Haze Formation and Behavior in the PUREX Process

Stuart T. Arm

Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, Richland, Washington, 99352

Aqueous haze formation and behavior was studied in the liquid-liquid system tri-n-butyl phosphate in odorless kerosene and 3M nitric acid with uranyl nitrate and cesium nitrate representing the major solute and an impurity, respectively. A pulsed column, mixer-settler and centrifugal contactor were chosen to investigate the effect of different turbulence characteristics on the manifestation of haze since these contactors exhibit distinct mixing phenomena. The dispersive processes of drop coalescence and breakage, and water precipitation in the organic phase were observed to lead to the formation of haze drops of ~1 μm in diameter. The interaction between the haze and primary drops of the dispersion was critical to the separation efficiency of the liquid-liquid extraction equipment. Conditions of high power input and spatially homogeneous mixing enabled the haze drops to become rapidly assimilated within the dispersion to maximize the scrub performance and separation efficiency of the equipment.

INTRODUCTION

This extended abstract describes the manifestation and significance of aqueous phase entrainment in the continuous organic phase of a liquid – liquid extraction process employed to separate uranium and plutonium from irradiated nuclear fuel (PUREX). The most widely used liquid – liquid extraction process employs an extractant, tri-n-butyl phosphate (TBP) dissolved in an organic diluent to selectively extract uranium and plutonium from impurities dissolved in a nitric acid solution. Examples of diluent include dodecane, used in the USA and odorless kerosene (OK) used in the United Kingdom. An organic phase consisting of 20 volume percent TBP in OK (20% TBP/OK) contacted with 3M nitric acid was used throughout this work.

Process Equipment for Liquid – Liquid Extraction

The entrainment characteristics of dispersed aqueous phase drops into the continuous organic phase product was expected to be affected by the turbulence structure within the dispersion. In turn, the turbulence structure is dependent upon the geometric and dynamic characteristics of the process equipment. Therefore, three types of liquid – liquid contactor equipment commonly employed for irradiated fuel processing were studied and are described below.

The Gravity Mixer-Settler

The gravity mixer-settler is a discrete contactor that has been employed extensively from the earliest processing facilities. As illustrated in figure 1, it consists of a mixing chamber into which the aqueous and organic phases are fed. A dispersion of aqueous drops is formed by the action of an impeller. The dispersion flows over a weir and into the settling section where drops coalesce and settle by gravity. The length of the settler should be sufficient for drops to have settled out of the continuous phase.

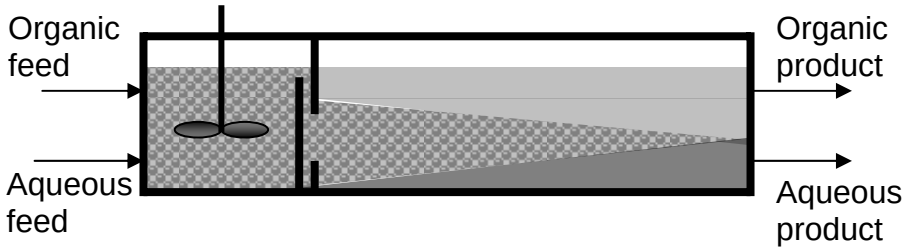

Figure 1. Schematic of the Gravity Mixer-Settler

The Centrifugal Contactor

Another discrete contactor is the centrifugal contactor, which is considered the base-line technology for future fuel processing facilities and is schematically illustrated in figure 2. The two liquid phases enter into an annulus bounded by the fixed contactor housing and an internal rotor that spins at several thousand revolutions per minute. The shear forces generated by the spinning rotor and the stationary vanes at the base produces the dispersion. It is in the annulus that the principal mass transfer takes place. The dispersion is then pumped up inside the rotor where the centrifugal forces facilitates separation of the dispersion into aqueous and organic phases. The separated phases pass over weirs, into their respective collector rings and thereby exit the contactor.

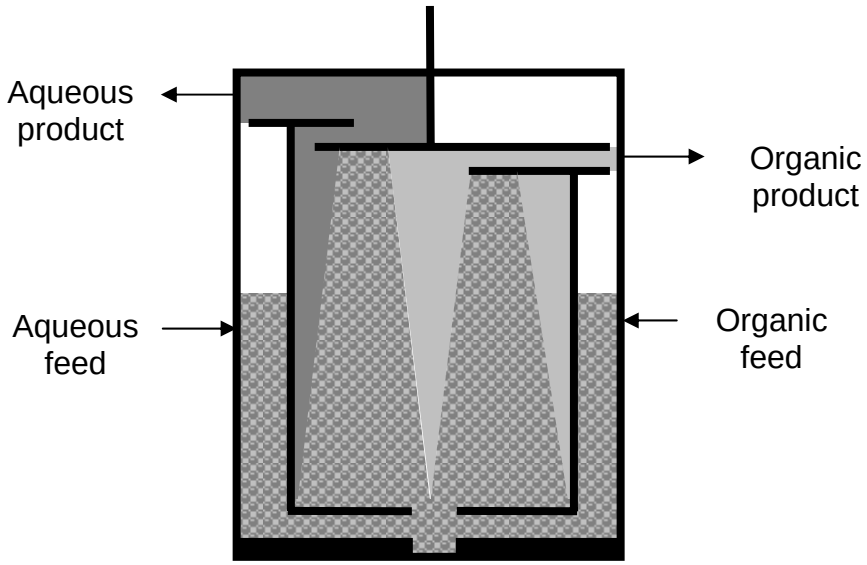

Figure 2. Schematic of the Centrifugal Contactor

Discrete contactors are typically connected to provide countercurrent contact of the organic and aqueous phases. Haze formation and behavior was studied in a bank of centrifugal contactors consisting of both extraction and scrub sections. Figure 3 illustrates the process. In the extraction section of four contactors, aqueous feed is countercurrently contacted with the organic phase. For the PUREX process, uranium, plutonium and small quantities of fission products are extracted into the organic phase in the extraction section. The organic phase exits the extraction section and feeds the scrub section where it is countercurrently contacted with dilute (~0.1M) nitric acid to strip

extracted fission products. The scrub section shown consists of eight contactors.

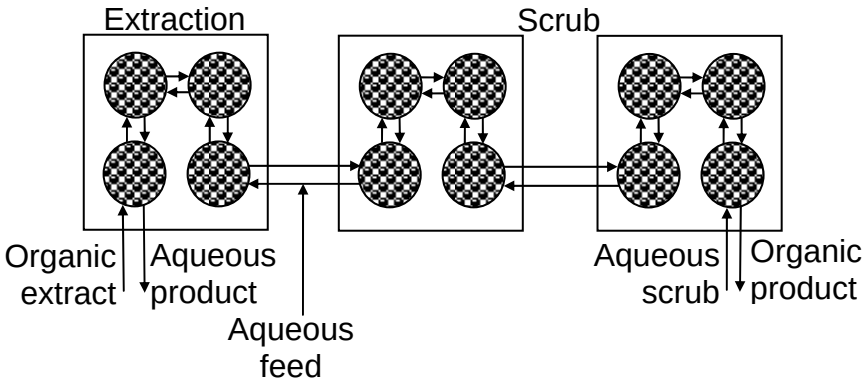

Figure 3. Countercurrent connection of discrete contactors

The Pulsed Column

The pulsed column is a differential type of contactor employed in the most modern commercial irradiated fuel processing facilities (e.g. the Thermal Oxide Reprocessing Plant, operated by British Nuclear Fuels, plc.). The pulsed column, illustrated in figure 4, consists of a column containing an axial arrangement of perforated plates, top and bottom settlers and a pulse limb. The light, organic phase is fed just above the bottom settler and forms the continuous phase. The heavy aqueous phase enters below the top settler and forms the dispersed phase as it passes through the nozzles of the perforated plates. The pulse, applied to the continuous phase, provides the dynamic force for the dispersed phase to overcome the surface tension forces that would otherwise retain the heavy phase on the plates. Drops of the dispersed phase coalesce in the bottom settler before the heavy phase passes from the column. The height of the top settler should be sufficient for drops to settle from the continuous phase before it also passes from the column.

Extraction and scrub sections may be incorporated into a single pulsed column, as illustrated in figure 4. In this case, the organic feed enters the bottom of the column, the aqueous feed part way up and then the scrub feed enters at the top. Aqueous and organic products exit the column at the column's bottom and top, respectively.

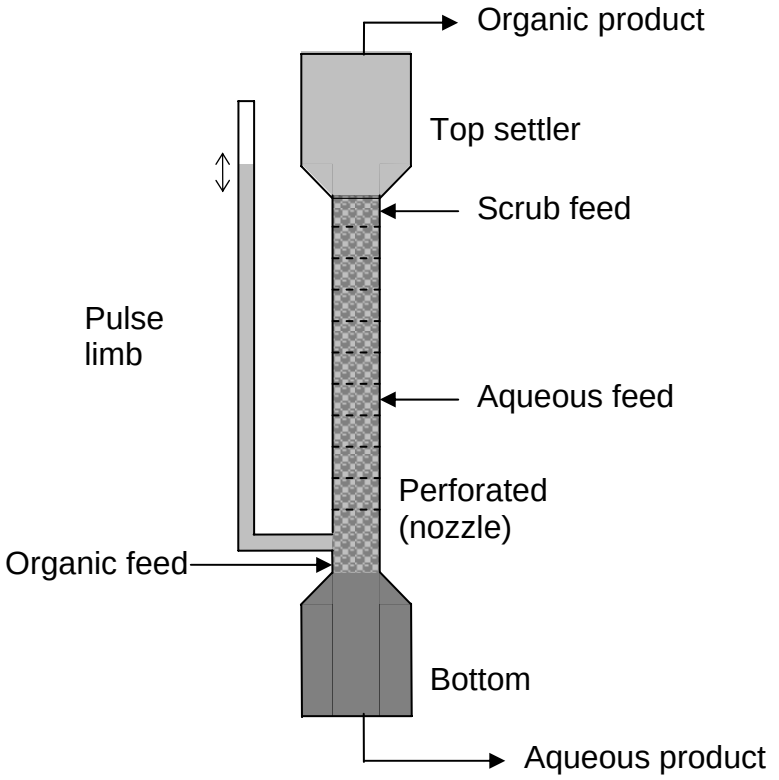

Figure 4. Schematic of a pulsed column

HYPOTHESES FOR HAZE FORMATION AND BEHAVIOR

This section defines haze and discusses hypotheses for its formation and behavior that can be compared to the phenomena experienced in actual process equipment.

Haze Formation

Haze Definition

For the purposes of this study, haze drops are defined as the secondary drops of a dispersion with diameters of approximately 1 μm since they will be most easily entrained into the continuous phase product. Primary drop breakage and water precipitation are the primary means of haze formation in the 20% TBP/OK – 3M nitric acid system.

Haze Formation by Primary Drop Breakage

Secondary or haze drops will be formed as the fluid inertial, or turbulent, forces overcome the surface tension forces constraining the primary drops such that they break apart. Turbulence consists of the apparently random motion of fluid eddies that act to generate shear forces across drops. As illustrated in figure 5, the eddy causes the drop to deform, generating a neck that breaks at a critical eddy size, as a result of Rayleigh instabilities, to produce primary and secondary drops.

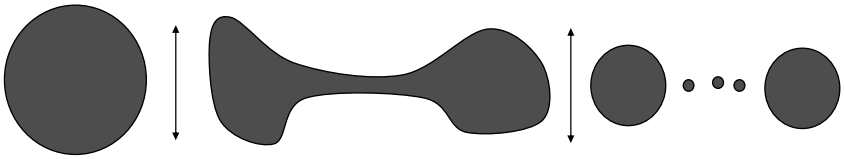

Figure 5. Illustrative Mechanism of Drop Deformation and Breakage

The size of the secondary drops can be approximately predicted by considering equations for thin film rupture and jet break-up. Ruckenstein and Jain (1974) considered the Navier Stokes equations and intermolecular forces to derive the critical wavelength of perturbations that would rupture a free thin film,

$$\lambda_{crit} = h_d^2 \sqrt{\left(\frac{4\pi^3 \gamma}{A_H} \right)} \qquad (1)$$

In equation 1, A_H is the Hamaker Constant (~10^{-20}J), h_d is the average film thickness (m) and γ is the interfacial tension (Nm^{-1}). In addition, Coyle et al. (1981) derived the volume of a drop formed from a jet breaking as a result of Rayleigh instabilities, $v_d = \pi\lambda h_j^2$, where h_j is the jet radius (m) and λ is the wavelength of the disturbance. A wavelength, or eddy size, of size 45 μm is therefore calculated to create secondary drops of 1μm diameter by putting $h_j = h_d$.

In the spectrum of eddy sizes, the smallest eddies have a size such that their Reynolds number is unity. On this basis, Kolmogoroff (1941) defined the length of the smallest eddy size, l_k, as

$$l_k = \left(\frac{\mu_c^3}{\rho_c^2 P_v} \right)^{1/4} \qquad (2)$$

In equation 2, μ_c is the continuous phase viscosity (Nsm^{-2}), ρ_c is the continuous phase density (kgm^{-3}) and P_v is the power input per unit volume (Wm^{-3}), which is a characteristic operating parameter of the process mixing equipment. Therefore, the secondary drop size can be predicted from the operating characteristics of the process equipment. The value of P_v for a l_k of 45 μm is 2400 Wm^{-3} for the system 20% TBP/OK – 3M nitric acid.

Haze Formation by Precipitation

Haze drops are also formed in the organic phase by water precipitation as a result of metal extraction. The solubility of water in 20% TBP/OK decreases as the concentrations of extracted metals, particularly uranium, increases. Therefore, the organic phase becomes increasingly super-saturated in water as uranium extraction proceeds and this is relieved by precipitation of the excess water. In a combined extraction – scrub counter-current process, most haze drops will precipitate close to the aqueous phase feed point.

Haze Behavior

Haze drops are important in considering the performance of liquid – liquid

extraction processes because they act as ‘sinks’ for relatively inextractable metals and may become easily entrained into the organic phase product due to their small size. Entrainment into the organic phase becomes increasingly probable the larger the smallest turbulent eddies compared to the haze drops because the haze drops will exist in a viscous fluid regime. In a viscous fluid regime, the haze drops are more likely to follow the fluid streamlines around the primary drops than to collide and coalesce. An important concept in considering the contactor performance is to recognize that precipitated haze represents a deviation from the equilibrium drop dispersion generated from the drop breakage and coalescence processes. The rate at which the equilibrium dispersion is re-established after haze precipitation will depend upon the turbulence characteristics of the equipment.

OVERVIEW OF EXPERIMENTAL METHODS

Gravity Mixer-Settler Experiments

Gravity mixer-settler experiments were performed batch-wise in a baffled 200-mL capacity beaker. A Rushton-type impeller provided fluid agitation with its speed measured by an optical tachometer. Experiments were performed by first adding the organic phase and then the aqueous phase beneath the organic phase by pipette. Agitation was initiated and continued for the desired time. The phases were allowed to separate for the desired time once agitation was terminated.

Pulsed Column Experiments

Pulsed column experiments were performed in a pilot plant consisting of a glass column 11-m tall and 10-cm diameter packed with nozzle plates spaced 5 cm apart. The aqueous feed was introduced to the column 3 m below the scrub feed. Organic phase samples were extracted from the column using a sampler constructed from PTFE.

Centrifugal Contactor Experiments

Centrifugal contactor experiments were performed using a single contactor with a rotor 5.5-cm diameter and 12 cm tall providing a mixing annulus 6.4 mm wide. Experiments were also performed in a pilot plant consisting of four extraction and eight scrub contactors. Sampling of the organic phase exiting each contactor was performed from a drain valve.

Analytical Techniques

Samples of the organic phase were analyzed by Karl Fischer titration for their dissolved and total (i.e. dissolved and entrained) water content. The dissolved water concentration was determined on a sub-sample from near the surface of the sample, after allowing entrained water to settle. The total water concentration was then determined by performing the titration on the entire sample.

The size distribution of drops entrained in the organic phase were analyzed using a Malvern Mastersizer laser spectrometer. Samples were analyzed for drop size distribution within a few minutes of th sampling event.

RESULTS FROM GRAVITY MIXER-SETTLER

Haze formation by drop breakage were expected from the gravity mixer-settler since the predicted power input was typically 1200 Wm^{-3} providing smallest eddies of size 50 μm. Some persistence of precipitated haze was expected since the turbulence

energy is distributed in a spatially inhomogeneous manner. Figure 6 confirms these expectations. A first set of experiments were performed with organic and aqueous phases pre-equilibrated with uranium (i.e. no mass transfer) to investigate the formation of haze drops from only the dispersive processes. Concentrations of entrained haze were approximately 0.04 volume% for mixing times up to 120 seconds. A further set of mass transfer experiments were performed to investigate haze precipitation. Figure 6 shows the concentration of entrained precipitated haze (the difference between the profiles) decreased from 0.08 volume% to 0.03 volume% for mixing times of 23 seconds to 120 seconds. The precipitated haze represents a deviation from the equilibrium drop dispersion and the latter becomes re-established and the haze concentration decreases as mixing progresses.

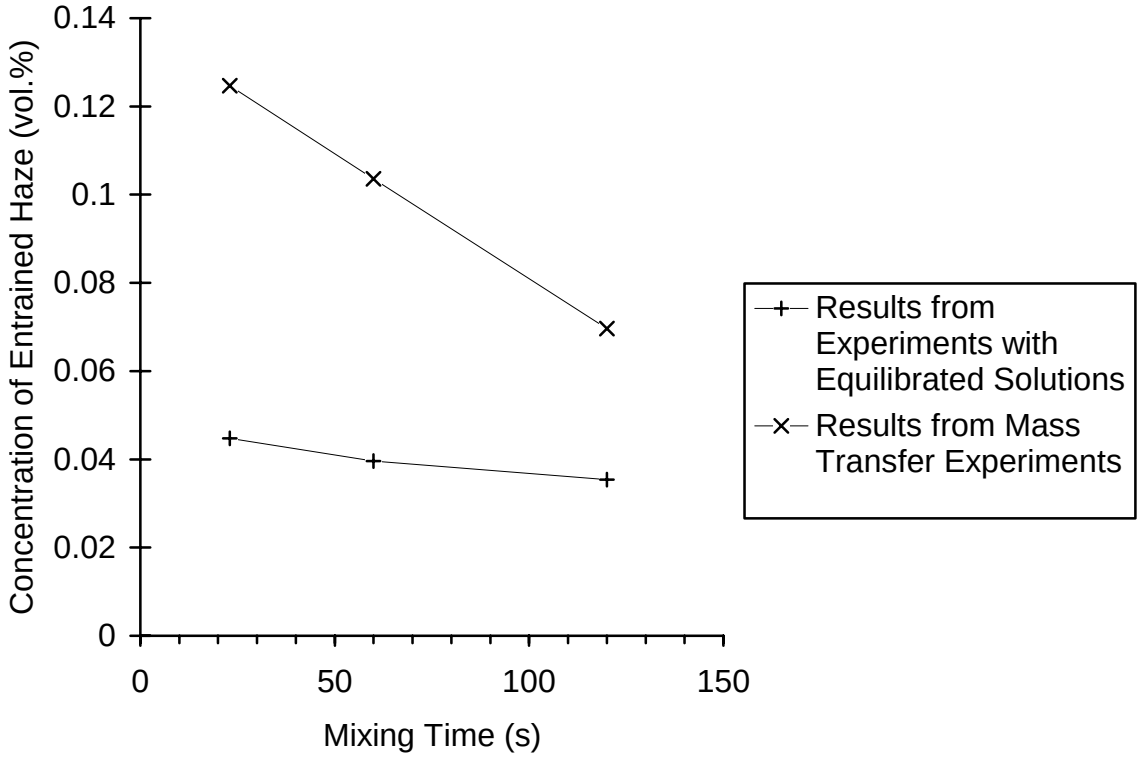

Figure 6. Concentration of Entrained Haze as a Function of Mixing Time

Figures 7 and 8 illustrate the results from the laser spectrometer for the mixing times of 23 and 120 seconds. Drops of diameter greater than approximately 8 μm are primary drops and will not be discussed further. The figures show a difference in the proportion of entrained haze drops, typically 1 μm diameter, generated in the presence and absence of mass transfer that diminishes as mixing progresses. The results from the laser spectrometer again illustrate the equilibrium drop dispersion becoming re-established as mixing progresses.

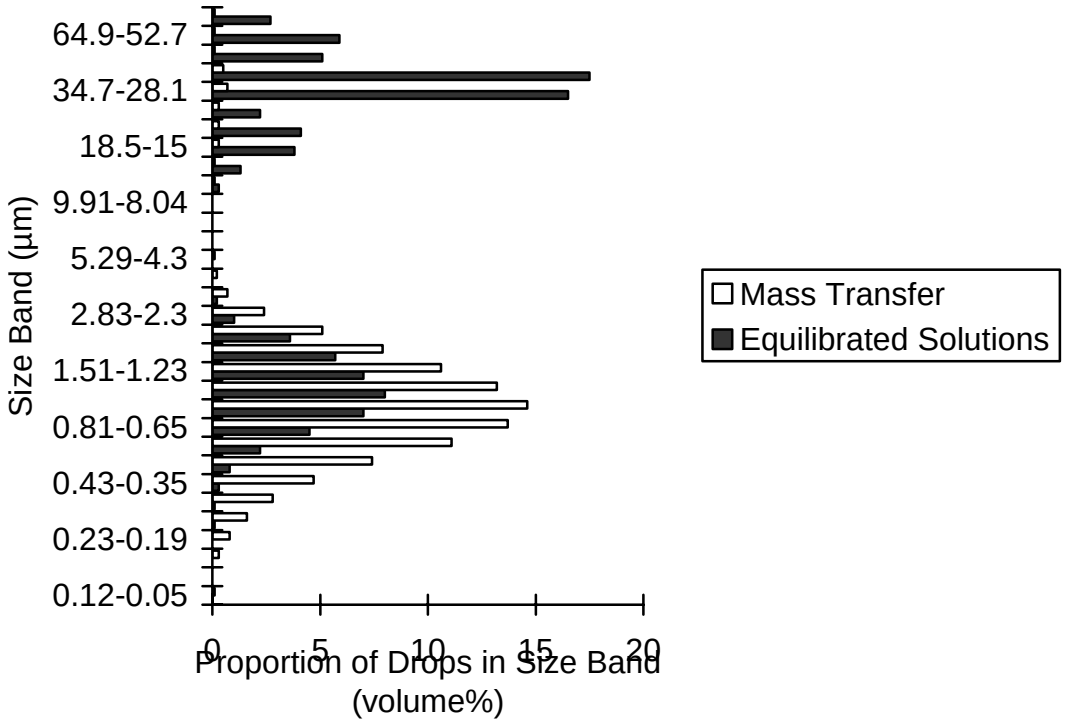

Figure 7. Entrained Drop Size Distribution in the Presence and Absence of Mass Transfer for a Mixing Time of 23 seconds

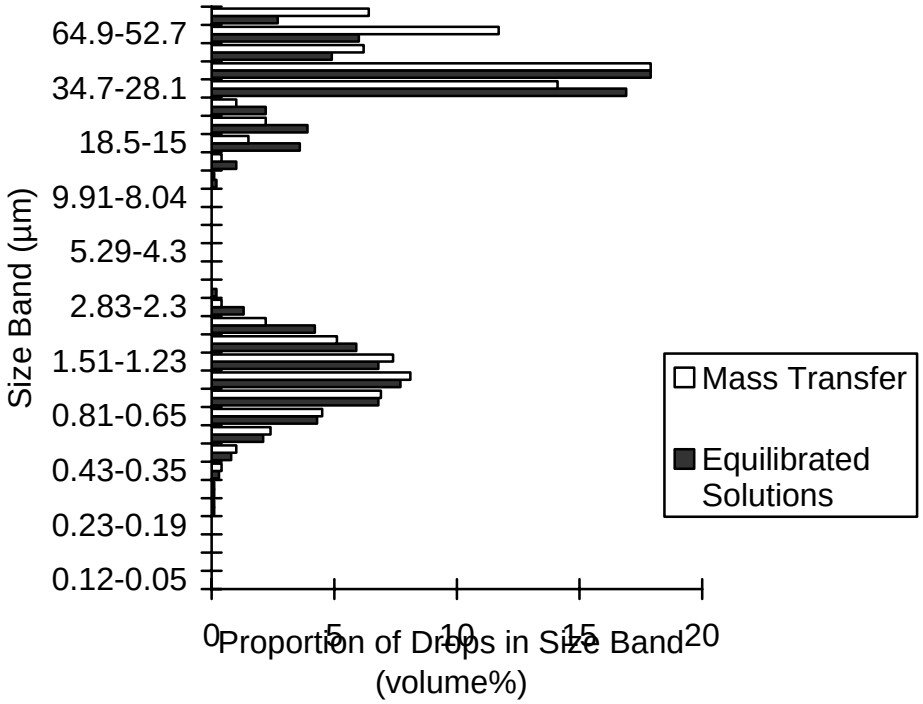

Figure 8. Entrained Drop Size Distribution in the Presence and Absence of Mass Transfer for a Mixing Time of 120 seconds

RESULTS FROM THE PULSED COLUMN

Precipitated haze was expected to persist through the scrub section of the column. The smallest eddy size of 150 μm generated from a power input of approximately 100 Wm^{-3} would not have generated haze drops by drop breakage. In addition, the precipitated haze drops exist in a viscous fluid regime and follow the fluid streamlines around the primary drops rather than undergoing coalescence.

Figure 9 presents the dissolved and entrained water concentration profiles from the pulsed column pilot plant. The uranium bearing aqueous feed is introduced approximately 3 m below the scrub feed. The dissolved water concentration decreases through the extraction section as uranium is extracted into the organic phase. The dissolved water concentration remains constant through the scrub section since there is no uranium extraction into the organic phase. The concentration of entrained aqueous phase is negligible through the extraction section 5 m below the scrub feed. However, the concentration of entrained aqueous phase increases to approximately 0.1 volume% closer to the aqueous feed point, where most of the uranium mass transfer occurs, as haze is precipitated and entrained. There is a spike in the entrained aqueous phase concentration at the aqueous feed point but this is considered mainly constituted of bulk aqueous phase entrained directly into the sample from the aqueous feed distributor. In the scrub section, the concentration of entrained aqueous phase remains constant at approximately 0.1 volume% indicating the persistence of haze precipitated close to the aqueous feed point.

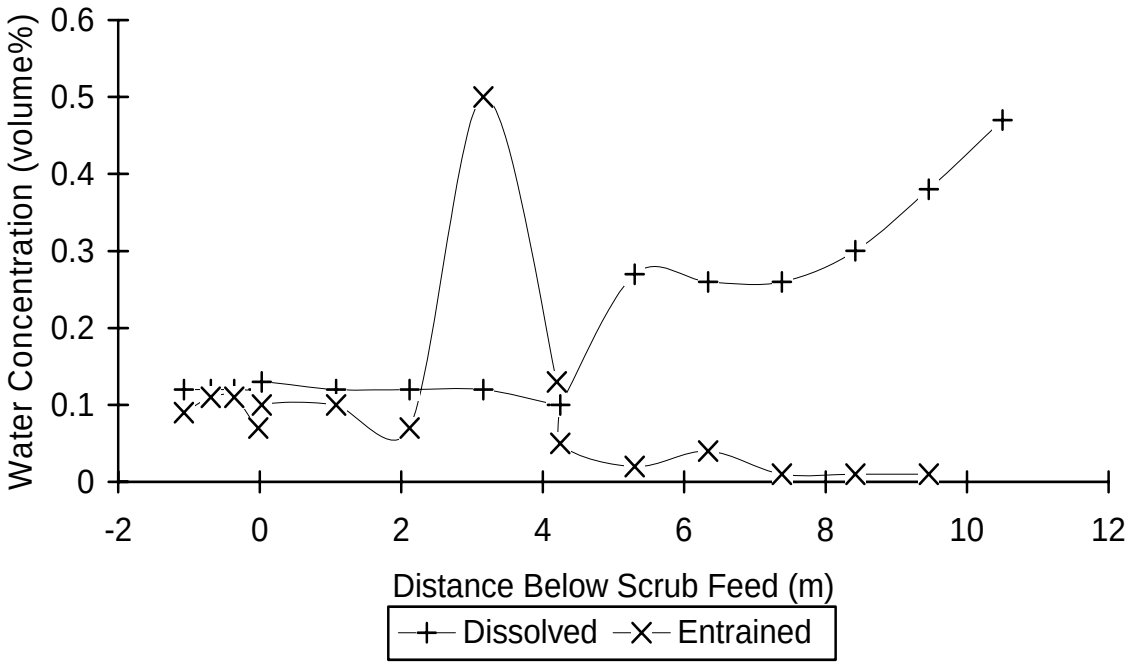

Figure 9. Water Concentration Profiles from the Pulsed Column Pilot Plant

RESULTS FROM THE CENTRIFUGAL CONTACTOR

Haze formation from drop breakage was expected to be significant in the centrifugal contactor since the smallest eddies generated from a power input of 40,000 Wm^{-3} were predicted to be approximately 20 μm diameter. The precipitated haze was expected to become rapidly assimilated with the haze drops formed by drop breakage since the mixing energy is concentrated into a small volume.

Figure 10 illustrates the size distribution of drops entrained from the centrifugal contactor in the absence of mass transfer. Drops of size greater than approximately 8 μm again represent the primary drops and are not discussed further. The figure clearly shows the generation and entrainment of haze from drop breakage. As expected, the haze drops become smaller with increasing rotor speed and, therefore, decreasing eddy size.

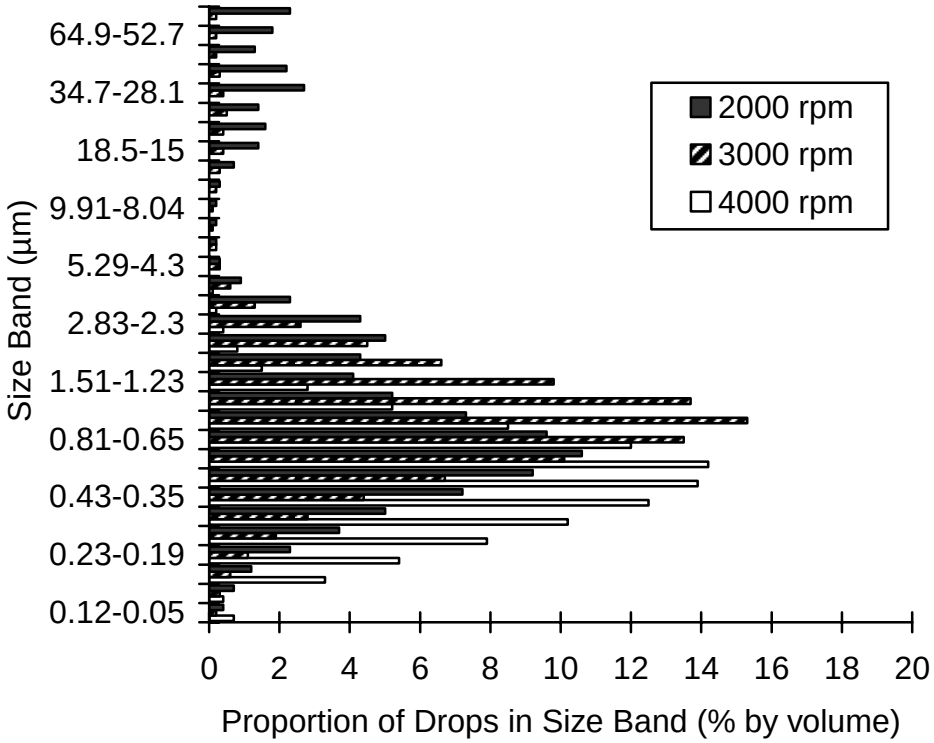

Figure 10. Size Distribution of Entrained Aqueous Drops in the Centrifugal Contactor (no mass transfer)

Haze entrainment is further illustrated in figure 11 as a function of rotor speed. At low rotor speeds, haze entrainment slightly decreases as the rotor speed is increased, which can be attributed to improved phase separation due to increased centrifugal forces inside the rotor. However, improving phase separation at higher rotor speeds is less significant than the increasing mixing intensity in generating smaller drops that are harder to separate. Therefore, the entrained haze concentration increases with increasing rotor speed at higher speeds.

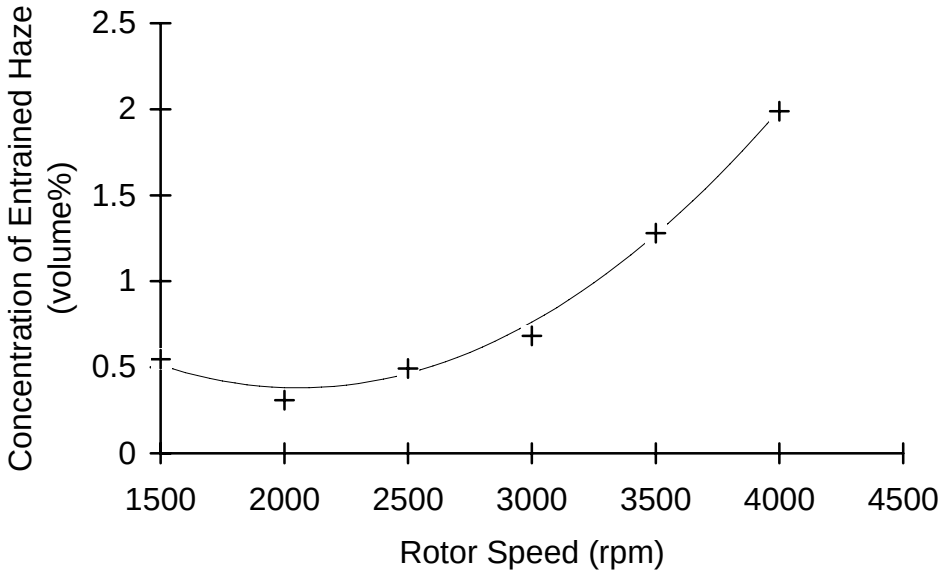

Figure 11. Entrained Haze in the Centrifugal Contactor as a Function of Rotor Speed

Figure 12 illustrates the profiles of dissolved and entrained water in the centrifugal contactor pilot plant. As in the pulsed column, the concentration of dissolved water decreased in the extraction section as uranium was extracted into the organic phase. As expected, there was no evidence of precipitated haze entrained into the organic phase product from the fourth stage where most of the uranium mass transfer occurred. The concentration of entrained haze increased in each of the scrub stages presumably due to contactor hydrodynamics since no significant mass transfer occurs throughout this section. However, the reason for this phenomenon is not readily explained. These results demonstrate the importance of haze generated from drop breakage for centrifugal contactors and that precipitated haze is an insignificant contributor to entrainment.

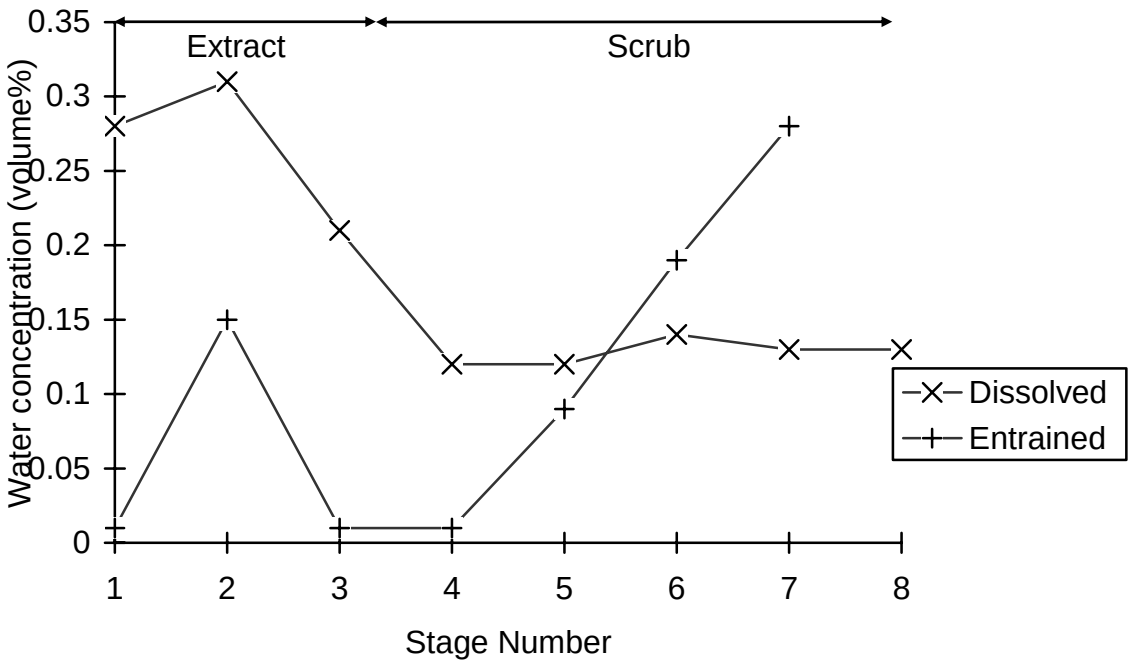

Figure 12. Entrained and dissolved water concentration profiles from the centrifugal contactor pilot plant

IMPLICATIONS OF HAZE ENTRAINMENT FOR ORGANIC PHASE PRODUCT PURITY

The major source of impurities in the organic phase product are in the entrained haze drops because they act as 'aqueous sinks' in which the impurities are dissolved. The mechanism by which these impurities are scrubbed from the organic phase depends upon the haze behavior and, therefore, the mixing intensity in the contactor.

Haze drops fully participate in the drop dispersal and coalescence processes in contactors for which the power input is greater than approximately 1000 Wm^{-3} (i.e. centrifugal contactors and gravity mixer-settlers). Impurities dissolved in the entrained drops are successively mixed with the bulk aqueous phase in each stage. Therefore, the concentration of impurities in the organic phase is successively reduced by dilution. Two dilution models were considered. In the dispersion – capture model, haze drops are first formed from the bulk aqueous phase and mixed with those entrained in the organic phase feed. Excess haze drops then coalesce with the bulk aqueous phase so that the equilibrium dispersion is generated. In the capture – dispersion model, haze drops entrained in the organic phase feed are first captured by the bulk aqueous phase. Haze drops are then generated from the bulk aqueous phase to establish the equilibrium dispersion. The dispersion – capture model better described operations with low dispersed phase holdup, presumably because of a low coalescence rate. At high dispersed phase holdup when the coalescence rate is higher, however, the capture – dispersion model was better.

For pulsed columns and other contactors with power inputs less than

approximately 1000 Wm^{-3}, haze drops are only formed by precipitation and they do not participate in the drop dispersal and coalescence processes. The concentration of impurities in the haze drops can only be reduced by mass transfer through the organic phase and into the scrub aqueous phase. However, such mass transfer is insignificant due to the low extractability of impurities into the organic phase and the low bulk interfacial area of scrub drops. Therefore, haze drops and their impurity content persist through the scrub section into the organic phase product.

CONCLUSIONS

The formation and behavior of aqueous hazes is determined by the mixing characteristics of the contactor type.

- Haze drops are generated from primary drop breakage in contactors of high mixing intensity, such as centrifugal contactors and gravity mixer-settlers. In addition, haze is precipitated in all equipment when water super-saturation in the organic phase is relieved during uranium extraction.
- Precipitated haze drops persist in a laminar flow environment in contactors of low mixing intensity, such as pulsed columns. In contactors of high mixing intensity, the haze drops fully participate in the drop dispersal and coalescence processes.

The impact of haze entrainment on product purity was investigated by measuring the concentrations of impurities (e.g. cesium) in haze drops and the organic phase. These results show the purity of the organic phase product is largely determined by the presence of entrained aqueous hazes because they act as ‘sinks’ for impurities of low extractability.

- The impurity content of haze drops is reduced by dilution with the bulk aqueous phase in contactors of high mixing intensity.
- In contactors of low mixing intensity, there is no significant reduction in the impurity concentration.

REFERENCES

Coyle, R.W.; Berg, J.C.; Niwa, J.C. Liquid-liquid Jet Break-up Under Conditions of Relative Motion, Mass Transfer and Solute Adsorption. Chem. Eng. Sci. **1981**, *36*.

Kolmogoroff, AN, Compt. Rend. Acad. Sci. URSS **1941** *30, 32*

Ruckenstein, E.; Jain, R. K. Spontaneous Rupture of Thin Liquid Films. J. Chem. Soc., Faraday Trans. II **1974**, *70*.