATION
6410 IF J6<A6(1) GOTO 6445
6420 'FIND PROPER INTERVAL
6430 FOR X6=2 TO N6 :IF J6<=A6(X6) THEN 6450
6440 NEXT X6
6450 X6=X6-1 :K6=(J6-A6(X6))/(A6(X6+1)-A6(X6))
6460 L6=B6(X6)+F6(X6)*K6+G6(X6)*K6*K6+H6(X6)*K6*K6*K6
6470 RETURN
10000 'DROP SIZES TO BE STUDIED
10010 DATA 300,285,245,225,175,135,97,74
10020 DATA 850,800,640,540,410,275,170,120
```

A.7.5 MASS TRANSFER COEFFICIENT MODELA.7.5.1 Summary of the Mass Transfer Coefficient Model**Mass Transfer Coefficients**

The overall stage efficiency may be predicted from the conditions of agitation and the size of drops in the mixer. The model assumes that the rate of mass transfer is related to the bulk phase concentrations of uranium, a characteristic interfacial concentration for each phase, and the mass transfer coefficients for each phase.

For a given stage efficiency, E , the (characteristic) aqueous phase interfacial concentration, x_{ao} , is determined by:

$$x_{ao} = \frac{k_y}{k_x} (1 - x_{ao}) \left[\frac{g(x_{ao}) - h(x_{ao})}{1 - g(x_{ao})} \right] + x_{ab}$$

The mean residence time, τ , may then be calculated from:

$$\tau = \frac{c_{aq}}{S k_x (1 + O/A)} \frac{(x_{ai} - x_{ab})(1 - x_{ao})}{(x_{ao} - x_{ab})}$$

The continuous phase mass transfer coefficient, k_c , is calculated from:

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$$

The dispersed phase mass transfer coefficient, k_d , is estimated by Elzinga's correlation (56p21-62):

$$k_d = \frac{-d}{6\phi} \ln \left[\frac{3}{8} \sum \beta_n \exp \left[\frac{-\alpha_n 64 D \phi}{d^2} \right] \right]$$

Controlling Resistance

Equilibrium considerations and calculated values for mass transfer coefficients suggest that the aqueous (dispersed) phase resistance should be the more important when the initial aqueous concentration of uranium is less than 5 to 10 g/L.

Table A.7.10 Predicted Mass Transfer Efficiencies
Mass Transfer Coefficient Model

Impellor Speed (s ⁻¹)	Fast Extraction				Slow Extraction			
	d (μm)	kd (10 ⁻³ cms ⁻¹)	kc (10 ⁻³ cms ⁻¹)	E %	d (μm)	kd (10 ⁻³ cms ⁻¹)	kc (10 ⁻³ cms ⁻¹)	E %
7.5	300	3.33	2.18	97.5	850	1.01	1.60	81.0
8	285	3.51	2.29	97.8	800	1.10	1.60	83.1
9	245	4.11	2.56	98.3	600	1.45	1.82	89.2
10	225	4.48	2.78	98.6	540	1.77	2.02	91.6
12	175	5.78	3.33	99.1	410	2.40	2.43	95.0
15	135	7.52	4.07	99.5	275	3.64	3.12	97.6
20	97	10.5	5.28	99.7	170	5.96	4.26	99.0
25	74	13.8	6.50	99.8	120	8.46	5.40	99.5

A.7.5.2 Development of the Mass Transfer Coefficient Model

W_a , the total molar flux of component 'a' across all interfaces, may be related to the Murphree stage efficiency, E_{MS} , for a continuous process;

$$E_{MS} = \frac{\text{rate of transfer of 'a' for given conditions}}{\text{rate that would be required to establish equilibrium}}$$

$$= W_a / W_{a.\text{equil}}$$

$$\text{but } W_a = Q_{aq} C_{aq} (x_{af} - x_{ab}) \quad (1)$$

where f indicates concentrations in the feed

Q_{aq} is the aqueous flow rate

x_{ab} is the bulk aqueous phase concentration of uranium which is equal to the exit aqueous uranium concentration

C_{aq} is the molar concentration of all species in the phase

$$W_{a.\text{equil}} = Q_{aq} C_{aq} (x_{af} - x_{a.\text{equil}})$$

where

$x_{a.\text{equil}}$ is the aqueous phase concentration if equilibrium was established between the phases. This will be a function of the feed phases, and is known experimentally for the fast and slow extraction runs.

$$\text{also } E_{MS} = \frac{x_{af} - x_{ab}}{x_{af} - x_{a.\text{equil}}} \quad (2)$$

In order to calculate E , x_{ab} must be determined. This requires some means of determining the rate of mass transfer for given conditions in terms of the total molar flux as defined above. Mass transfer coefficients are formulated in a manner that is compatible with this problem.

A mass transfer coefficient model for the stage

efficiency of the mixer assumes that the total mass transfer rate across all interfaces may be expressed in terms of characteristic concentration driving forces and predictable values of the "conductivity" (or diffusivity) of the solute through each phase.

Diffusional flux of A = "diffusivity" * driving force

$$W_{ai} - x_{ai}(W_{ai} + W_{bi}) = k_x A (x_{ai} - x_{ab})$$

for the aqueous phase

where

- x_a = mole fraction of A in the aqueous phase
- i - indicates conditions at the interface
- b - indicates conditions in the bulk phase
- k_x = mass transfer coefficient for the aqueous phase ($\text{gmol cm}^{-2} \text{ s}^{-1}$)

Note that the characteristic concentration gradient is simply taken to be the difference in concentrations between the bulk phase and the interface, divided by a characteristic length which is incorporated into k_x . (This length is later related to the average drop size.) While the bulk concentrations are easily definable, characteristic interfacial concentration must be calculated indirectly.

The above equation is written for mass transfer in a binary mixture. Under certain conditions (diffusion of a dilute component through a mostly pure phase with minor impurities, or where all "diffusional" coefficients are equal for the different components) a multicomponent mixture as used in this project may be treated as a binary mixture. This is assumed without proof in the following analysis.

The present problem is one of "unicomponent diffusion" where

$$W_{bi} = 0$$

$$\text{so } W_{ai} (1 - x_{ai}) = k_x A (x_{ai} - x_{ab}) \quad (3)$$

Likewise for the organic phase;

$$-W_{ai} (1 - y_{ai}) = k_y A (y_{ai} - y_{ab}) \quad (4)$$

Assuming that reasonable estimates of k_x , k_y , and A are available, there are 5 unknowns in equations 3 and 4. Two more equations are provided by a mass balance and by the assumption that the "characteristic" aqueous phase interfacial concentration, (x_{ai}) , is in equilibrium with the "characteristic" organic phase interfacial concentration, y_{ao} . This assumption is not a rigorous application of physical or chemical laws. It is a very rough generalization of the same nature as the assumed characteristic driving forces and conductivities.

Mass balance

initial U present = uranium present at time t

$$x_{abf} (cv)_{aq} + y_{abi} (cv)_{org} = x_{ab} (cv)_{aq} + y_{ab} (cv)_{org}$$

where V is the phase volume.

Rearranging:

$$y_{ab} = h(x_{ab}) = y_{abf} + \frac{(cv)_{aq}}{(cv)_{org}} (x_{abi} - x_{ab}) \quad (5)$$

Chemical equilibrium;

$$y_{ao} = g(x_{ao}) \quad \text{The equilibrium relationship was established in Chapter III.} \quad (6)$$

By suitable manipulation of (3) through (6), x_{ao} is obtained

as an implicit function of x_{ab} ;

$$x_{ai} = \frac{k_y}{k_x} (1 - x_{ai}) \left[\frac{g(x_{ai}) - h(x_{ab})}{(1 - g(x_{ai}))} \right] + x_{ab} \quad (7)$$

The aqueous bulk phase concentration, x_{ab} , may be related to the given feed conditions by combining equations (1) and (3);

$$(Q_c)_{aq} (x_{af} - x_{ab}) = k_x A \left[\frac{x_{ai} - x_{ab}}{1 - x_{ai}} \right] \quad (8)$$

This may be expressed in terms of the average residence time;

$$\begin{aligned} \tau &= \frac{V_{\text{mixer}}}{Q_{aq} + Q_{org}} & \tau &= \text{average residence time} \\ &= \frac{V_{\text{mixer}}}{Q_{aq} (1 + O/A)} & O/A &= \text{organic to aqueous} \\ & & & \text{volumetric feed ratio} \end{aligned}$$

also

$$S = \frac{A}{V_{\text{mixer}}} \quad S = \text{the interfacial area per unit volume of the dispersion (from drop size and } O/A \text{ ratio)}$$

$$\text{rearranging (8)} \quad \frac{A}{Q_{aq}} = \frac{c_{aq} (x_{af} - x_{ab})}{k_x (x_{ai} - x_{ab})} (1 - x_{ai})$$

$$S \frac{V_{\text{mixer}}}{Q_{aq}} = "$$

$$S \tau (1 + O/A) = "$$

$$\text{or} \quad \tau = \frac{c_{aq}}{S k_x (1 + O/A)} \frac{(x_{af} - x_{ab}) (1 - x_{ai})}{(x_{ai} - x_{ab})} \quad (9)$$

The method of solution of the mass transfer problem can now be summarized as:

1) Known conditions

- Initial feed concentrations x_{af}, y_{af}
- Feed phase ratio O/A
- Total molar concentrations of the phases c_{aq}, c_{org}
- Interfacial area per unit volume S
- Mass transfer coefficients k_x, k_y
- Mass balance (equation (5))
- Chemical equilibrium (equation (6))

2) Given

- Stage efficiency E

3) Determine x_{ab} from equation (2)

x_{ai} from equation (7)

L " " (9)

A computer program is included in this section for solving the problem.

A.7.5.3 Overall Mass Transfer Coefficients and Controlling Resistances

It is informative to calculate which phase is mass transfer "controlling", and why. The approach below first calculates the overall mass transfer coefficient based on the aqueous phase. Substituting for values from the experimental runs will suggest which variables are predominant in controlling mass transfer between the aqueous and the organic phases.

Overall mass transfer coefficient
(based on the aqueous phase)

$$W_a / A = k_a (c_{ab} - c_{a*})$$

where

k_a = overall coefficient
 c_{ab} = aqueous phase bulk concentration of A
 c_{a*} = aqueous phase concentration that would be in equilibrium with c_{ob}

then

$$\frac{1}{K_a} = \frac{1}{k_x} + \frac{1}{M_a K_y} \quad M_a = \frac{c_{oi} - c_{ob}}{c_{ai} - c_{a*}}$$

i-denotes interfacial concentration

The expression above relates the overall resistance to mass transfer to the ~~aqueous~~^o and organic resistances which are in series. It will predict which phase "controls" mass transfer.

In the slow extraction runs (approximate numbers are from mass transfer calculations);

$k_x = 1.3E-3$	$c_{ab} = 0.52$	$c_{ai} = 0.20$	$c_{o*} = 3.2$	
$k_y = 4.9E-3$	$c_{ob} = 2.85$	$c_{oi} = 2.9$	$c_{a*} = 0.19$	$c_{oi} = 0$

Therefore $M_a = \frac{2.9 - 2.85}{0.2 - 0.19} = 5$ (note- very sensitive to errors)

$$\frac{1}{K_a} = \frac{1}{k_x} + \frac{1}{M_a k_y} = 769 + 41$$

So the aqueous phase resistance controls the slow extraction runs. Note, however, the sensitivity of M_a to errors in the concentrations. For slightly higher concentrations of uranium it appears as though the organic phase resistance would be controlling.

In the fast extraction runs;

$$c_{ab}=0.040 \quad c_{ai}=8E-3 \quad c_{o*}=1.9 \quad c_{ai}=1.4$$

$$c_{ob}=0.935 \quad c_{oi}=2.4 \quad c_{a*}=8E-3 \quad c_{oi}=0$$

$M_a \Rightarrow$ INDETERMINATE

From the calculation of M_a above, or simply by looking at the slope of the equilibrium line in the region of interest to the fast extraction runs, it is obvious that the controlling resistance is in the aqueous phase for the fast extraction runs.

A.7.6.4 k_c - Continuous Phase Mass Transfer Coefficient

Slip Velocity Analogy

The slip velocity analogy as explained by Harriot (28) was used to calculate the continuous phase mass transfer coefficients.

$$Sh = .2 + 0.6 Re^{1/2} Sc^{1/3}$$

The Reynold's number was calculated according to my own interpretation;

$$v = \sqrt{(v_t^2 + v_s^2)}$$

v - slip velocity (for Re)
 v_t - particle terminal velocity
 v_s - Shinnar's velocity for $Re \gg N$ (inertial subrange)

Table A.7.10 Estimates of the Continuous Phase Mass Transfer Coefficient, k_c

Impellor Speed	Fast Extraction Series			Slow Extraction Series		
	d_{32}	Re	k_c	d_{32}	Re	k_c
	(μm)	- ($10^{-3} cm^2 s^{-1}$)		(μm)	- ($10^{-3} cm^2 s^{-1}$)	
7.5	300	4.9	2.18	850	20.3	1.52
8	285	4.8	2.29	800	19.8	1.60
9	245	4.4	2.56	640	16.2	1.82
10	225	4.4	2.78	540	14.3	2.02
12	175	3.8	3.33	410	11.8	2.43
15	135	3.3	4.07	275	8.6	3.12
20	97	2.8	5.28	170	6.0	4.26
25	74	2.5	6.50	120	4.7	5.40

A.7.5.5 k_d - Dispersed Phase Mass Transfer Coefficients

Elzingua's correlation (see Perry's Chemical Engineer's Handbook) was used for estimating the dispersed phase mass transfer coefficient. His correlation assumes a Hadamard-like circulation of fluid within the drops, and is corrected for the continuous phase mass transfer coefficient.

β_n and α_n from Table 21-2 Perry (55p21-17)

τ = residence time (60 seconds)

D - diffusivity

Table A.7.11 Estimates of the Dispersed Phase Mass Transfer Coefficient, k_d

Impellor Speed (s ⁻¹)	Fast Extraction		Slow Extraction	
	d ₃₂ (μ m)	k_d (10 ⁻³ cm ² s ⁻¹)	d ₃₂ (μ m)	k_d (10 ⁻³ cm ² s ⁻¹)
7.5	300	3.33	850	1.01
8	285	3.51	800	1.10
9	245	4.11	600	1.45
10	225	4.48	540	1.77
12	175	5.78	410	2.40
15	135	7.52	275	3.64
20	97	10.5	170	5.96
25	74	13.8	120	8.46

Listing A.7.2 A Program for the Mass Transfer Coefficient
Model

```

2 * "BAK"-- RELATING BULK AND INTERFACIAL CONCENTRATIONS WITH MASS TRANSFER COEFF
ICIENT CONCEPTS
3 CLS :POKE 16553,255
10 DIM X(50),Y(50),D7(50),F7(50),G7(50),H7(50)
100 CO=5.2E-3 :CA=5.5E-2 :MW=238
105 CS=1E-3/MW/CA :C6=1E-3/MW/CO
110 OA=1.5 :XV=1/(1+OA)
150 'CUBIC SPLINE FIT OF EQUILIBRIUM DATA
151 PRINT "COMMENCE CUBIC SPLINE SETUP"
160 GOSUB 10000
200 'GENERAL INFORMATION
210 TM=60 :XI=4.8
220 XI=XI*CS :GOSUB 3000
250 LPRINT "GIVEN CONDITIONS"
255 LPRINT "      MEAN RES TIME (SECS)=":TM
260 LPRINT USING "      URANIUM CONC (G/L)      INIT. AQ. ##.###":XI/CS
265 LPRINT TAB(26); :LPRINT USING "EQUIL AQ. ##.###":XE/CS
270 LPRINT TAB(26); :LPRINT USING "EQUIL ORG ##.###":YE/C6
275 LPRINT :LPRINT "D","KD","KC","N"
300 'PARTICULAR INFO
310 READ D,KD,KC,W
320 D=D*1E-4 :S=6*XV/D :KD=KD*CA :KC=KC*CO
400 'DETERMINE EFFICIENCY FOR PARTICULAR CONDITIONS
405 E5=0.05
410 NL=0.70 :NR=1.00 :NM=(NL+NR)/2
420 NG=NL :GOSUB 2000 :F5=TM-TG
430 NG=NM :GOSUB 2000 :F6=TM-TG
440 C7=F5*F6 :IF C7<0 GOTO 460
450 NL=NM :NM=(NL+NR)/2 :F5=F6 :GOTO 470
460 NR=NM :NM=(NL+NR)/2
470 E6=ABS(F6/2) :IF E6<=E5 GOTO 490
480 GOTO 430
490 N=NM
500 'PRINTOUT OF A PARTICULAR RESULT
510 LPRINT D*1E4,KD/CA,KC/CO,N
520 GOTO 300
1000 END
--
2000 'RESIDENCE TIME FOR A GIVEN EFFICIENCY
2010 XB=(1-NG)*XI+NG*XE :YB=(XI-XB)*CA/CO/OA
2020 GOSUB 4000
2030 TG=CA/S/KD*(XI-XB)*(1-XO)/(XB-XO)/(1+OA)
2090 PRINT NG,TG
2100 RETURN
3000 'PHASE CONCENTRATIONS AT COMPLETION
3010 E=1E-6 :E=E*CS
3020 XL=0 :XR=XI :XM=(XL+XR)/2
3030 XG=XR :GOSUB 5000 :YE=YG
3040 YM=(XI-XG)*CA/CO/OA :F1=YM-YE
3100 XG=XM :GOSUB 5000 :YE=YG
3110 YM=(XI-XG)*CA/CO/OA :F2=YM-YE
3200 C1=F1*F2 :IF C1<0 GOTO 3220

```

Listing A.7.2 (continued)

```

3210 XR=XM :XM=(XL+XR)/2 :F1=F2 :GOTO 3300
3220 XL=XM :XM=(XL+XR)/2
3300 E2=(XR-XL)/2 :IF E2<=E GOTO 3400
3310 GOTO 3100
3400 XE=XM
3499 RETURN
4000 'IMPLICIT INTERFACIAL CONCENTRATION- ROOT FINDING WITH THE METHOD OF BISECT
IONS
4005 E=2E-4 :E=E*CS
4010 XL=0 :XR=XI :XM=(XL+XR)/2
4020 XG=XR :GOSUB 5000 :YO=YG
4030 XC=XG-KC/KD*(1-XG)*(YO-YB)/(1-YO) :F1=XC-XG
4100 XG=XM :GOSUB 5000 :YO=YG
4105 XC=XG-KC/KD*(1-XG)*(YO-YB)/(1-YO) :F2=XC-XG
4110 C1=F1+F2 :IF C1<0 GOTO 4130
4120 XR=XM :XM=(XL+XR)/2 :F1=F2 :GOTO 4140
4130 XL=XM :XM=(XL+XR)/2
4140 E2=(XR-XL)/2 :IF E2 <= E GOTO 4160
4150 GOTO 4100
4160 XG=XM
4170 RETURN
5000 'EQUILIBRIUM CONCENTRATIONS- CUBIC SPLINE INTERPOLATION
5010 XG=LOG(XG) :IF XG<X(1) GOTO 5045
5020 'FIND PROPER INTERVAL
5030 FOR J=2 TO P :IF XG<X(J) THEN 5050
5040 NEXT J
5045 PRINT "XG OUT OF BOUNDS" :GOTO 1000
5050 J=J-1 :W5=(XG-X(J))/(X(J+1)-X(J))
5060 YG=Y(J)+F7(J)*W5+G7(J)*W5*W5+H7(J)*W5*W5*W5
5070 XG=EXP(XG) :YG=EXP(YG)
5100 RETURN
10000 'CUBIC SPLINE FORMULATION
10005 P=14
10007 DATA 1E-4,1E-1,W
10010 DATA 1.5E-3,0.392,W,3E-3,0.56,W,6E-3,0.8,W,1E-2,1.03,W
10020 DATA 2E-2,1.4,W,4E-2,1.85,W,8E-2,2.46,W,0.16,2.8,W
10030 DATA 0.32,3.17,W,0.64,3.35,W,1.2,3.42,W,2.4,3.5,W
10040 DATA 4.8,3.51,W
10100 FOR J=1 TO P :READ X5,Y6,W6 :X(J)=LOG(X5*CS)
10110 Y(J)=LOG(Y6*CS) :NEXT J
10200 'COMPUTATION OF SLOPES
10210 J=2 :GOSUB 10500
10230 D7(1)=2*A7*X(1)+B7 :D7(2)=2*A7*X(2)+B7
10240 FOR J=3 TO P-1 :GOSUB 10500
10250 D7(J)=2*A7*X(J)+B7 :NEXT J
10260 D7(P)=2*A7*X(P)+B7
10300 'CUBIC SPLINE COEFFICIENTS
10310 FOR J=1 TO P-1
10320 F7(J)=D7(J)*(X(J+1)-X(J))
10330 G7(J)=3*Y(J+1)-D7(J+1)*(X(J+1)-X(J))
10340 G7(J)=G7(J)-3*Y(J)-2*F7(J)
10350 H7(J)=Y(J+1)-Y(J)-F7(J)-G7(J) :NEXT J
10500 'COEFFICIENTS OF PARABOLA
10510 M7=(Y(J-1)-Y(J))/(X(J-1)-X(J))
10520 A7=M7-(Y(J)-Y(J+1))/(X(J)-X(J+1))
10530 A7=A7/(X(J-1)-X(J+1))
10540 B7=M7-A7*(X(J-1)+X(J))
10550 RETURN
15000 'DROP SIZE & MATRAN COEFF DATA
15005 'FOR SLOW EXTRACTION SERIES XI=4.8

```

Listing A.7.2 (continued)

```
15010 DATA 850,1.01E-3,1.52E-3,Z,800,1.10E-3,1.60E-3,Z
15011 DATA 600,1.45E-3,1.82E-3,Z,540,1.77E-3,2.02E-3,Z
15012 DATA 410,2.40E-3,2.43E-3,Z,275,3.64E-3,3.12E-3,Z
15013 DATA 170,5.96E-3,4.26E-3,Z,120,8.46E-3,5.40E-3,Z
15100 'FOR FAST EXTRACTION SERIES XI=1.41
15110 DATA 300,3.33E-3,2.18E-3,Z,285,3.51E-3,2.29E-3,Z
15111 DATA 245,4.11E-3,2.56E-3,Z,225,4.48E-3,2.78E-3,Z
15112 DATA 175,5.78E-3,3.33E-3,Z,135,7.52E-3,4.07E-3,Z
15113 DATA 97,10.5E-3,5.28E-3,Z,074,13.8E-3,6.50E-3,Z
```

Listing A.7.3 A Program for the Calculation of
Dispersed Phase Mass Transfer Coefficients

```

5  * "KAK" DISPERSED PHASE MATRAN COEFF- ELZINGUA
10 CLS :POKE 16553,255 :POKE 16425,58
20 T=60
25 PC=0.80 :UC=1.65E-2 :DC=2.2E-6
30 PD=1.03 :UD=1.03E-2 :DD=9E-6
40 DATA 300,2.18E-3,Z,285,2.29E-3,Z,245,2.56E-3,Z
41 DATA 225,2.78E-3,Z,175,3.33E-3,Z,135,4.07E-3,Z
42 DATA 97,3.28E-3,Z,74,6.50E-3,Z
43 DATA 850,1.52E-3,Z,800,1.40E-3,Z,640,1.82E-3,Z
44 DATA 540,2.02E-3,Z,410,2.43E-3,Z,275,3.12E-3,Z
47 DATA 170,4.26E-3,Z,120,5.40E-3,Z
90 LPRINT "PHYSICAL PROP"PC;UC;DC;DD
92 LPRINT "RES TIME"IT
94 LPRINT
97 LPRINT "D      KC      SHC      KD"
100 'INPUTS
110 READ D,KC,WS :D=D*1E-4 :W=0
200 'SHERWOOD N- CONTINUOUS PHASE
210 SHC=KC*D/DC
400 'SELECTION OF EIGENVALUES & COEFFICIENTS
410 IF SHC > 5.3 GOTO 420
413 L(1)=0.262 :L(2)=4.24 :L(3)=0
416 B(1)=1.49 :B(2)=0.107 :B(3)=0 :GOTO 500
420 IF SHC > 10.7 GOTO 430
423 L(1)=0.534 :L(2)=4.24 :L(3)=0
426 B(1)=1.49 :B(2)=0.107 :B(3)=0 :GOTO 500
430 IF SHC > 107 GOTO 440
433 L(1)=1.082 :L(2)=5.9 :L(3)=15.7
436 B(1)=1.49 :B(2)=0.495 :B(3)=0.205 :GOTO 500
440 L(1)=1.656 :L(2)=9.08 :L(3)=22.2
443 B(1)=1.29 :B(2)=0.596 :B(3)=0.386
500 'DISPERSED PHASE MASS TRANS. COEFF.
510 'HADAMARD-TYPE CIRCULATION- ELZINGA (PERRY)
520 'ONLY THE FIRST TERMS COUNT
530 A1=-L(1)*64*DD*T/D/D
540 B1=LOG(B(1))
550 W=2*B1+A1
560 KD=D*W/6/T*LOG(3/8)
1000 'PRINTOUT
1010 LPRINT USING "NNN  NN.NNNNN  NNNN  NN.NNNNN";D*1E4,KC,SHC,KD
1100 GOTO 100
2000 END

```

Listing A.7.4 A Program for the Calculation of
Continuous Phase Mass Transfer Coefficients

```

5 * "SLAK" CONTINUOUS PHASE MASS TRANS COEFF BASED ON SLIP V
6 CLS :POKE 16553,255 :POKE 16425,58
20 PM=0.89 :UM=3.41E-2 :VM=830 :D=4 :NP=5.3
30 C1=2 :C2=1/18 :G=980 :PC=0.8 :PD=1.05 :UC=1.65E-2
35 DC=2.2E-6 :SC=UC/DC/PC
40 LPRINT "PHYSICAL PROP" :PC :PD :PM :UC :UM
42 LPRINT "MATRAN PROP" :DC :SC
44 LPRINT "MIXER GEOM" :DIVMINP
46 LPRINT :LPRINT "N      D      N1      VC      RE      KC"
50 'DATA- N,R,UM
55 DATA 7.5,300,2,8,285,2,9,245,2,10,225,2,12,175,2
56 DATA 15,135,2,20,97,2,25,74,2
60 DATA 7.5,850,2,8,800,2,9,640,2,10,540,2,12,410,2
61 DATA 15,275,2,20,170,2,25,120,2
100 'DATA INPUT
110 READ N,R,UM :R=R*1E-4
200 'TURBULENCE CALC
210 'POWER DISS
220 E=NP*NI3*D[3/VM :N1=(UM/PM)[0.75*(C2*E)](-0.25
300 'SHINNAR'S VELOCITY (R>>N)
310 RS=C1[0.5*E[0.333*R[1.333*PM/UM
320 VS=RS*UM/PM/R
400 'TERMINAL VELOCITY
410 VT=G*R*R*(PD-PC)/18/UC :RT=R*PC*VT/UC
420 IF RT>2 THEN VT=0.153*G[0.71*R[1.14*(PD-PC)[0.71/PC[0.29/UC[0.43 :RT=R*PC*V
T/UC
430 IF RT>500 THEN VT=1.75*SQR(G*R*(PD-PC)/PC) :RT=R*PC*VT/UC
500 'COMPOSITE VELOCITY
510 VC=SQR(VT*VT+VS*VS) :RE=R*PM*VC/UM
700 'MASS TRANSFER COEFF- SLIP VELOCITY ANALOGY
710 SH=2+0.6*RE[0.5*SC[0.333 :KC=SH*DC/R
1000 'PRINT OUT
1010 LPRINT USING "##.##  ####  ###  ###.##  ##.##  ##.##[[[[" :N,R*1E4,N1*1E4,
VC,RE,KC
1020 GOTO 100
2000 END

```

A.7.6 The Correction Factor For High Rates of Mass Transfer

The importance of the bulk flow term at the interface on the mass transfer coefficient may be estimated by following the analysis of Bird, Stewart, and Lightfoot (10p656).

$$\theta = \frac{N_{ao} + N_{bo}}{k_{x,local}} \quad \text{correction factor}$$

$$= \theta(R_{ab}) \quad \text{where } R_{ab} = \text{flux ratio}$$

$$= \frac{x_{ao} - x_{ab}}{\frac{N_{ao}}{N_{ao} + N_{bo}} - x_{ao}}$$

The largest value of R_{ab} and of θ would occur for a maximum value of x_{ao} and a minimum value of x_{ab} , which are 4 g/L and zero g/L respectively. Converting x_{ao} to a mole fraction;

$$x_{ao} = M \quad F_{ao}$$

$$\begin{aligned} \rho &= \text{density of organic} = 0.8 \text{ g/cm}^3 \\ F_{ao} &= \text{mass concentration of uranyl complex} \\ &\quad (R_3NH)_4UO_2(SO_4)_3 \\ &= 3 \text{ g/l} * \frac{1790 \text{ g complex}}{238 \text{ g uranium}} \\ &= 2.3 * 10^{-2} \text{ gcm}^{-3} \\ M_a &= \text{molecular wght. of complex} \\ &= 1790 \text{ g/gmole} \\ M &= \text{average molecular wght.} \\ &\quad \text{of the organic phase} \\ &= 144 \text{ g/gmole} \end{aligned}$$

$$\text{so } R_{ab} = 2 * 10^{-3}$$

According to Figure 21.7-3 of B.S.L. p.675, the mass transfer across the interface for a small R as above would have no effect on the mass transfer coefficient.

A.7.7 Conversion Factors for Uranium Concentrations

The table below includes factors that are useful when converting from molar to mass concentrations for the phases of this project.

Table A.7.12
Conversion Factors for Uranium Concentrations

Phase	Molar Concentration	Mass Concentration to Mole Fraction of Uranium
Aqueous	5.5×10^{-2}	$x_U = 7.6 \times 10^{-2} * F_{Uaq} \text{ (cm}^3\text{g}^{-1}\text{)}$
Organic	5.2×10^{-3}	$y_U = 0.808 * F_{Uorg}$
+		

Appendix A.8
The Settler Dispersion Band

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A.8.0 INTRODUCTION

This appendix supplies supporting data and calculations for Section 8 in the main body of the report, which is concerned with the settler dispersion band height and phase entrainment. The approach of the dispersion band heights to a steady state value is first presented, followed by details of how the dispersion band height at the end of each run was "normalized" to permit easy comparison of the results for different runs. Finally, data relating the settler dispersion band heights and the coalescing time in the mixer is reported.

A.8.1 APPROACH TO THE STEADY STATE DISPERSION BAND HEIGHT

The table on the following page shows the behaviour of the dispersion band height with time for the different runs.

t (minutes) = time from the start of the run

H (cm) = the actual dispersion band height, at any time t

H_r = the reduced dispersion band height = $\frac{H}{H_{\text{end of run}}}$

The data is also used later for calculating the normalized dispersion band heights.

Table A.8.1 - Approach to the Steady State Dispersion Band Height

NO EXTRACTION SERIES

8	t	(7.5)	-	14	20.5			
	H	4.9	5.2	5.5	5.6			
	Hr	0.88	0.93	0.98	1.0			
9	t	2	4	6.5	8	17.5	20	
	H	4.4	5.4	5.7	5.8	6.2	6.25	
	Hr	0.70	0.86	0.91	0.93	1.0	1.0	
10	t	2	4	6	8	14	17	20
	H	5.4	6.3	6.9	7.3	7.45	7.5	7.6
	Hr	0.71	0.83	0.91	0.96	0.98	0.99	1.0
11	t	2.3	4.2	6.0	8.0	14.5	17	20
	H	4.2	5.35	5.7	5.9	6.15	6.20	6.30
	Hr	0.67	0.85	0.90	0.94	0.98	0.98	1.0

FAST EXTRACTION SERIES

1	t	2	3.2	6	8	16	17.5	19.5
	H	2.7	3.0	3.1	3.1	2.9	2.6	2.8
	Hr	0.96	1.07	1.11	1.11	1.09	0.93	1.00
2	t	2	4	6	8	16.5	18.75	
	H	2.1	2.15	2.8	2.9	2.95	2.9	
	Hr	0.72	0.74	0.97	1.0	1.02	1.00	
3	t	2	4	6	8	16	18	
	H	2.05	2.5	2.52	2.75	2.45	2.4	
	Hr	0.85	1.04	1.05	1.15	1.02	1.00	
4	t	2	4	6.5	8	15	17.3	20
	H	2.6	3.05	3.2	3.2	2.9	2.85	3.0
	Hr	0.87	1.02	1.07	1.07	0.97	0.95	1.00
5	t	1	2.7	3.8	9.2	11.3		
	H	4.6	9.5	11.2	15.0	15.1		
	Hr	0.30	0.63	0.74	0.99	1.0		
6	t	0.8	2	3.5	4.2	6	7.5	
	H	5.7	9.9	12.9	14.2	16.5	(OVERFLOW+1.7)	
	Hr	-----						
7	t	1	2	3	4.6	10		
	H	5.0	8.9	11.2	14.7	16.8	+ 10.5 OVERFLOW	
	Hr	-----						
8	t	0.5	0.9	2.1	3.15	4.25	8.1	9.2
	H	4.0	5.8	10.4	12.9	15.0	16.7	16.7
	Hr	-----			OVERFLOW		3.1	2.8
								2.4

Table A.8.1 (continued)

SLOW EXTRACTION SERIES

1	t	1.3	4.5	7	9	14.5	17	
	H	2.3	2.7	2.95	2.90	2.9	2.95	
	Hr	0.78	0.92	1.00	0.98	0.98	1.00	
2	t	1	4.5	6	9.5	15.5	17	19
	H	(1.05)	3.1	3.5	3.6	3.4	3.7	3.2
	Hr	-	0.97	1.09	1.13	1.06	1.16	1.00
3	t	1.25	3	6	9.5	14.25	17	19
	H	3.7	4.1	5.25	5.1	5.2	5.4	5.5
	Hr	0.67	0.74	0.95	0.93	0.95	0.98	1.00
4	t	2.5	4	6	8	16	17.5	19
	H	2.2	1.4	1.5	1.5	1.6	1.2	1.4
	Hr	1.57	1.00	1.07	1.07	1.14	0.86	1.00
5	t	1.5	4	7	10	14	17	19.8
	H	0.3	0.4	0.2	0.2	0.4	0.1	0.1
	Hr	-----						
6	t	0.5	3	5	7	9.6	12	14
	H	2.3	3.1	3.15	3.1	3.1	3.1	3.2
	Hr	0.72	0.97	0.98	0.97	0.97	0.97	0.94

STRIPPING SERIES

1	t	1.6	3	5	8.3	15.4	17	
	H	3.1	3.4	3.7	4.5	4.1	4.1	
	Hr	0.76	0.83	0.90	1.10	1.00	1.00	
2	t	1	3.2	5.0	7.0	17.8	19.4	
	H	3.4	3.9	4.25	4.8	4.5	4.4	
	Hr	0.77	0.89	0.97	1.09	1.02	1.00	
3	t	0.65	1.80	3.1	5	7	16.0	18.0
	H	3.6	5.1	5.6	6.3	6.1	7.1	7.1
	Hr	0.51	0.72	0.79	0.89	0.86	1.00	1.03
4	t	1.5	3.25	5	7.4	17	19	
	H	1.4	2.3	2.1	1.6	1.1	1.0	
	Hr	1.4	2.3	2.1	1.6	1.1	1.00	
5	t	0.6	1.0	1.6	5.0	5.5		
	H	3.3	4.0	4.9	6.7	7.0		
	Hr	0.47	0.57	0.7	0.96	1.00		
6	t	0.7	1.5	5.2				
	H	1.2	0.7	0.6				
	Hr	2.0	1.12	1.00				
7	t	0.35	0.8	1.5	5.6			
	H	1.7	1.9	2.4	2.8			
	Hr	0.61	0.68	0.86	1.00			
8	t	0.5	1.0	1.45	2.8	6.1		
	H	3.4	5.1	6.3	8.4	9.3		
	Hr	0.37	0.55	0.68	0.90	1.00		

A.8.2 H_N - NORMALIZED SETTLER DISPERSION BAND HEIGHTS

Settler Design Equation

$$H = c * (Q/A_s)^q$$

c, q - constants

q - 2.5 to 7 (Glasser et al (32))

Q - total volumetric throughput

A_s - settling area (horizontal cross sectional area of the settler (24 cm² per section))

The purpose of these calculations is to put the experimental dispersion band heights on a comparable basis; i.e. what would the dispersion band height have been if a standard specific flowrate (Q/A_s) was used for each run? (Experimentally it was not possible to maintain a constant specific flowrate for each run, as that would have required a much larger settling unit.)

The constants c and q may actually vary with H for the small settler used in this project. They may also be different for the different series of runs. However, by assuming reasonable values for these constants a rough qualitative comparison of the variations in settling characteristics is obtained. In three of the no extraction runs the settling areas were varied while flowrates remained constant. This allows an estimate of q.

run	first set		second set		q
	A _s (cm ²)	H (cm)	A _s (cm ²)	H (cm)	
1,2,3	72	13.6, 12.5 12.3	96	6	2.55
5	72	13.6	96	6.1	2.79
V-1	72	6.9	48	16.9	2.21

The average value of q is about 2.5, which is close to the results of other workers obtained with some other systems. A common basis of a specific flowrate of 0.144 cm^{-1} was chosen. This is equivalent to a mixer residence time of 60 seconds and a settler area of 4 sections (96 cm^2). The correction factors to convert the actual height to a normalized height for each series of runs are:

series	residence time (min)	A_s (cm^2)	correction factor, K	($H_N = K \cdot H$)
no extraction	1	72	0.49	
fast extraction	1	96	1.00	
"	1/2+	120	0.31	
slow extraction	1	48	0.18	
stripping	1	48	0.18	
"	1/2	144	0.18	

+ In fact, there was some dispersion overflow for this series. Rough corrections were made to the results to put them on a comparable basis with other results.

Table A.8.2- H_N - Normalized Dispersion Bank Heights

Series

no extraction	N	24.8	21.7	34.3	
	H	16.8	12.5	12.3	
	H_N	8.2	6.1	6.0	
fast extraction (60 s)	N	7.5	18.2	24.8	33.3
	H	2.4	3.0	2.9	2.8
	H_N	2.4	3.0	2.9	2.8
(30 s)	H	16.8	16.7	16.5	
		+10.5	+2.4	+1.7	
	H_N	7.61	6.42	6.18	
slow extraction (100 ppm)	N	7.5	14.5	24.8	
	H	0.1	3.6	3.1	
	H_N	0.02	0.63	0.56	
(14.5 s ⁻¹)	solids	0	50	100	500
	H	2.9	5.5	3.5	1.4
	H_N	2.9*	1.0	0.63	0.25
stripping (60 s)	N	7.5	11	14.5	24.8
	H	1.1	4.1	4.5	7.1
	H_N	0.20	0.74	0.81	1.28
(20 s)	H	0.6	2.8	7	9.3
	H_N	0.11	0.60	1.26	1.67

N (s⁻¹) = impellor speed

H (cm) = final dispersion band height at the end of the run

 H_N (cm) = normalized dispersion band height

solids - in ppm

* - This run was done with a settler area of 96 cm² instead of 48 cm², so the correction factor is different from other runs in the set.

**A.8.3 CORRELATING THE NORMALIZED DISPERSION BAND HEIGHT
WITH THE MIXER COALESCING TIMES**

At the end of each mixer/settler run, the time required for complete phase separation in the mixer was noted (i.e. the time at which the first clear interface appeared). This is compared to the normalized dispersion band height at different impellor speeds in the table below.

Table A.8.3 - Correlating the Normalized Dispersion Band Height with the Mixer Coalescing Time

series					
fast extraction (60 s)	N	7.5	18.2	24.8	33.3
	H _N	2.4	3.0	2.9	2.8
	t _{mix}	107.1	97.1	93.6	84.5
(30 s)	H _N	6.4	-	7.6	6.2
	t _{mix}	132	-	108	103
slow extraction (14.5 s ⁻¹)	solids	0	50	100	500
	H _N	2.9	0.63	1.0	0.25
	t _{mix}	95	43	33	<15
(100 ppm)	N	7.5	28.2		
	H _N	0.02	0.56		
	t _{mix}	<19	<29		
stripping (60 s)	N	7.5	11	14.5	24.8
	H _N	0.20	0.74	0.81	1.28
	t _{mix}	58	-	61	57
(20 s)	H _N	0.11	0.50	1.26	1.67
	t _{mix}	23	48	55	54

t_{mix} = mixer coalescence time (to the first clear interface)
in seconds

Appendix A.9

CRUD

This appendix supplies the background calculations for the concentration factors of impurities in crud as presented in the literature review of Section 9. Also included are photographs of crud that formed in the settler during the slow extraction runs. The crud is visible as a blackish "blob" at the interface between the aqueous and the organic phases in the settler.

Table A.9.1- A Comparison of the Analysis of Solids Present
in Crud with the Analysis of the Feed Solution
(from Ritcey (57))

	feed		extraction crud			stripping crud		
	raw %	rel. %	raw %	rel. %	F _{conc}	raw %	rel. %	F _{conc}
U	1.87	11.6	11.3	31.0	2.7	12.1	36.8	3.2
Mo	8E-4	5E-3	0.11	0.30	60	0.72	2.2	440
Fe	1.84	11.4	5.4	14.8	1.3	8.0	24.3	2.1
Si	0.44	2.7	13.1	36.0	13	7.5	22.8	8.4
Al	2.11	13.1	4.0	11.0	0.85	0.077	0.23	0.02
Mg	9.9	61.3	2.5	6.9	0.11	4.5	13.7	0.22
Tot.	16.16	100	36.41	100				

raw % = $\frac{\text{amount of a component in the phase (g/L)}}{\text{total amount of phase (g/L = density)}}$

rel. % = relative %

= $\frac{\text{amount of component in the phase (g/L)}}{\text{total amount of listed components in the phase (g/L)}}$

F_{conc} = concentration factor

= $\frac{\text{relative \% in the crud}}{\text{relative \% in the feed}}$

Note - Many other elements were identified in some of the phases
(feed, extraction crud, stripping crud)

Figure A.9.1 PHOTOGRAPHS OF THE SETTLER DISPERSION BAND

Effect of the Solids Content
(14.5 rev/s impellor speed)



0 ppm



50 ppm



100 ppm



500 ppm

Effect of the Impellor Speed
(100 ppm solids)



7.5 rev/s



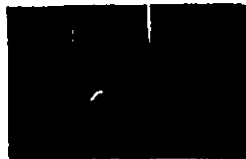
24.5 rev/s

The Progression of Crud Formation
and Crud Details

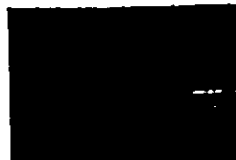
(500 ppm solids 14.5 rev/s impellor speed)



@ 10 minutes



@ 20 minutes



details