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**Predispersed Solvent Extraction**

by

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(ABSTRACT)

A new solvent extraction method has been developed for the extraction of metal and organic ions from very dilute aqueous solutions. The new method, which has been named Predispersed Solvent Extraction (PDSE), is based on the principle that there is no need to comminute both phases. All that is necessary is to comminute the solvent phase prior to contacting it with the feed. This is done by converting the solvent into aphrons, which are micron-sized globules encapsulated in a soapy film. Since the aphrons are so small, it takes a long time for the solvent to rise to the surface under the influence of gravity alone. Therefore, the separation is expedited by piggy-back flotation of the aphrons on specially prepared gas bubbles, which are somewhat larger than aphrons and are called colloidal gas aphrons (CGA).

Copper, uranium and chromium ions, and alizarin yellow were extracted from very dilute aqueous solutions using PDSE. Tests were performed in a vertical glass column in both batch and continuous modes, and in a continuous horizontal trough. The new solvent extraction procedure worked very efficiently and very quickly under laboratory conditions. Higher than 99% extraction was achieved in many of the tests performed.

## **Dedication**

I dedicate this thesis to the memory of my beloved son, Walter Anthony (Nono).

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## **1.0 INTRODUCTION**

### **1.1 Preamble**

Due to depletion of high grade ore reserves, environmental legislation and political factors, increasingly significant proportions of metals production are obtained through hydrometallurgy. In hydrometallurgy, the leaching process is always followed by a separation process to selectively remove components from the mixture. A separation method commonly used is solvent extraction.

The main advantage of solvent extraction lies in its extreme versatility because of the large range of choice of solvents. Whereas, distillation and gas absorption processes impose rigid requirements as to the vapor pressures and solubilities of the various components, solvent extraction can be adapted to many more systems.

In the process of solvent extraction it is important to create a large surface area between the extracting solvent and the feed solution containing the solute in order to achieve rapid approach to equilibrium by facilitating mass transfer of solute across the interface. Although new and improved contactors that employ mechanical energy input to achieve high rates of mass transfer have been developed during the past 40 years, these can be expensive and for very dilute feed solutions the power costs can be significantly high and wasteful. Predispersed Solvent Extraction (PDSE), is a new solvent extraction procedure, which has shown promise for extraction from very dilute solution very efficiently and very quickly.

This thesis presents a study of extraction of copper, chromium, and uranium ions; and alizarin yellow from dilute aqueous solution using PDSE. With this new solvent extraction process, higher than 99% extraction was achieved in many of the tests performed.

## **1.2 Description of the PDSE Process**

### **1.2.1 Principles of PDSE**

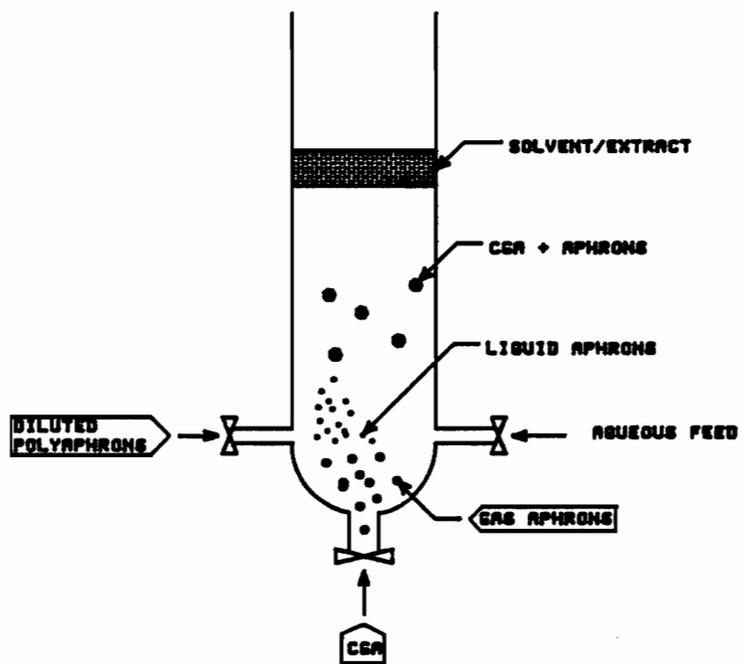
In conventional solvent extraction mass transfer of solute across the interface is achieved by vigorous mixing of the aqueous and solvent phases, followed by a settling stage during which the droplets coalesce; or alternatively by breaking up a stream of one phase as it enters the second. But there is really no need to comminute both phases. In fact, all that is necessary is to comminute one phase and clearly, with energy conservation in mind, that would be the minor phase, namely the solvent. In PDSE only the solvent phase is comminuted, using mainly surface forces, prior to contacting the feed solution. The process requires the conversion of the solvent into aphrons, (Sebba, 1984), which are micron-sized globules encapsulated in a soapy film which stabilizes them. A concentrate of aphrons containing 90 to 95% oil dispersed in water as the continuous phase is easily made and is known as a polyaphron. Polyaphrons are very stable and can be stored for long periods of time (several years), without deterioration, until they are required for use.

Polyaphrons of high PVR, phase volume ratio, have too much cohesion and take too long to disperse. Therefore, in order to be suitable for PDSE, polyaphrons have

to be diluted previously to being used. Since water is the continuous phase in all polyaphrons used so far for solvent extraction purposes, addition of the polyaphron to water breaks it down into individual aphrons that are dispersed in the water.

In the settling stage of conventional solvent extraction the solvent rises because it is lighter than water, and it then coalesces so that in a short time two distinct layers form; the heavier aqueous layer on the bottom with the lighter solvent layer floating on top. In the case of predispersed solvent extraction the solvent is previously aphronized; therefore, the globules are so small that it would take a very long time for the solvent to rise to the surface under the influence of gravity alone. For this reason, separation is expedited by piggy-back flotation of aphrons on specially prepared gas bubbles, which are somewhat larger than aphrons, and are called colloidal gas aphrons (CGA). These, as described by Sebba and Barnett (1981), are 25-50  $\mu\text{m}$  bubbles dispersed to the extent of 60% by volume of gas in water. Since this work was done, an improved method for generating CGAs has been developed by Sebba (1985a), using a rapidly spinning horizontal disc mounted between two vertical baffles. The CGAs are made very quickly in this way and can be pumped and metered into the feed solution at any desired rate. They rise more rapidly than aphrons through the aqueous pregnant solution, because of their low density, and in so doing they capture the solvent aphrons which adhere to the outside of the bubble shell. This adherence occurs because the outside of each bubble is hydrophobic because of the orientation of the surfactant molecules in the encapsulating soap film (Aggarwal et al, in press). On reaching the surface of the pregnant aqueous phase the bubbles burst, the gas escapes and the solvent remains as a thin layer on the surface. Figure 1 illustrates the predispersed solvent extraction process.

The possibility of foam formation at any stage of the process can be avoided by an adequate choice of surfactant for the CGA. As reported by Sebba (1963), a foam



**Figure 1. Predispersed Solvent Extraction.**

can often be broken by contacting it with a foam of opposite charge. Therefore, taking advantage of this phenomenon, if the polyaphron is made using an anionic surfactant for the encapsulating soapy film, then the CGA that is to be used in the flotation stage should be made with a cationic surfactant. In this manner, the amount of foam that is left floating on the solvent is negligible, provided that the amount of CGA used is not in excess of that necessary to achieve complete flotation.

### **1.2.2 Theory**

There is a very important distinction between the theory of conventional solvent extraction and that of predispersed solvent extraction. Both depend, of course, on a favourable distribution coefficient of the solute between solvent and water. This will be referred to as the extraction coefficient,  $E$ . However, in a mixing-settling extraction, transfer from the solution to the solvent will cease as soon as the equilibrium is established, so there is a limit to the amount of extraction at each stage. On the other hand, in predispersed solvent extraction the equilibrium is between each aphron and the pregnant solution at the point when the aphron is just about to leave the solution and enter the surface, effectively removing it from equilibrium. Each aphron therefore leaves a portion of the solution that is slightly depleted in solute. Clearly each aphron cannot be in equilibrium with the total volume of pregnant solution, so it is convenient to define a depletion volume, which is that volume of pregnant solution with which the aphron has time to establish equilibrium just prior to leaving it.

The depletion volume would, of course, be dependent upon factors such as temperature, diffusion coefficient and concentration, and would be an extremely small volume. However, there are an enormous number of aphrons, all following one

another, with each extracting irreversibly a small amount of solute. The net effect is that extraction in this way can be virtually complete. A useful analogy would be what happens in analytical chemistry when a precipitate is washed. In such a case it has been established that it is more efficient to wash a few times, each with a small volume of the wash liquid, than to extract once with a full amount.

Suppose the volume of pregnant solution is  $V_p$   $\langle ml \rangle$ , and this is extracted by a succession of  $N$  aphrons, each of which has a volume of  $v$   $\langle ml \rangle$ . Then

$$\text{Total volume of solvent } V_s = Nv \quad [1]$$

If  $f$  is the ratio of volume of total solvent to that of the pregnant solution,

$$V_s = fV_p \quad [2]$$

Each aphron prior to bursting through the surface of the pregnant solution is presumed to have reached equilibrium with the depletion volume,  $V_D$ .

If  $a$  is the initial number of moles of solute in volume  $V_D$ , and  $x_1$  moles of solute left after extraction by aphron 1, then the amount extracted will be  $(a - x_1)$  moles. If at any stage,  $C_s$  is the molar concentration of solute in solvent, and  $C_w$  is its molar concentration in the water, then the extraction coefficient  $E$  is  $\frac{C_s}{C_w}$ . After extraction by the first aphron,

$$C_s = \frac{(a - x_1)}{v}, \text{ and } C_w = \frac{x_1}{V_D} \quad [3]$$

Then

$$E = \left[ \frac{(a - x_1)}{v} \right] \left( \frac{x_1}{V_D} \right)^{-1}$$

$$= \frac{(a - x_1)V_D}{x_1 v}$$

so

$$x_1 = aV_D(Ev + V_D)^{-1} \quad [4]$$

After extraction by aphaon 2,  $x_2$  is left, and the amount extracted is  $(x_1 - x_2)$ . Then

$$C_s = \frac{(x_1 - x_2)}{v}, \text{ and } C_w = \frac{x_2}{V_D} \quad [5]$$

and

$$E = \frac{C_s}{C_w}$$

$$= (x_1 - x_2) \left( \frac{v x_2}{V_D} \right)^{-1}$$

whence

$$x_2 = \frac{x_1 V_D}{(Ev + V_D)}$$

$$= a \left[ \frac{V_D}{(Ev + V_D)} \right]^2 \quad [6]$$

After extraction by aphaon  $n$ ,

$$x_n = a \left[ \frac{V_D}{(Ev + V_D)} \right]^n \quad [7]$$

or

$$\frac{x_n}{a} = p^n$$

where  $p = \frac{V_D}{(Ev + V_D)}$ . It is the exponent  $n$  which makes this form of solvent extraction so efficient.

If  $f$  is the ratio of total volume of solvent to total volume of pregnant,

$$n = \frac{fV_D}{v} \quad [8]$$

If the aphron is delayed at the interface for 0.5 seconds and diffusivity is  $10^{-5}$  cm<sup>2</sup>/sec, then  $V_D$  is approximately  $400\mu\text{m}^3$ . Assume  $f = 0.3$  and  $v = 1\mu\text{m}^3$ ; then  $n = 120$ . Then, if  $E = 10$ ,  $x_n/a = 0.052$ , whereas for a single conventional extraction it would be 0.25.

On the other hand, if  $E = 100$ ,  $x_n/a$  would be  $2.3 \times 10^{-12}$ , whereas for a single conventional extraction it would be 0.032.

There are two factors that determine the efficiency of the extraction. One is the value of  $p$  which must be as small a fraction as possible. Thus the larger the value of  $E$  (the extraction coefficient), the smaller  $p$  will be. Secondly the value of  $n$ , (the exponent) must be as large as possible. This would be determined by the ratio of volume of extracting solvent to the volume of the pregnant solution,  $f$ , and by the size of the aphrons. The smaller the aphrons, the larger  $n$  would be. As the aphrons are removed by flotation, a reduction in the size of the aphrons does not pose a problem, unless they are made so small that they are virtually solubilized. It must be made

clear that the above equations have not yet been tested quantitatively (Sebba, 1987).

### **1.3 Research Objectives**

The objectives of this study may be broadly classified as follows:

1. To test the PDSE process as a means of extracting metal and organic ions from dilute aqueous solution.
2. To investigate the efficiency of the PDSE process in batch and continuous modes.
3. To study the effect of the following process variables on the extraction efficiency of the PDSE process:
  - a. Size of polyaphrons
  - b. Type of solvent used
  - c. Type of surfactant used to make polyaphrons and CGAs
  - d. Volume of polyaphrons added
  - e. Volume of CGA added
  - f. Residence time
4. To determine analytical techniques to measure the percent of solid extracted.

## **1.4 Summary of Chapters**

This thesis is divided into six major chapters. A summary of the remaining chapters follows.

Chapter 2 contains a comprehensive review of liquid extraction. The principles, physical and chemical equilibria, and advances in process equipment are summarized, along with some background and new developments on the solvent recovery of uranium, copper, chromium, and color removal from textile mill effluents.

Chapter 3 gives a description of the apparatus used for predispersed solvent extraction in this study. The chapter also contains a detailed procedure of the experimental work done.

Chapter 4 includes a detailed discussion of the experimental work done. It outlines some of the problems encountered with the analytical techniques used and gives a description of the results obtained.

Chapter 5, summarizes the conclusions and Chapter 6 lists some ideas for future work in the area of predispersed solvent extraction.

## 2.0 LITERATURE REVIEW

### 2.1 Liquid Extraction

Liquid extraction, sometimes called solvent extraction, is the separation of the constituents of a liquid solution by contact with another insoluble liquid. If the substances constituting the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result, and this can be enhanced by use of multiple contacts or their equivalent in the manner of gas absorption and distillation.

In all such operations, the solution which is to be extracted is called the feed, and the liquid with which the feed is contacted is the *solvent*. The solute-enriched product of the operation is called the *extract*, and the residual liquid from which solute has been removed is the *raffinate*.

Applications of liquid extraction fall into several categories: those where extraction is in direct competition with other separation methods and those where it seems uniquely qualified (Treybal, 1980). When in competition with other mass-transfer operations, relative costs are important. Distillation and evaporation are direct separation methods, the products of which are composed of essentially pure substances. Liquid extraction, on the other hand, produces new solutions which must in turn be separated, often by distillation and evaporation. Nevertheless, there are separations that can be performed with difficulty by distillation or with relative ease by extraction into a suitable solvent followed by distillation of the extract. For

the most dilute solutions particularly, where water must be vaporized in distillation, extraction is more economical, especially since the heat of vaporization of most organic solvents is substantially less than that of water. Extraction may also be attractive as an alternative to distillation under high vacuum at very low temperatures to avoid thermal decomposition (Treybal, 1980). For example, long-chain fatty acids can be separated from vegetable oils by high vacuum distillation but more economically by extraction with liquid propane (Treybal, 1980).

Liquid extraction is also used as a substitute for chemical methods. Chemical methods consume reagents and frequently lead to expensive disposal problems for chemical by-products. Liquid extraction, which incurs no chemical consumption or by-product production, can be less costly (Treybal, 1980). Metal separations such as uranium-vanadium, the fission products of atomic-energy processes and even lower-cost metals such as copper and inorganic chemicals such as phosphoric acid are economically purified by liquid extraction, despite the fact that the cost of solvent recovery must be included in the final reckoning.

There are separations that presently cannot be performed by any other method than liquid extraction. Among these are the separation of substances that are nearly of the same molecular weight and are impossible to separate by distillation because their vapor pressures are approximately the same. On the other hand, these substances can be readily separated by extraction with any number of solvents.

The main advantage of liquid-liquid extraction lies in its extreme versatility because of the enormous range of choice solvents. Whereas distillation and gas absorption processes impose rigid requirements as to the vapor pressures and solubilities of the various components, solvent extraction can be adapted to many more systems. It is increasingly common for solvent extraction processes to involve a chemical reaction of the extracted component with a component (the extractant)

dissolved in the solvent; this has led to major new applications in hydrometallurgical processing (Mark et al 1987).

Like many other chemical engineering unit operations, liquid- liquid extraction was developed in the 1920's and 1930's as part of the petrochemicals industry. Important applications were also developed for the recovery of vegetable oils and the purification of penicillin and other heat-sensitive pharmaceutical products that cannot be separated easily by distillation.

The growth in the nuclear industry has resulted in many applications of liquid-liquid extraction in the refining of uranium, plutonium, and other radioisotopes. Since about 1960, extractants for nonnuclear metals, in particular copper, cobalt, and nickel, have been developed. A recent survey (Flett, 1977), listed 19 plants or proposed plants using liquid-liquid extraction for copper alone.

The growth in the industrial application of liquid-liquid extraction has been paralleled by increased research aimed at an understanding of the fundamentals. In the 1920's and 1930's liquid-liquid extraction was usually treated as an equilibrium-stage process analogous to distillation. However, many types of extraction columns (e.g., packed columns and spray columns) do not contain discrete stages, and this has led to increasing use of the transfer unit concept and more emphasis on mass transfer rate estimation using transport phenomena models. The importance of hydrodynamic effects such as droplet breakup and coalescence and axial mixing has been increasingly realized in the past decade. Finally, the chemistry of solvent extraction reactions has come under even closer scrutiny (Mark et al, 1987).

## 2.1.1 Principles of Liquid-Liquid Extraction

### 2.1.1.1 Physical Equilibria

Extraction involves the use of systems composed of at least three substances, and although for the most part the insoluble phases are chemically very different, generally all three components appear at least to some extent in both phases. Liquid-liquid equilibria are governed by the phase rule:

$$F = C - P + 2 \quad [9]$$

where  $C$  is the number of components,  $P$  is the number of phases (two in this case), and  $F$  is the number of degrees of freedom, *i.e.*, independent variables permitted by the system.

Ternary liquid-liquid systems are, therefore, allowed three degrees of freedom according to the phase rule. At a given temperature and pressure, the composition of one phase determines the composition of the other phase at equilibrium. Several graphical methods for representing equilibrium data have been proposed and are described by Treybal (1980).

A large and ever-growing amount of experimental liquid-liquid equilibrium data are available (Francis, 1963). Alternatively, data can be obtained experimentally by manually shaking the solution and solvent and then separating the layers, followed by analysis. Recently, an automated device, the AKUFVE apparatus, has been developed for the collection of large quantities of equilibrium data (Rydberg et al, 1973). The prediction of liquid-liquid distribution data from activity considerations for nondilute systems with partial miscibility has been developed to a considerable

extent (Laddha and Degaleesan,1976). However, the number of systems tested is still rather limited, and these methods are recommended only as an approximate but inexpensive alternative to experimental measurement (Mark et al, 1987).

### 2.1.1.2 Chemical Equilibria

In many cases, equilibria in liquid-liquid systems are affected by chemical changes; e.g., (1) equilibrium with a chemical change occurring in the bulk of one or both of the phases but with components transferring between phases without chemical change; and (2) equilibrium with a chemical change occurring at the interface itself; no molecular species has significant solubility in both phases (Mark et al, 1987).

The majority of hydrometallurgical extraction processes belong to the second type, in which an equilibrium is considered to exist at the interface between ionized species in the aqueous phase and unionized species in the organic phase. For this purpose, there are numerous commercially available metal extractants that act as liquid-liquid cation exchangers (Kolarik, 1971). The extraction is represented by the following equation:



where,  $M^{n+}$  is the metal cation and RH is the extractant which is normally dissolved in an inert organic diluent such as kerosine.  $R_nM$  is an organic-soluble salt or complex of the metal and the extractant, which may be an acid or an acidic chelating agent.

The distribution ratio of the metal (organic to aqueous phases) decreases strongly as the hydrogen ion concentration in the aqueous phase increases. Thus the

pH control is crucial to the point that a metal that is almost completely extracted into the organic phase at pH 4 can be reextracted by the aqueous phase at pH 1 (Cook and Szmokaluk, 1971).

### 2.1.1.3 Interfacial Mass Transfer

Just as important as the equilibrium relationships are in determining the ultimate separation obtainable in a liquid-liquid system, is the rate of equilibrium attainment in the design or operation of extraction processes (Mark et al, 1987). In a batch process, this rate determines the contact time required; in a continuous process, the required size of the equipment and the residence time (volume of equipment divided by volume flow rate of phases) depend on mass transfer rates as well as on equilibrium process.

In the absence of any chemical reactions, the rate of transfer of a component to be separated from one phase to another is governed by the diffusion laws. The diffusional mass transfer rate of solute per unit area, relative to a stationary medium, is given by Fick's first law:

$$N = D \frac{\partial c}{\partial z} \quad [11]$$

where  $N$  refers to transport in the  $z$  direction,  $c$  is the concentration of the component to be separated, and  $D$  is its molecular diffusivity with respect to the solvent. Values of  $D$  for many systems are available on the literature or can be predicted by various correlations which are accurate to within  $\pm 10\%$  or better (Reid and Sherwood, 1958). In general, molecular diffusivities of solutes in liquids are within the range of  $10^{-6}$  to  $10^{-5} \text{ cm}^2/\text{s}$ .

Due to the low values of diffusivity,  $D$ , molecular diffusion is a very slow process; however, its effect is practically always enhanced by turbulent eddies and circulation currents. These provide almost perfect mixing in the bulk phases but their effect tends to be retarded in the vicinity of a liquid-liquid interface. Consequently, the important role of molecular diffusion is confined to very narrow regions, sometimes referred to as films, on either side of the interface.

In accordance with Fick's first law, the transfer across each film occurs in the direction of decreasing concentration. It is usually assumed that the solute concentrations  $c_{A_i}$  and  $c_{B_i}$  in the A-rich and B-rich phases at the interface are in equilibrium. If the system obeys the distribution law, then:

$$c_{B_i} = mc_{A_i} \quad [12]$$

where  $m$  is the appropriate distribution factor. This assumption of interfacial equilibrium is reasonable in practice, except for some cases where a physical barrier of a surface-active contaminant (Lindland and Terjesen, 1956) or reaction product (Yagodin et al, 1979) accumulates at the interface. In these cases, an allowance has to be made for interfacial resistance.

The thicknesses of the regions across which the concentration varies are on the order of  $10^{-3}$  cm and depend upon hydrodynamic conditions. These thicknesses are extremely hard to measure directly and the flux of solute is, therefore, expressed in terms of mass transfer coefficients which combine the effects of molecular diffusivity and film thickness:

$$N = k_A(c_A - c_{A_i}) = k_B(c_{B_i} - c_B) \quad [13]$$

where,  $N$  is the mass transfer rate per unit interfacial area.

The order of magnitude of  $k_A$  and  $k_B$  is usually within the range of  $10^{-3}$  to  $10^{-2}$  cm/s in liquid-liquid systems.

The flux may also be expressed in terms of bulk concentration driving forces. If  $c_A^*$  is defined as  $c_B/m$ , *i.e.*, the concentration that phase A would have if it were in equilibrium with phase B, then an overall mass transfer coefficient  $K_A$  based on phase A is defined by:

$$N = K_A(c_A - c_A^*) \quad [14]$$

From this equation it can be seen that:

$$\left\{ \frac{\text{mass transfer rate}}{\text{unit volume of equipment}} \right\} = Na = K_A a (c_A - c_A^*) \quad [15]$$

where  $a$  is the interfacial area available per unit volume. If the transfer space contains a volume fraction  $h$  (the holdup) of the dispersed phase in the form of spherical droplets of diameter  $d_m$ , it can be shown that:

$$a = 6h/d_m \quad [16]$$

Thus  $a$ , and therefore the mass transfer effectiveness, can be maximized by increasing the holdup and reducing the drop size, subject to certain limits. Considerable experimental and theoretical work has been done on mass transfer to and from an isolated drop moving through a continuous phase (Laddha and Degaleesan, 1976). Mass transfer coefficients are generally much greater for drops that circulate internally because of their motion through the surrounding liquid than for drops that circulate internally because of their motion through the surrounding liquid than for drops in which circulation is inhibited by the presence of surface-active contaminants. Table 1 summarizes the main relationships that have been put forward

for the dispersed-phase and continuous phase mass transfer coefficients under circulating and noncirculating conditions.

### **2.1.2 Equipment**

Industrial applications of solvent extraction have increased rapidly in the last 25 years. Simple mixer-settlers, packed columns, and spray columns were widely used in the process industries during the 1930's and 1940's. New and improved multistage and differential contactors employing mechanical energy input to achieve a high rate of mass transfer have been developed since the late 1940's and have found wide commercial application. Because of the great variety available, the choice of a commercial extractor for a new process can be confusing. The following criteria should be taken into consideration when selecting a contactor for a particular application (Reissinger and Schroter, 1978): (1) stability and residence time, (2) settling characteristics of the solvent system, (3) number of stages required, (4) capital cost and maintenance, (5) available space and building height, and (6) throughput.

Contactors can be classified according to the methods applied for interdispersing the phases and producing the countercurrent flow pattern. Figure 2 summarizes the classification of major types of commercial extractors and Table 2 summarizes their main characteristics.

The mixer-settler has been the most widely used contactor in solvent extraction processing, originating with the gravity type design, followed by the pump-mix design and its many modifications in pump design and settler configuration (Ritcey and Ashbrook, 1979). The mixer settlers are claimed to be ideal as they are inexpensive,

**Table 1. Mass Transfer Coefficients in Freely Moving Single Droplets.<sup>1 2</sup>**

	Dispersed phase, $k_1$	Ref.	Continuous phase, $k_2$
circulating single drops	laminar circulation $k_1 \approx 17.9 \frac{D_1}{d_m}$	41	$k_2 = \sqrt{\frac{2D_2 U_t}{\pi d_m}}$
	turbulent circulation $K_1 = \frac{0.00375 u_t}{1 + \mu_1/\mu_2}$	42	penetration theory, taking exposure time as $d_m/u_t$
rigid single drops <sup>3</sup>	$K_s = 2 \pi^2 \frac{D_1}{3 d_m}$	1	
	$\frac{K_2 d_m}{D_2} = 2.0 + 0.6 \left( \frac{u_t d_m \rho_1}{\mu_1} \right)^{0.5} \left( \frac{\mu_1}{\rho_1 D_1} \right)^{0.33}$		

<sup>1</sup> Source: Laddha and Degaleesan, 1976.

<sup>2</sup> Symbols:  $k_1$  and  $k_2$  = mass transfer coefficients;  $D_1$  and  $D_2$  = molecular diffusivities;  $\mu_1$  and  $\mu_2$  = viscosities;  $\rho_1$  and  $\rho_2$  = densities;  $d_m$  = diameter of drop

$u_t$  = terminal velocity of drops; subscript 1 = dispersed phase and subscript 2 = continuous phase.

<sup>3</sup> The value 0.6 varies between 0.56 and 0.70 (43-44).

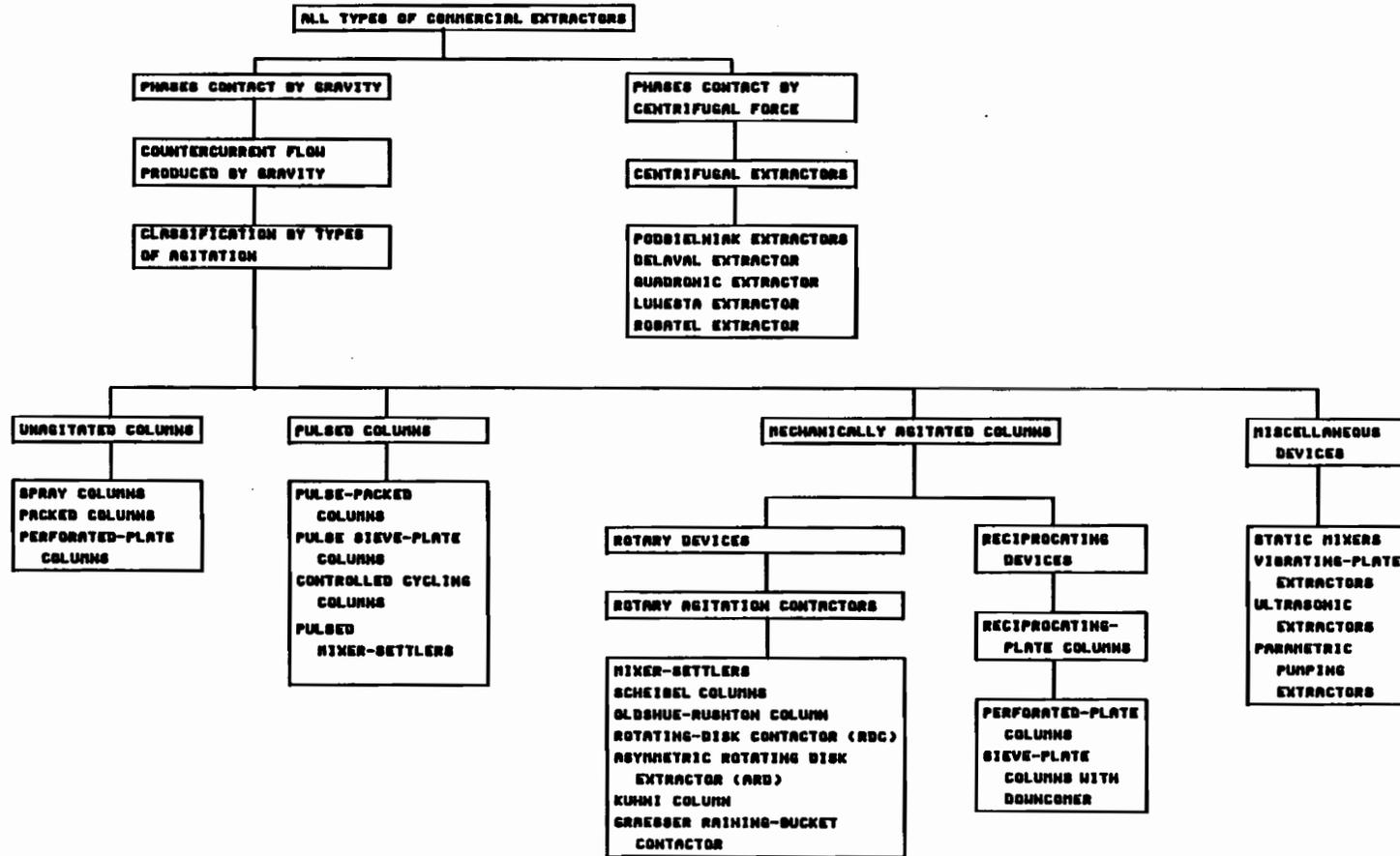


Figure 2. Classification of Commercial Extractors

**Table 2. Summary of Features and Fields of Industrial Application of Commercial Extractors.<sup>1</sup>**

<b>Types of extractor</b>	<b>General features</b>	<b>Fields of industrial application</b>
unagitated columns	low capital cost, low operating and maintenance cost, simplicity in construction, handles corrosive material	petrochemical, chemical
mixer-settlers	high-stage efficiency, handles wide solvent ratios, high capacity, good flexibility, reliable scale-up, handles liquids with high viscosity	petrochemical, nuclear, fertilizer, metallurgical
pulsed columns	low HETS, no internal moving parts, many stages possible	nuclear, petrochemical, metallurgical
rotary agitation columns	reasonable capacity, reasonable HETS, many stages possible, reasonable construction cost, low operating and maintenance cost	petrochemical, metallurgical, pharmaceutical, fertilizer
reciprocating-plate columns	high throughput, low HETS, great versatility and flexibility, simplicity in construction, handles liquids containing suspended solids, handles mixtures with emulsifying tendencies	pharmaceutical, petrochemical, metallurgical, chemical
centrifugal extractors	short contacting time for unstable material, limited space required, handles easily-emulsified material, handles systems with little liquid density difference	pharmaceutical, nuclear, petrochemical

<sup>1</sup>Source: Lo, 1975.

easy to fabricate, usually easy to cleanse of entrained solids or cruds, easily scaled-up and simple to operate and control. However, they do have a large solvent hold-up, occupy a large area, which can be expensive if requiring a heated building, and the combined pumping-mixing provides an extremely high shear to the process solution and solvent mixture and so droplets are produced which are often much smaller than necessary to effect the required mass transfer. Consequently stable emulsions, and often cruds, are produced.

The performance of gravity settlers has been improved by the use of vertical baffles and picket fences (Bonney et al, 1981; Roberts et al, 1977) and the general aspects of mixer settler design have been well documented in recent years (Orjans et al, 1977; Barnea, 1977; Roberts and McKee, 1980). In addition to baffles to improve coalescence, work on packing, or coalescing material has increased the capacity of settlers (Barnea and Mizrahi, 1977).

Many plants using high shear types of mixer settlers must clarify the feed to less than 30 ppm solids to minimize crud formation. In the past few years there has therefore been more concern as to the generation of crud, its cost in solvent loss, as well as the concern for the environment receiving the solvent discharged to tailings. The crud often contains up to 80% or more of organic phase. Solvent losses, and those attributed to crud, can be caused by many variables in the process, both chemical and physical, and various crud treatment methods have been proposed (Young, 1979).

The equipment manufacturers now have a better appreciation of the problem of high shear and stable emulsions and cruds, and the designs of the past couple of years have demonstrated equipment having minimum shear, but sufficient to provide for mass transfer. The Krebs mixer-settler (Castillon et al, 1981) is gaining fast acceptance since 1975. The design permits for 3-4 times the flow capacity of the

usual pump-mix design and could probably tolerate more solids in the feed solution. Also, Davy McKee have developed a contactor, the Combined Mixer Settler (CMS) to minimize turbulence (Rowden et al, 1981). It can accommodate up to 300 ppm of solids without generation and accumulation of crud. A capital cost saving of about 30% over conventional mixer settlers is claimed, together with lower operating costs.

### **2.1.3 Solvent Recovery**

An interesting approach to solvent recovery from the raffinate is to wash with the diluent (Langdon et al, 1977). Mixer settlers or centrifugal contactors can be used. The system reported was TBP-HNO<sub>3</sub>, but amine-H<sub>2</sub>SO<sub>4</sub> should be equally viable. Activated carbon and various types of coalescers have been tried. One design, demonstrated on kerosine dispersed in water consisted of a fibrous medium treated with isobutyl methacrylate resin to form a rigid and stable structure (Prestridge et al, 1981). Regeneration of the coalescer is by steam. Solvent can also be recovered by the use of electrostatic coalescence (Wang and Zhang, 1981).

### **2.1.4 Environment**

Although the development and optimization of the metallurgical processes, including solvent extraction, has progressed through phases of concern for economics and energy, a more recent concern is for industrial plant hygiene and the environment. Therefore, the proper selection of the contactor design and proper operation is necessary to minimize solvent losses in the plant and in the effluents

discharged. Poorly vented work areas and the use of volatile solvents cause hygiene concerns in the plant but these can easily be eliminated. Waste raffinates, often containing large amounts of entrained solvents, may be discharged to the environment if the equipment and its operation are not optimal. Future environmental constraints may well force the operator to provide for in-plant treatment of such raffinates to minimize the environmental impact. Coalescers, centrifuges or perhaps activated carbon treatment may be necessary to control the amount of organic released to the environment (Ritcey and Silver, 1982).

## **2.2 Status Of Liquid-Liquid Extraction In Dilute Metals**

### **Recovery In Hydrometallurgical Processes**

Both pyrometallurgy and hydrometallurgy have been used for extracting metals from ores. Pyrometallurgy consists of processes with elevated temperatures, such as roasting, smelting, converting and refining. This method deals with process streams that are concentrated with respect to metal content. However, hydrometallurgy consists of a combination of chemical unit processes such as leaching, solvent extraction, precipitation and electrowinning. This method usually deals with far less concentrated process streams. Some metals, such as aluminum, uranium, gold, cobalt and cadmium can be produced only through the application of hydrometallurgy. Recently, due to depletion of high grade ore reserves, environmental legislation and political factors, increasingly significant proportions of metals production are obtained through hydrometallurgy. Examples include copper,

zinc, nickel, tungsten, molybdenum, vanadium, rare earths and platinum group metals (Flett, 1981).

In hydrometallurgy, the leaching process is always followed by a separation process to selectively remove components from the mixture. A separation or purification method commonly used for copper, nickel, zinc, cobalt, uranium and rare earth elements is solvent extraction. This is a continuous process where the transfer of metals depends on extraction with simultaneous chemical reaction. The reaction is reversible, and therefore solvent recovery can be accomplished by changing the chemical conditions. The development of solvent extraction processes along with novel extractants has aroused significant attention both from academia and industry in the past four decades and has resulted in processing of nuclear fuel, transition metals, and conventional non-ferrous metals. The most successful and commercially available processes are copper and uranium extraction (Tavlarides et al, 1987).

### **2.2.1 Uranium**

Uranium has become a valuable mineral resource in the past three decades with the development and growth of nuclear power to meet worldwide energy demands. It is used almost exclusively as an energy source in nuclear power plants. The technology for uranium extraction is essentially modern, although elements of the technology have evolved from that used for other metals such as gold and vanadium.

The uranium industry has grown dramatically in thirty years from virtually no production in the early 1950's to around 40,000 tons of uranium in 1981. However, this growth has not been steady or predictable. The boom in uranium demand in the late 1950's led to a remarkable amount of exploration and a build-up of uranium extraction

plants: some 26 opened in the United States in the 1960-1962 period, 19 in Canada in 1959, and many more in other countries, notably South Africa. By 1970, the majority of these plants had closed as the anticipated market demand did not materialize in the 1960's.

A second period of growth began in the early 1970's as more nuclear power plants were built. The nuclear power demand was accelerated by the "Energy Crisis" of the mid-1970's. Uranium demand increased, exploration increased, prices increased, new uranium mines and mills were started, and old mills were refurbished. By 1980, a record production of uranium, some 40,000 tons, was established.

The buoyant market of 1980 did not last, however, as the worldwide recession deepened, the growth in energy demand slowed and nuclear power developments were curtailed. The uranium industry once again found itself in a dangerous position with an oversupply of uranium and rapidly declining prices. This resulted again in mine and mill closures, a decline in exploration and the postponement of new mine and mill developments (OECD and IAEA, 1983).

In 1985, while production capability was still above demand, actual production was estimated at 35,000 tons. Beyond this period, the outlook will be influenced by a variety of complex market factors among the most important of which are the actual level of surplus consumer inventories and policies regarding their disposition, the growth in uncommitted demand, the uncertainties related to government import and export policies, and the impact of such factors on uranium prices (OECD and IAEA, 1986).

The present weakness in uranium market demand might well be interpreted as a signal that new technologies and continuing research and development are unnecessary. Undoubtedly, this was the conclusion when the uranium boom ended

in the 1960's. However, when the demand rebounded in the 1970's, the only technology available was that which had been developed in the 1950's. New and restarted old plants incorporated little new technology because it was important to get into production quickly and the investors did not wish to risk money on untried and unproven techniques. With the accelerated growth and activity there was inadequate time to fully test, design, and incorporate much new technology into the plants (OECD and IAEA, 1983). Such a situation should not be allowed to occur again.

Solvent extraction affords an efficient method for separating elements on a commercial scale (Burkin, 1966). In practice metal ions in an aqueous medium are brought into contact with an organic solvent, which is sparingly soluble in water. The enhanced stability of the undissociated species in the organic phase results in a transfer of the compound from the aqueous to the non-aqueous phase. Transfer in the reverse direction from the organic back to the aqueous phase correspondingly requires a shift of chemical equilibrium in the reverse direction and this process is known as *stripping*.

The extraction of uranium from one aqueous solution (the lixiviant), with its subsequent purification and eventual transfer to another aqueous solution, (the strip liquor) involves the use of various reagents (extractants, diluents and modifiers), and requires a suitable apparatus to bring about intimate contact between the aqueous and non-aqueous phases which is necessary to accomplish extraction, scrubbing and stripping of the leached uranium.

The recovery of uranium from ores by using solvent extraction began in 1955 with the use of DEHPA (DAPEX Process), (Brown and Coleman, 1958), and since 1957, the tertiary amines (Amex Process), (Crouse and Brown, 1959) have been the most popular extractants.

The most common lixiviant for uranium ores has been sulphuric acid, although at least one plant has used nitric acid with TBP extraction (Tunley and Nel, 1974), and a few plants have used alkaline leaching with direct precipitation of the yellowcake (Canadian Mining Journal, 1960). Several plants use a combination of ion exchange with solvent extraction (Eluex or Bufflex process) in treating sulphuric acid leach solutions containing uranium (Fisher and Vivyurka, 1970; Cross, 1968).

### **2.2.1.1 Extractants and Modifiers Used in Uranium Recovery**

The tertiary amines continue to be the most widely used for treating process solutions resulting from sulphuric acid leaching of uranium-bearing ores. The major impurity that is extracted preferentially to uranium is molybdenum, and it can be removed by carbonate stripping after first selectively stripping the uranium with a chloride solution. Oxidized vanadium if present, will be co-extracted and stripped with molybdenum (Sialino et al, 1977). Zirconium extraction can be suppressed by the addition of phosphate. Iron is water scrubbed and any arsenic present may be removed in a scrub stage (The Key Lake Uranium Process, 1980). Feed solutions having high chloride levels present, as in the case where the solution results from chloride elution of an ion exchange resin, may be treated using an alkylphosphate, amine (after dilution of the feed) or by TOPO (Ritcey et al, 1981). The use of TOPO as a synergist with the tertiary amine provides for increased kinetics. The stripping is difficult, but can be accomplished with an  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$  mixture (Ritcey et al, 1983). The TOPO replaces the long chain alcohol as a modifier in such a system. As for modifiers, there have been no satisfactory replacements for the long chain alcohols. However, the use of TOPO for the treatment of phosphoric acid has been

successful, and one can anticipate its use in the future for recovery of uranium from sulphuric acid solutions (Logsdail, 1985).

### **2.2.1.2 Diluents Used in Uranium Recovery**

For many years the diluent was considered to be only the carrier for the active extractant, with no other function in the extraction system. This myth has been dispelled over the past few years and indeed the diluent does play an important part in the extraction process, with aromaticity, solubility parameter, naphthene content, etc. exhibiting effects (Ritcey and Lucas, 1974). Diluents other than the kerosine type have been investigated, particularly perchloroethylene which is heavier than water (Manfroy and Gunkler, 1974; Verhaege et al., 1982). With the latter type, the phase separation is usually faster, and metals' discrimination is often improved as compared to aliphatic and aromatic diluents. Flash point is an important criterion in the choice of diluent, and most plants select one with a flash point greater than 120°F. Because of the diluent composition affecting the solvency and chemical properties of the extraction, some diluents are now supplied by the manufacturer in a blended form to contain 15-20% aromatic content in an aliphatic diluent. Such a diluent is the Escaid 100 by Exxon. The diluent should be selected only after sufficient tests have indicated it to be compatible with the process (Logsdail et al, 1985).

### **2.2.1.3 Scrubbing**

In the early uranium operations in the 1950's and 1960's the solvent extraction plants were designed to include a scrub process prior to stripping for uranium

recovery. The purpose of the scrub process was to remove any entrained or absorbed impurities that might be carried with the loaded solvent and which could adversely affect the subsequent stripping and phase separation characteristics. The impurities were generally Ca, Mg, Fe, Al, Si (Trembley and Bramwell, 1959). Water was found to be a satisfactory scrub solution. However in the second generation of uranium plants there is a high percentage of processes not incorporating the scrub stage. The results have been poor phase disengagement, high solvent losses due to entrainment in the aqueous phase, crud formation and losses of solvent, and in general increased operating cost (Logsdail et al, 1985).

#### **2.2.1.4 Stripping**

Much of the emphasis in solvent extraction development research on new processes is directed towards the extraction circuit, with minimum consideration often given to the stripping circuit. In the uranium circuit the stripping agents have included the following:  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{CO}_3$ .

Because of the poor pH control often encountered when using ammonia addition, uranium precipitation can occur within such circuits. The result is the formation of excessive cruds and high solvent losses. This reflects adversely on the economics of the plant. Apart from a few plants that employ the chloride stripping in the presence of co-extracted molybdenum (Merritt, 1971), the majority of the uranium circuits use controlled pH stripping with  $(\text{NH}_4)_2\text{SO}_4$  and ammonia addition. For example, ammonia-ammonium sulphate stripping is used in Canada, Australia, United States and South Africa. Sodium chloride stripping is effectively used in mills in the United States, France, Niger and Gabon (Grimes, 1984). One plant in the United States and one in Niger use sodium carbonate stripping.

## 2.2.2 Copper

Despite an oversupply of copper on the world market from 1975 to 1978, significant new copper deposits are being explored or known reserves are being expanded. A high-grade deposit described as one of the top ten known massive sulfide deposits in North America was discovered in 1975 near Crandon, Wisconsin. The identification and drilling of three small to medium porphyry copper deposits in Pakistan were announced in 1976; and in Argentina, St. Joe Minerals Corporation expanded reserves at the Pachon porphyry copper deposit to approximately 725,000,000 tons at 0.59% copper (Mark et al, 1987).

The major copper production in the United States is from processing copper sulfide ores by such procedures as milling, smelting and refining. This processing scheme accounts for about 82% of the primary production. Leaching yields about 15% of annual new copper production in the United States. Most of the remainder is derived as a byproduct from other ores.

Milling for concentration of copper sulfide ores is a well-established technology, and improvements in this area have been incremental. Improvements have been made primarily by incorporating more automation in concentrators and by using larger crushers, grinding mills, and flotation cells. It is not likely that technological changes will be made in milling, but minor technological advances will continue to increase metal recovery and reduce beneficiation costs (McKinney and Groves, 1977).

On the other hand, there has been more room for improvement in copper hydrometallurgy practices. For many years the method employed for recovering copper from dilute leach liquor has been copper cementation in which shredded

detinned scrap iron cans are contacted with copper-bearing solutions to precipitate a cement copper product containing 60 to 80% copper (McKinney and Groves, 1977). Standard practice is to smelt the impure cement copper in a reverberatory furnace along with copper sulfide flotation concentrates. The development of solvent extraction of copper from dilute leach liquors accompanied by electrowinning offered the opportunity to produce a marketable copper directly at the leach plant site.

### **2.2.2.1 Solvent Extraction-Electrowinning of Copper**

The biggest change in US copper industry hydrometallurgy practices in the past 15 years has been the trend towards solvent extraction-electrowinning as a means of recovering copper from dilute leach liquors in place of copper cementation. Heap and agitation leaching of oxidized copper ores, dump leaching of open-pit mine waste, and in situ leaching of caved mine workings all produce low-concentration copper solutions. Historically, cementation on scrap iron has been the only practical method for recovering copper from these process streams. Recent advances in solvent extraction technology and the development of copper selective, pH sensitive organic liquid ion-exchange reagents provide an alternative to cementation. Copper can be extracted from dilute leach liquors, a high-grade solution can be produced for feed to an electrowinning circuit, and marketable copper can then be recovered from the solution by electrodeposition.

Although the capital investment for a solvent extraction-electrowinning plant is considerably greater than for a cementation operation, the process has many advantages. The most important advantage is that high-quality cathode copper is produced at the mine site. Cement copper is an impure product that must be shipped to a smelter for additional processing.

Another consideration in favor of solvent extraction- electrowinning is the dwindling supply of suitable scrap iron for cementation. Shredded tinplate scrap is the preferred product, and it is becoming more difficult and costly to obtain (McKinney and Groves, 1977). In addition, in the solvent extraction process, the spent liquor from the extraction stage contains a useful amount of acid that can be used to leach additional copper. This is particularly important in the case of leaching oxidized copper ores since acid is not produced in the leach. In a copper cementation process, the copper in the leach solution is replaced by iron so that the liquor returned to the dump contains excess iron. This may lead to deposition of iron salts and eventual plugging of the leach dump. Such iron buildup does not occur in a solvent-extraction plant except for the small amount of iron leached from the ore (McKinney and Groves, 1977).

#### **2.2.2.2 Reagents for Copper Solvent Extraction**

Copper recovery from dilute sulfuric acid leach solutions using solvent extraction-electrowinning technology was first practiced commercially in 1968 at the Bluebird Mine of Ranchers Exploration and Development Company (Power, 1970). Since that time, the technology has gained wide acceptance in the metallurgical community as a way to produce very high quality copper at attractive costs from appropriate leach solutions. Over the years a large number of molecules with a variety of extractive functionalities have been suggested as possible copper extractants to be used in this technology (Kordosky et al., 1987). Of all the reagents that have been tested, only the hydroxy oximes have been used in commercial plants for this task.

Hydroxy oxime reagents can be divided by structure and properties into two distinct classes: the salicylaldoximes, which are very strong copper extractants, and the ketoximes, which are moderately strong copper extractants. The strength of a copper extractant is based on the degree to which the copper extraction- stripping equilibrium is driven toward extraction by the reagent. Another class of extractant combines a ketoxime with a salicylaldoxime in an approximate 1:1 mole ratio. This third class of extractant is based on the distinct properties the mixtures possess (Kordosky et al., 1987).

The Henkel hydroxy oxime reagents LIX 64, LIX 63 and LIX 64N were the first to achieve commercial acceptance. During the early 1970s, the reagent LIX 64N became the standard extractant for copper solvent extraction. Today the copper industry has available more solvent extraction reagents than at any time so that the reagent with the best overall properties to fit the specific leach liquor, circuit design and operating parameters of a plant can be selected.

In spite of its commercial success the copper solvent extraction process is not completely understood (Kordosky et al., 1987). The kinetics have been studied in detail, yet a consensus on the mechanism of the extraction has not been achieved. Several papers have addressed the relationship between the extraction ability of hydroxyoximes and the electronic steric effects of the chelating functionality, but further work remains (Dalton and Price, 1983).

### **2.2.3 Chromium**

The military and economic strength of the US is dependent to a large degree upon importation of metals from Southern Africa and from communist bloc countries.

Congress's office of Technology Assessment underscores four minerals - chromium, cobalt, manganese, and the platinum-group metals - as being critical to America's defense program (Tavlarides et al., 1987). All four come primarily from South Africa, Zaire, and the Soviet Union. Chromium, manganese and cobalt are used in high strength alloys vital to the manufacture of engines and parts of aircraft and missiles. Platinum is needed in a wide range of chemical processes. Thus it becomes imperative that the United States develop the technology, regardless of cost, to produce these crucial metals with nationally based ores or resources in politically aligned nations (Tavlarides et al., 1987).

### **2.2.3.1 Solvent Extraction Processes for Chromium**

The solvent extraction chemistry and processing of chromium is dominated by its aqueous-phase behaviour and especially the multiplicity of oxidation states that occur (Aylward and Findlay, 1974). Furthermore, there are complications as a result of the hydrolysis and polymerization of anionic species in the highest stable oxidation states as a function of pH and concentration (Hughes and Lever, 1974) and of complex formation, such as with sulfate and chloride. All affect the extractability of the metals.

The behaviour of chromium(VI) is comparatively simple and well established (Pourbaix, 1966). Below pH 1-2, it exists as unionized  $\text{H}_2\text{CrO}_4$ . Between pH values of about 2 and 7, it exists as  $\text{Cr}_2\text{O}_7^{2-}$  above 1 g/l, whereas  $\text{HCrO}_4^-$  predominates below this concentration independently of pH. At pH values above about 7, the  $\text{CrO}_4^{2-}$  ion is stable.

The quaternary amines, Aliquat 336 or Adogen 464 and primary amine, N-1923 have been used for chromium(VI)/vanadium(V) separation. Pilot plants for recovering chromium from titaniferous magnetic iron ores have been operated using the amine

extractants in Canada, China and South Africa. There are two possible types of extractants, tributylphosphoric acid (TBP) and amines for chromium (VI)- sulfuric acid separation systems. Amines are used for dilute acid feed systems. The selectivity of TBP for chromium(VI) over sulfate and other metal ions is excellent. A commercial process is in operation for this system in France (Rice, 1983).

Mathematical models have been fitted to binary equilibrium data for the extraction of chromium(VI) by Aliquat 336 from chloride media of pH 2-13 (Henkel Corp., 1961). Empirical constants were found, but no extraction equilibrium constants are available in the literature (Kertes et al., 1974). Kinetics for extraction with Aliquat 336 are rapid, and equilibrium established within three minutes of contact time. Aliquat 336 can be stripped effectively with mixtures of 1.5M  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  (Henkel Corp., 1961).

## **2.3 Color Removal From Textile Mill Effluents**

The first commercial textile plant in the United States began to operate in the mid 1600s near Boston, Massachusetts. Due to the abundance of fast-flowing streams throughout New England, the industry became well established and prosperous in the region by the time of the American Revolution. During the Great Depression of the 1930s many mills migrated from the northeastern United States to the east-central and southern states. The industry presently consists of some 7100 plants in 47 states, ranging from highly integrated manufacturing complexes to small contract firms (US EPA, 1974).

Although cotton and wool are still important fibers, the demand for synthetics has experienced a phenomenal growth in the past several decades. The widespread acceptance of synthetics has led to significant changes in the industry, stimulating the development of new processes and chemicals. Each year hundreds of new dyes, pigments and auxiliary chemicals are introduced.

Pollution from textile mills is a problem of great dimensions. An estimated 135 billion gallons of wastewater are discharged from textile mills in the United States each year (Porter et al., 1972). Of the 100 million pounds of dyes consumed by the American textile industry, 90% end up on the fabrics and 10% in the effluents (Porter et al., 1972).

Many mills discharge their effluents into municipal sewage works. For example, in the United States about 35% of the textile mills use municipal treatment facilities (US EPA, 1974). While biological treatment is still very popular, increasingly stringent environmental regulations have stimulated the development and/or adaptation of advanced treatment processes. Activated carbon adsorption, chemical coagulation, reverse osmosis and solvent extraction are some of these novel techniques (Beszedits et al., 1980). Recycling of treated effluents is also gaining in popularity.

Color is the single most perplexing problem facing environmental engineers designing appropriate treatment facilities for textile mill wastewaters. Available processes for color removal have been described in a number of recent articles (Alspaugh, 1973; Sandman, 1977; McKay, 1979). While there are numerous techniques, it is difficult to make generalizations about color removal since each effluent is unique and requires a careful study to determine the best and least costly treatment alternative.

### 2.3.1 Color Removal Using Liquid-Liquid Extraction

Liquid-liquid extraction is finding an ever-growing application in pollution control. Todd and Hooper (1971), recovered azo dyes from a dilute aqueous solution using Alamine 336, a tertiary amine, as the extractant. A kerosine-type solvent was used as the diluent and a long-chain alcohol was added as the modifier. The aqueous stream containing 0.1 - 0.5% azo dyes was introduced into a centrifugal rotor extractor where it was contacted with the solvent mixture (*i.e.* 5% Alamine 336, 90% kerosine and 5% alcohol). Solute dyes were extracted into the organic phase as amine salts. About 93 - 97% of the azo dyes could be recovered if the organic phase was at least 5% of the aqueous phase. Stripping of the dyes from the organic phase was accomplished with a dilute basic solution. Both soda ash and ammonium hydroxide solution were found satisfactory for this purpose.

## **3.0 MATERIALS AND METHODS**

### **3.1 Equipment for Extraction**

Generally extraction equipment constitutes a mixer-settler assembly or a packed extraction tower. However, as mentioned earlier, the use of aphron technology avoids the need for any mixing devices for contacting the feed with the solvent. In fact, predispersed solvent extraction can be achieved with very simple equipment.

#### **3.1.1 Description of Batch Cell**

The batch experiments were performed in a glass column 58 cm long and 9.5 cm in diameter. The total volume of the cell is approximately 4 liters. The column was positioned vertically via a ring stand and secured with clamps. The glass cell has three entry points in the bottom; one for the introduction of the feed or pregnant solution, one for the introduction of the diluted polyaphrons, and the other for the CGA introduction. The entry point used to introduce the CGA was also used to decant the raffinate after the separation was completed in order to separate it from the loaded solvent. All three entry points are fitted with stopcocks. As mentioned earlier, due to the high cohesion forces of polyaphrons, they have to be diluted previously to being used. This was done by adding the polyaphrons and water into a 50 ml beaker which had been placed on a magnetic stirrer. Peristaltic pumps were used to

introduce the feed, diluted polyaphrons, and CGA into the vessel. A schematic of the laboratory cell is shown in Figure 3.

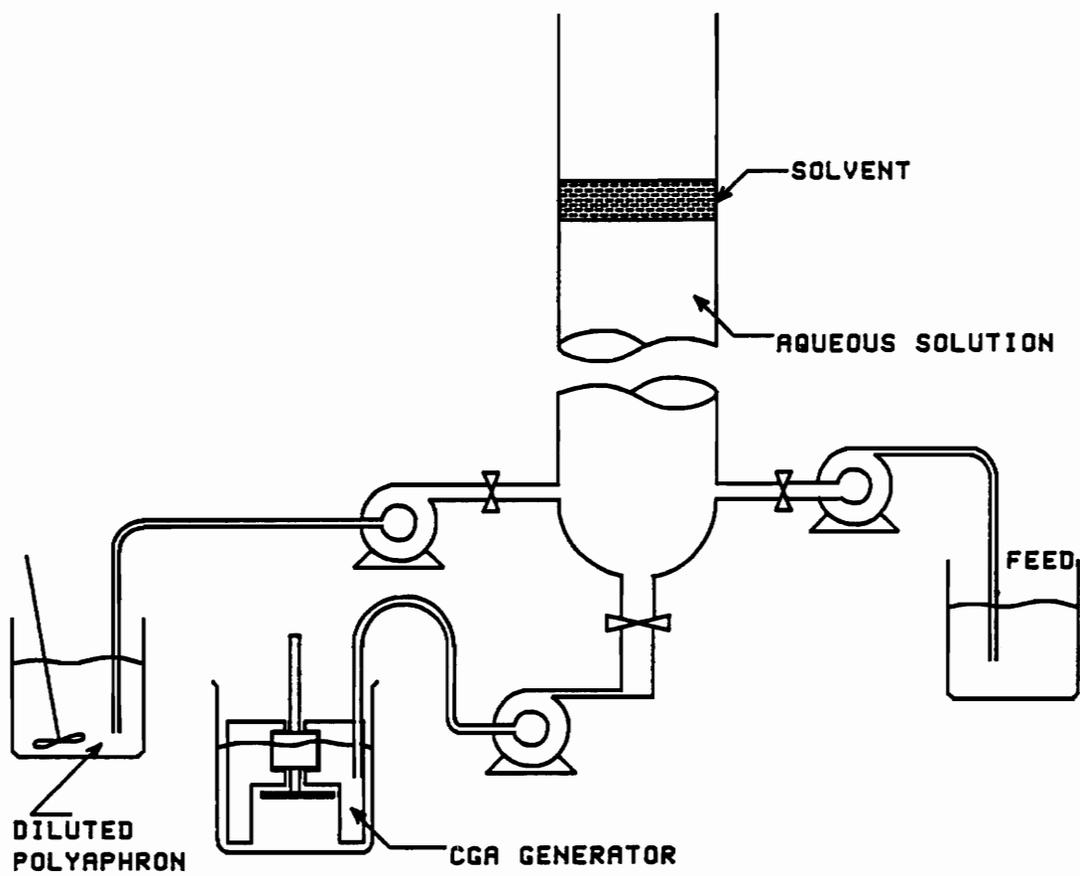
### **3.1.2 Description of Apparatus for Continuous Modes**

#### **3.1.2.1 Upright Column**

A semi-pilot plant unit was designed and built incorporating a glass extraction cell with a diameter of 12 cm and a height of 55 cm. For the purposes of this study, this apparatus was operated only in a continuous mode, but if desired it could also be operated in batch mode.

The cell was mounted on a mobile stand, the objective being not only to have a semi-pilot plant unit which could be used to obtain operating data, but also that it could be transported to a site for preliminary investigations, in cases where samples could not satisfactorily be sent away for testing purposes.

The feed, diluted polyaphrons, and CGA were introduced into the extraction cell through three entry ports located in the bottom of the cell. The solvent was continuously pumped out from the top right hand side of the extraction column, which was open to the atmosphere, via a draw tube. On the left hand side of the cell, another draw tube was positioned to continuously pump out the raffinate. Both draw tubes were adjustable in a manner that they could be positioned at various distances from the bottom of the cell. In this manner, the raffinate and solvent can be removed from various points of the extraction column. All solutions were pumped from one stage to the other using Masterflex peristaltic pumps. A schematic design of the layout is shown in Figure 4.



**Figure 3. Apparatus for Batch PDSE Experiments.**

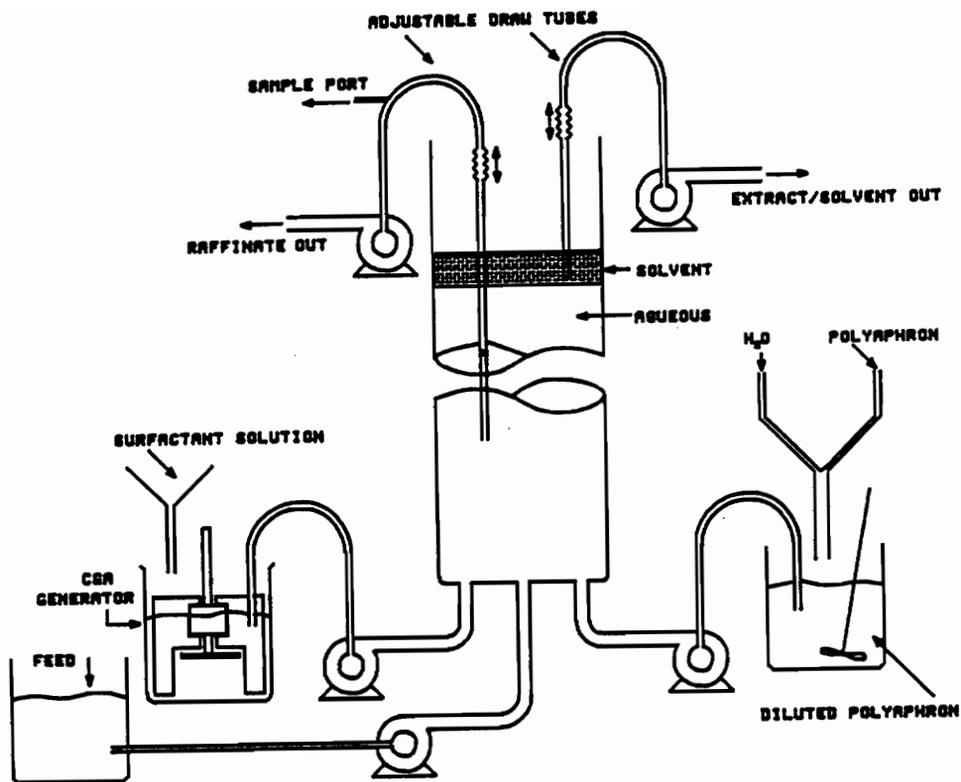


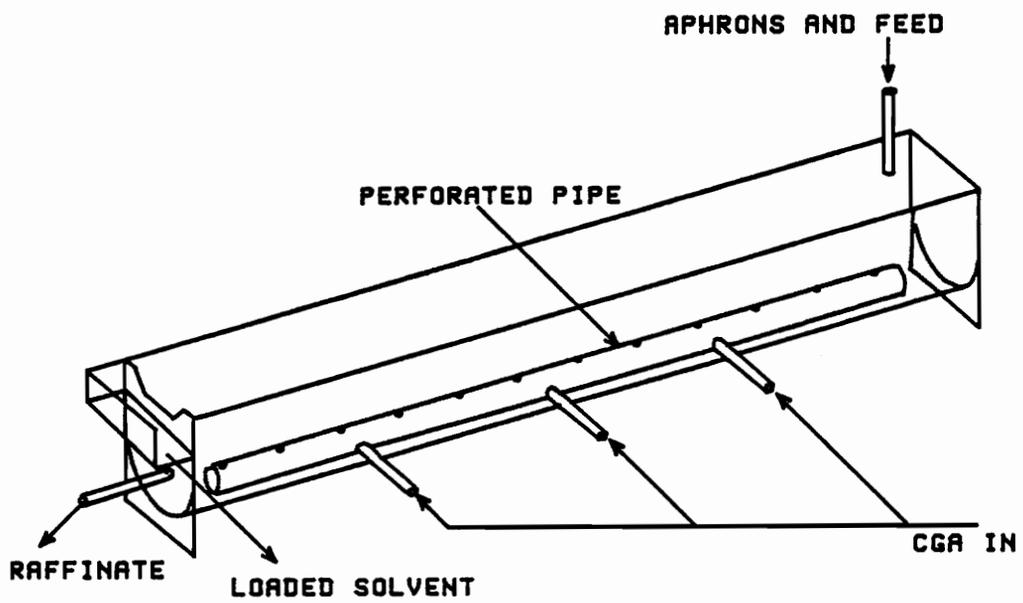
Figure 4. Semi-pilot Plant Unit for PDSE Experiments.

### **3.1.2.2 Horizontal Trough**

A horizontal trough with a 15 liter capacity was built out of plexi-glass. The trough was shaped like a U in order to facilitate visualization. From previous experience it was known that a V-shaped trough does not allow the experimenter to observe adequately the happenings in the lower part of the trough. Due to the shape of the trough, it was necessary to build a wood frame where the cell was imbedded. A 3/4 in. diameter plexi-glass tube with both ends closed, was attached horizontally on the inside bottom of the cell. The tube was perforated with 1/8 in. diameter holes set approximately 1/4 in. apart, and three entry points positioned equi-distant from each other were fitted with swedgelock fittings for the introduction of the CGA. On one end of the trough and 3 in. above the bottom of the cell, another entry was made for the introduction of the polyaphrons and the feed or pregnant solution. On the opposite end from the feed entrance and at the top of the cell, a weir, also made out of plexi-glass, was positioned for the purpose of allowing the solvent to overflow. Also, about 1 in. below the weir, an exit point was designed to run off the raffinate. Again, all solutions were pumped using Masterflex peristaltic pumps. A diagram of the apparatus is shown in Figure 5.

### **3.1.3 CGA Generator**

To make the colloidal gas aphrons, a CGA generator developed by Sebba (1985a), was used. The generator consists of a thin metal disc of approximately 5 cm in diameter, mounted horizontally about 2 - 3 cm below the surface of the surfactant solution. The disc is fixed to a vertical shaft connected to an electric 1/2 hp motor.



**Figure 5. Horizontal Trough Used for PDSE.**

Two rigid baffles made of perspex are mounted vertically and around the disc. The generator is depicted in Figure 6.

To form CGAs, the disc must spin at more than 4,000 r.p.m. Once the disc is spinning faster than 4,000 r.p.m., the CGAs form almost instantaneously. Therefore, the generator can be operated as a batch or continuous mode. To operate it continuously all that is necessary are two pumps; one for feeding surfactant solution into the vessel where the CGAs are being generated and the other to remove the newly formed CGAs.

#### **3.1.4 Polyaphron Generator**

The machine used to make the polyaphrons is illustrated in Figure 7. The apparatus consists of a cylindrical Plexiglas tube approximately 10 cm in diameter, and a rotating shaft centered along the tube axis. Four Plexiglas blades, perpendicular to the shaft, are attached to the rotating shaft. The organic feed is added through entry ports B to D, and the aqueous feed is added through entry port A. The polyaphrons are collected through exit port E. Polyaphrons at different PVR can be made by changing the feed flow rates. This machine was developed by Bergeron and Sebba (1987).

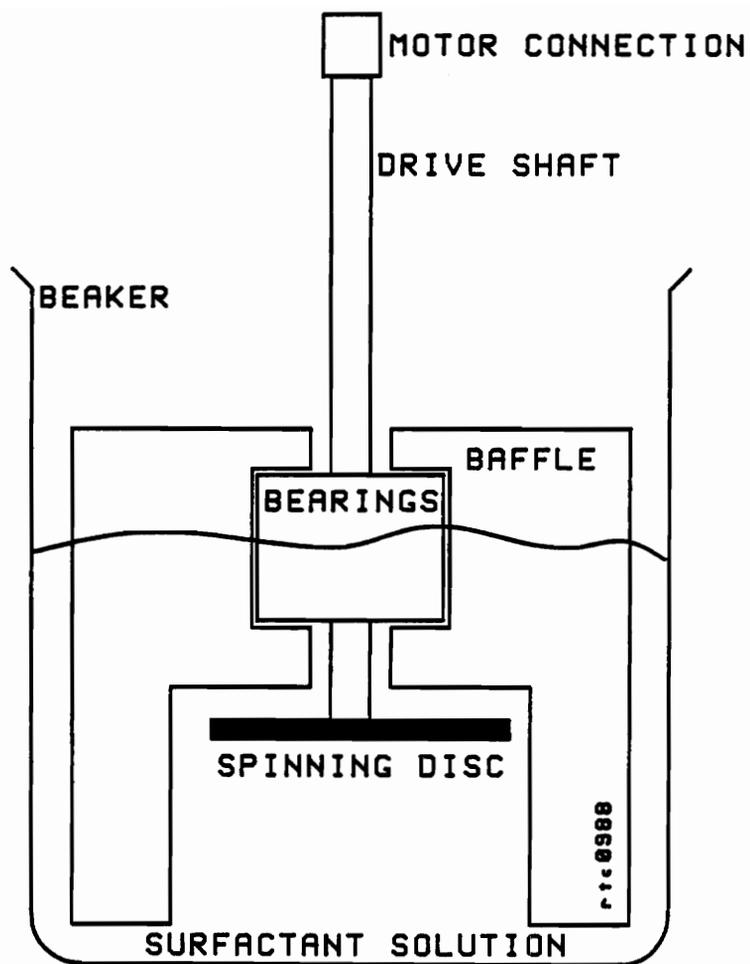
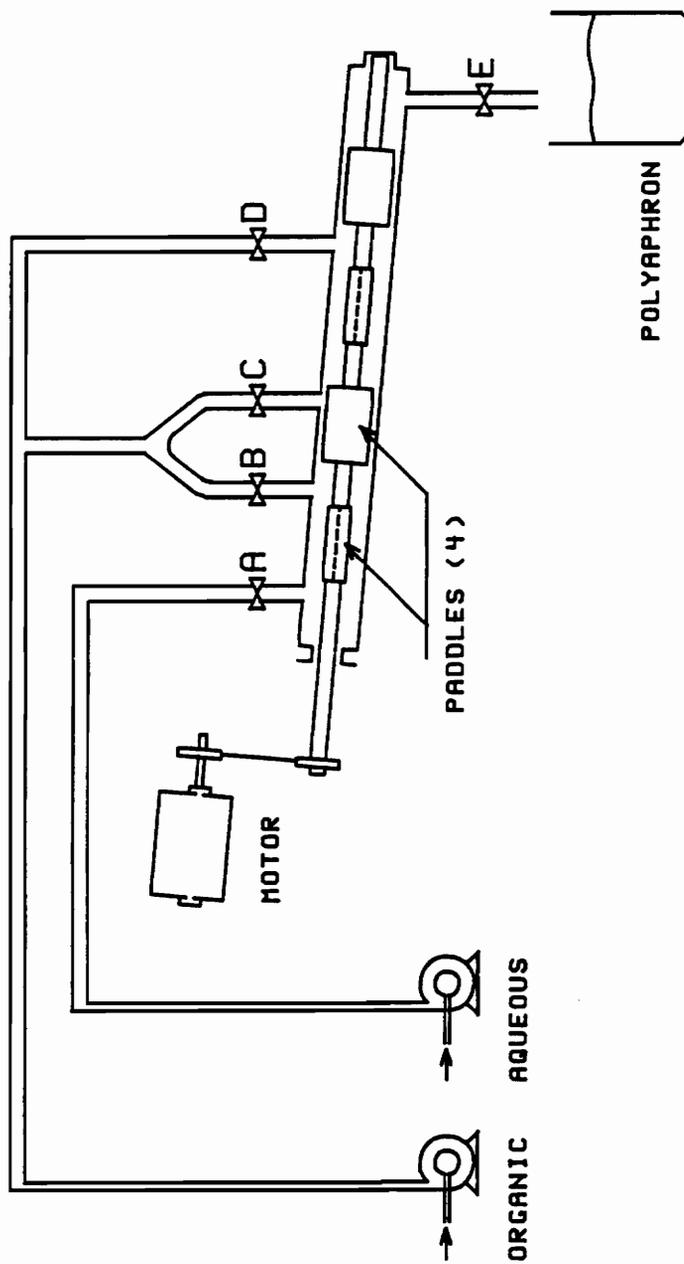


Figure 6. CGA Generator.



**Figure 7. Continuous Polyaphron Generator.**

## **3.2 Experimental Procedure**

### **3.2.1 Batch Experiments**

Polyaphrons were made by hand or with the continuous polyaphron apparatus illustrated in Figure. Both methods of preparation are described in Appendix B.

The method used for making the CGA was that of the spinning disc described in Appendix A.

All batch tests were carried out in the apparatus illustrated in Figure 3. Approximately 2 liters of feed solution were pumped into the extraction cell via a Masterflex peristaltic pump through one of the entry ports located at the bottom of the cell. A measured volume of previously made polyaphrons and a volume of distilled water equivalent to five times the volume of the polyaphrons was placed in a beaker and stirred with a magnetic stirrer for about two minutes. The diluted polyaphrons were then pumped into the feed containing extraction cell through another of the cell's entry ports. After all the diluted polyaphrons were introduced into the cell, the CGA generator, which contained a dilute surfactant solution, was turned on. The desired volume of CGAs, which form almost instantaneously, was introduced into the column. After allowing the contents of the extraction cell to remain undisturbed for a few minutes (5 - 15), a sample of the raffinate was removed through one of the cell's entry ports. In some cases, more CGAs were added to the system after the raffinate sample was removed, and another sample collected. This was done to determine the effect of CGA volume on percent extraction.

The raffinate samples and a sample of the feed were analyzed for solute content. The copper concentration was determined with a cupric ion selective electrode and

the chromium, uranium, and alizarin yellow concentrations were determined spectrophotometrically.

## **3.2.2 Experimental Procedure for Continuous Flow Experiments**

### **3.2.2.1 Upright Column**

The continuous flow experiments were carried out in the pilot plant unit previously described in the apparatus section of this paper. All CGAs and polyaphrons were generated continuously as described in Appendices A and B respectively.

The feed tank, and surfactant solution and diluted polyaphron beakers were filled with the necessary solutions. The feed pump was started and the solution allowed to fill the extraction cell to a desired volume. The pump that removes the raffinate from the extraction cell was started. Next, the diluted polyaphron pump was started and the polyaphrons allowed to flow into the system. Lastly, the CGA generator was started and the CGAs were pumped into the system. All the pump controllers were set to the desired flow rates, and the raffinate flow rate out of the cell was adjusted so as to maintain the liquid in the column at a steady level. The pump used to remove the solvent was started as soon as the layer of the solvent level reached a height of approximately 2 in. The volume of liquid in the containers that hold the feed, diluted polyaphrons, and CGAs was kept from depleting by continuously pumping solutions into the containers.

As illustrated in Figure 4, the draw tubes used to remove the raffinate and solvent from the extraction cell are adjustable so that the two phases can be removed from

any desired liquid level. This was done to determine the effect of residence time on extraction efficiency. The process was allowed to run for several hours and raffinate samples were collected from the sample port as desired for analysis. The copper concentration in the raffinate was determined with a cupric ion selective electrode. The concentration of the other elements was determined spectrophotometrically. In the determination of the final concentrations, the dilution factor due to the addition of water to the system was taken into consideration.

### **3.2.2.2 Horizontal Trough**

The trough illustrated in Figure 5 was used to gather preliminary data on the continuous extraction of copper ions and alizarin yellow from dilute aqueous solutions. Polyaphrons and CGAs were prepared continuously in the continuous polyaphron and CGA generators (Appendices B and A).

The trough was filled with feed solution through the entry port located in the bottom right-hand side of the trough designed for both feed and diluted polyaphron entrance (Figure 5). The raffinate exit port located on the left-hand side of the trough was kept closed at this point. A beaker was placed under the solvent run-off ramp to collect the loaded solvent. When the trough was approximately half way full, the diluted polyaphron pump was started and the polyaphrons allowed to flow into the system. Immediately after, the CGA generator was started and CGAs were pumped into the system through the three entry ports located in the bottom of the trough. All pumps were adjusted to the desired flow rates. When the trough was full to its capacity, the raffinate exit port was opened and adjusted so as to maintain a steady liquid level in the trough and a steady overflow of loaded solvent. Periodically,

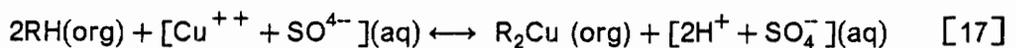
samples of the raffinate were collected and analyzed. The process was allowed to run for several hours.

## 4.0 RESULTS AND DISCUSSION

### 4.1 Batch Experiments

#### 4.1.1 Extraction of Copper

Copper was extracted from a dilute solution of copper sulphate using a 10% solution of a liquid ion exchanger, LIX-64N, an alpha-hydroxyoxime, in kerosine. The use of LIX in the hydrometallurgical field has met with considerable success, especially in the area of extraction of metallic ions from solutions. The extraction of copper using LIX-64N involves the contacting of a solvent containing LIX-64N with the copper containing feed, to yield a LIX-copper complex. The chelating action of LIX-64N can be represented in an equation form as:



As can be seen, the reaction is reversible, but for the reverse reaction to be important, the pH has to be in the range of 0.5 - 0.9.

Information on this system revealed that provided the feed solution was free of ferric compounds, there would be only one product for the reaction. The reason for this is that in spite of showing high selectivity for copper ions, LIX-64N has a slight affinity for ferric ions as well. Therefore in order to avoid any possible side products, it was decided to use an aqueous solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as the feed.

For the extraction of copper, two surfactants were selected to make the aphrons: sodium dodecylbenzenesulphonate and Arquad 12-50, dodecyltrimethyl ammonium chloride, obtained from Armak Chemicals. 10 ml of a solution containing 5 g/l of sodium dodecylbenzenesulphonate (NaDBS) in water was shaken up into a foam in a bottle and 100 ml of a 10% solution of the LIX-64N in kerosine was added in small quantities, with shaking, to form an anionic polyaphron of PVR 10 which was stable enough to be stored. Before use it was diluted fivefold with water. For cationic aphrons, the aqueous solution contained 5 ml/l of Arquad 12-50.

The cationic CGA was made in an aqueous solution containing 1 ml/l of Arquad 12-50, and the anionic CGA was made in an aqueous solution containing 1 g/l NaDBS.

For this work the feed solution was a solution of copper sulfate of concentration varying between  $10^{-3}$  and  $10^{-5}$  M adjusted with sulfuric acid to pH between 2 and 3, the most suitable for extraction according to the manufacturers of the LIX reagent. For each batch experiment, 2 liters of feed solution were placed in the cell.

Because of the limited analytical equipment available, it was decided to study the separations by analyzing for copper in the feed and in the raffinate. For this purpose an Orion cupric ion selective electrode, model 94-29 and a Fisher Acumet pH meter, model 825 MP were used. As the solutions to be analyzed inevitably contained some oil as well as surfactant, it was necessary to confirm the accuracy of the ion selective electrode under these circumstances. Initially some difficulties were experienced due to interference of the solvent which could not be entirely eliminated. However, a routine was developed for cleaning the electrode with ethyl alcohol and distilled water, and this has enabled consistent and reproducible results to be obtained.

A further problem developed because the cationic surfactant also interfered with the analyses. Eventually this was overcome by removal of the cationic surfactant before the ion selective electrode was used. This was achieved by an ion flotation

procedure by Sebba (1962) using a modification of a method described by Tomlinson and Sebba (1962). The sample solution into which the ion selective electrode would later be placed is first put into a 50 ml glass Buchner funnel with a fine pore fritted glass disc forming the base. An excess of a dye, of opposite charge to that of the surfactant to be removed, was added and a thin layer of isooctanol was added to the surface of the solution. Since the troublesome surfactant was cationic, the dye had to be anionic and methyl orange worked very well. 2 ml of a 300 mg/l solution of methyl orange, 1 ml of a 0.5 N solution of sodium carbonate and a few drops of ethanol was added for each 50 ml of sample taken. By introducing nitrogen under pressure through the stem of the funnel, very fine bubbles were generated and these, by the process of ion flotation, buoyed a compound between the dye and the surfactant to the surface where it was retained in the octanol and removed from the solution which was now able to be analyzed for copper by the ion selective electrode. The bubbling continued for 45 minutes.

The results for the batch tests are shown in Table 3. In all cases the volume of the feed solution was 2 liters. The solvent aphrons were introduced into the feed solution at the rate of 0.4 ml/s followed by CGA in bursts of 100 ml at a time, metered in at the same rate. Although in the runs a total of 400 ml of CGA was added to ensure complete extraction, the concentration of remaining copper was so small as to have reached the limit of accuracy of the ion selective electrode; therefore, the percent extraction is given after addition of 200 ml of CGA. The results listed are the averages of from 8 to 10 separate experiments for each set.

It will be seen from these results that the smaller aphrons are more effective in extracting the copper than the larger aphrons. This is in conformity with the theory discussed in Sebba (1985b). The only problem with the smaller aphrons is that the

**Table 3. Results From Batch Tests.**

Vol. of aphrons	Diam. of aphrons	Charge of aphron	Charge of CGA	Cu conc. Initial	(mol x 10 <sup>-6</sup> /l)		% CU Extracted
					Vol. CGA added 100 ml	200 ml	
10 ml	< 25 $\mu\text{m}$	anionic	SET 1 cationic	49	3.0	0.45	99.1
15 ml	< 25 $\mu\text{m}$	anionic	SET 2 cationic	61	0.83	0.43	99.3
50 ml	25-50 $\mu\text{m}$	anionic	SET 3 cationic	2200	270	190	91.4
50 ml	< 25 $\mu\text{m}$	cationic	SET 4 anionic	11900	191	144	98.8
50 ml	25-50 $\mu\text{m}$	cationic	SET 5 anionic	2200	277	177	92.0

time needed for these smaller bubbles to rise to the surface is greater than that for the larger bubbles.

In the batch experiments there had to be a delay time before determining the extent of extraction as the small CGA bubbles needed time to rise to the surface. Ten minutes was found to be adequate for this, but experiments would be needed to determine whether the loss of copper and solvent, if this time were to be reduced, was significant or not.

#### **4.1.2 Extraction of Uranium**

It was decided to extract uranium as the complex uranyl sulfato ion since this is typical of many of the heavy metal ions, which are difficult to extract. The solvent chosen was kerosine as this is the one most used in industrial separations. However, for the extraction of uranium a suitable reagent, which can complex with the uranium and make it soluble in the non-aqueous solvent, has to be added to the kerosine. One such reagent examined was Alamine 336, a commercial long chain tertiary amine obtainable from the Henkel Corporation. This is supplied as a solution in kerosine, and for this project it was further diluted tenfold with kerosine. The other extractant examined was tributylphosphate (TBP), also as a ten percent solution in kerosine. Both Alamine 336 and TBP are well-known uranium extractants; therefore, it was decided to compare their extracting effectiveness when used in PDSE.

Alamine 336 belongs to a class of extractants known as ion-pair extractants which are based on the principle of ion association whereby a large positively charged organic moiety causes the extraction of a large anionic metal complex into

the organic phase with concomitant expulsion of a small common anion to the aqueous phase.

The Alamine series of reagents all contain a basic nitrogen capable of forming amine salts with a wide variety of inorganic and organic acids. The amines which find the widest use in metals recovery processing are the tertiary amines of the general formula  $R_3N$  where R can represent a variety of hydrocarbon chains. The equations below are representative of the extraction chemistry of the Alamine series of reagents:

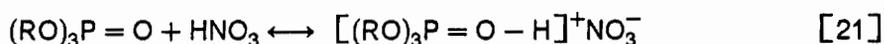


Equation [18] is simply amine salt formation while equation [19] represents true ion exchange. The extent to which  $B^-$  will exchange for  $A^-$  is a function of the relative affinity of the two anions for the organic cation and the relative stability of the anions in the the aqueous medium. The biggest commercial acceptance for Alamine type reagents has been in uranium recovery processes; however, any metal capable of forming anionic complexes in aqueous solutions is a candidate for extraction by an amine type extractant.

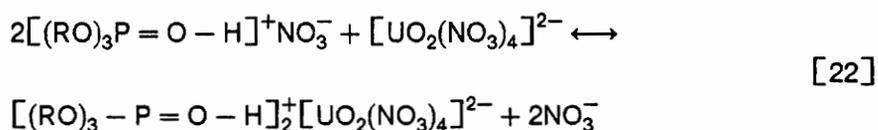
Tributylphosphate (TBP) is a well-known uranium extractant. In neutral or slightly acidic solutions, uranium is extracted as a solvate.



At very high nitric acid concentrations, protonation occurs:



Uranium extraction can then proceed under the alternative ion-exchange mechanism as follows:



The experimental method used for the extraction of uranium is exactly the same as the method used for the copper extraction. The same apparatus was used and the aphrons and CGAs were prepared in the same manner. Since this experiment was performed using two different types of extractants, two different polyaphrons were prepared. One set of polyaphrons was made with 100 ml of 10% Alamine 336 in kerosine as the organic phase and 10 ml of a 5 g/l aqueous solution of NaDBS. The other set of polyaphrons was made with 100 ml of 10% tributylphosphate in kerosine as the organic phase and 10 ml of a 5 ml/l Arquad 12-50 solution in water.

For this work the feed solution was a solution of uranium sulfate of concentration varying between  $10^{-1}$  and  $5 \times 10^{-5}$  g/l adjusted with sulfuric acid to pH between 2 and 3, the most suitable for extraction according to the manufacturers of the reagent. For each batch experiment, 2 liters of feed solution were placed in the cell.

In order to minimize the possibility of stable foams building up on top of the solution in the cell during the operation, it is desirable that the surfactant used for making the polyaphrons be of opposite charge to the surfactant used in making the CGA. With this in mind, the CGA used with the Alamine 336 extraction was made of a 1 g/l solution of NaDBS in water and the CGA used with the tributylphosphate extraction was made of a 1 ml/l solution of Arquad 12-50.

The uranium was analyzed spectrophotometrically using Arzenazo I. Arzenazo I and uranyl ions in slightly alkaline medium (pH 7.5 - 9.0) form a 1:1 blue complex that

is utilized for the spectrophotometric determination of uranium(VI). The reagent and its uranyl complex are soluble in water, owing to the sulphonate groups. Uranium (VI) is often determined with Arzenazo I, after separation by extraction or ion-exchange. Arzenazo I has been employed for the determination of uranium(VI) in natural water and ores and minerals. It must be noted that the limit of accuracy of the analytical method is  $1 \times 10^{-4}$  g/l.

The results for the batch tests are shown in Table 4. The solvent aphyrons were introduced into the pregnant solution at the rate of 0.4 ml/s of CGA followed by CGA in increments of 100 ml at a time, metered in at the same rate. The results listed are the averages of from 8 to 15 separate experiments for each set. The fact that there was not complete extraction at the highest concentrations is believed to be due to the fact that there was not sufficient extraction capacity in the small quantity of solvent which was kept constant for the series of runs.

The fact that virtually complete extraction is possible in one pass emphasizes the difference between predispersed solvent extraction and conventional extraction in which the concentrations in both the solvent and aqueous phases are fixed by the necessity to maintain the constancy of the extraction coefficient. In PDSE, because of the enormous number of aphyrons which move in sequence up the cell, each pass can be considered as made up of an extremely large number of stages and this is responsible for the high efficiency of the process.

### **4.1.3 Chromium Extraction**

The ability of the liquid ion exchange process to treat very dilute solutions and produce a high purity concentrate suggests the application of the process to the

**Table 4. Extraction of Uranium in Batch Cell.**

<b>Solvent</b>	<b>Initial conc. (g/l)</b>	<b>No. of runs</b>	<b>% extraction</b>
A	$1 \times 10^{-1}$	15	90
A	$1 \times 10^{-7}$	15	90
A	$2 \times 10^{-3}$	15	100
A	$1.5 \times 10^{-3}$	15	100
A	$1 \times 10^{-3}$	15	100
A	$5 \times 10^{-4}$	15	100
B	$1 \times 10^{-2}$	8	85
B	$2 \times 10^{-3}$	15	100
B	$1.5 \times 10^{-3}$	15	100
B	$1 \times 10^{-3}$	15	100
B	$5 \times 10^{-4}$	15	100

Solvent A: Polyaphrons made of 10% Alamine 336 in kerosine.  
Aqueous phase contains 5 g/l of sodium dodecyl benzene sulfonate.

Solvent B: Polyaphrons made of 10% tributylphosphate in kerosine.  
Aqueous phase contains 5 ml/l Arquad 12/50.  
CGA contains 1 g/l of sodium dodecyl benzene sulfonate.

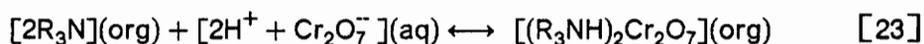
Volume of pregnant: 2 liters.  
Volume of polyaphrons, PVR 10: 50 ml.  
Volume of CGA: 200 ml.

treatment of waste streams containing the chromate or dichromate anion. The process would eliminate the hexavalent chromium waste treatment problem currently encountered and concentrate the chromate anion in a solution amenable to economic recovery.

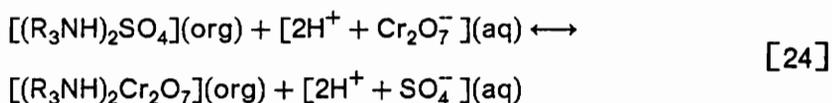
The extraction of chromium using a LIX reagent essentially involves the contacting of the organic phase, containing the LIX reagent in a suitable organic carrier, e.g. kerosine, with an aqueous chromate solution. The chromium values are extracted from the aqueous phase into the organic phase by the formation of a water insoluble amine or quarternary ammonium salt of chromium.

Alamine 336, a LIX reagent produced by Henkel Corporation, extracts dichromate by amine neutralization or salt formation:

1. Extraction by amine neutralization:



2. Extraction by salt formation:



Since extraction with Alamine 336 is dependent on sufficient hydrogen-ion concentration in the aqueous feed solution, it is applicable to acidic liquors. The exact extraction mechanism is dependent on the stripping agent employed. The dichromate may be stripped from the organic phase by employing either a base, an acid, or a salt. The salt may be either acidic or basic.

The extraction of chromium was carried out in the same manner as were the copper and uranium extractions. The polyaphron was made with 100 ml of a 10% Alamine 336 in kerosine solution and 10 ml/l of a 5 ml/l Tergitol 15-S-9 aqueous solution. Tergitol 15-S-9 is a nonionic surfactant produced by Union Carbide. The CGA was made with a 1 g/l NaDBS solution in water. For all experiments conducted, 2 liters of 0.001 g/l potassium chromate solution were placed in the extraction cell. 50 ml of polyaphron diluted in 200 ml of distilled water were pumped into the cell with a Masterflex peristaltic pump. 200 ml of CGA were then pumped with the same type of pump. After a chosen time interval, the raffinate was analyzed spectrophotometrically with diphenylcarbazide for chromium. Under the experimental conditions that these tests were carried out, it was noted that the analysis was sensitive to a concentration of 0.0001 g/l. The results for the tests are shown in Table 5.

Chromium is usually determined by the highly sensitive and selective diphenylcarbazide method. This method, which is more than one hundred times as sensitive as those based on the colors of the chromate or dichromate ions, is particularly useful for determining traces of chromium.

The percent of chromium extracted throughout all tests performed was 99%. It is probable that more was extracted but due to the limitations of the analysis it was impossible to quantitatively determine the extent of the extraction beyond 99%.

#### **4.1.4 Extraction of Alizarin Yellow**

In this experiment, predispersed solvent extraction was employed to separate alizarin yellow from a dilute ( $3.23 \times 10^{-5}$  M) aqueous solution. The solvent was a

**Table 5. Data for Chromium Extractions.**

<b>Test no.</b>	<b>Initial Conc. (g/l)</b>	<b>Final Conc. (g/l)</b>	<b>% extraction</b>
1	.001	.0001	99
2	.001	.0001	99
3	.001	.0001	99
4	.001	.0001	99
5	.001	.0001	99

Note: The spectrophotometric analysis used was sensitive only to a concentration of .0001 g/l.

solution of 10% octanone in light mineral oil and was converted to polyaphron of PVR 10 by using a 5 g/l NaDBS solution in water. To assist in the extraction, a CGA was made using a 5 ml/l Arquad 12-50 solution in water.

50 ml of polyaphron diluted in 200 ml of water and a total of 200 ml of CGA were pumped into the cell via Masterflex peristaltic pumps, to extract the alizarin yellow from a dilute alizarin yellow solution. The raffinate was then analyzed spectrophotometrically. The analysis was performed taking advantage of the fact that alizarin yellow at a pH of 10 turns from a pale yellow to a light orange. The darker orange color allows for data to be collected over a full range of transmittance levels.

The analysis of the raffinate presented difficulties at first because turbidity and suspended solids that were present in the samples interfered with the spectrophotometric readings. This was resolved by centrifuging the samples prior to the analysis. The results for these tests are shown in Table 6. As can be seen, the percent of alizarin yellow extracted was always 98 or higher.

## **4.2 Experiments Performed in Continuous Mode**

### **4.2.1 Upright Column**

Experiments for the continuous mode in a vertical column have been performed for the copper and alizarin yellow systems only. These two systems were selected because they are easier to work with and present less problems than the other two systems used in the batch mode. Uranium, because of its nature, poses problems that require special handling and strict measures for its disposal. For the batch

**Table 6. Results for the Extraction of Alizarin Yellow in Batch Mode.**

<b>Test no.</b>	<b>Initial Conc. (mol/l)</b>	<b>% extraction</b>
1	$3.5 \times 10^{-5}$	98.0
2	$3.5 \times 10^{-5}$	99.0
3	$3.5 \times 10^{-5}$	98.5
4	$3.5 \times 10^{-5}$	99.0
5	$3.5 \times 10^{-5}$	98.0

mode, small volumes of all solutions are necessary but for the continuous modes, much larger volumes are required; therefore, it was decided not to use it in the continuous mode experiments at the present time. Chromium on the other hand, is difficult to analyze and the best method that was available for this experiment was sensitive only to 0.0001 g/l. For this reason, it was decided that chromium would not be used until a better analytical technique can be implemented.

The continuous flow experiments were carried out in the pilot plant unit previously described in the apparatus section of this paper. The equipment functioned well over periods of 8 hours of continuous operation. The first objective was to obtain information on residence times for the pregnant copper solution. This was achieved by keeping the inflow of pregnant solution, aphrons (solvent), and CGA constant and sampling at different heights above the intake point (see Figure 4 and the description of the process in the procedure section). The results of a few runs are shown in Figure 8.

For all these runs the feed flow rate was 5.09 ml/s the CGA flow rate was 0.554 ml/s and the pH of the pregnant solution was 2.5.

Subsequently, the same type of experiment was performed for the extraction of alizarin yellow. The sampling for these tests was done at points even higher from those used for the copper extraction. The results of a few runs are shown on Figure 9.

For all these runs the feed flow rate was 190 ml/min., the CGA flow rate was 171 ml/min., and the polyaphron flow rate was 31.6 ml/min. Also, the pregnant solution concentration was  $3.23 \times 10^{-5}$  mol/l.

It is clear that a certain length of path is required before the extraction becomes efficient. In the above cases it is about 25 cm for the copper system and 35 cm for the alizarin yellow system. It must not be implied from these results that better

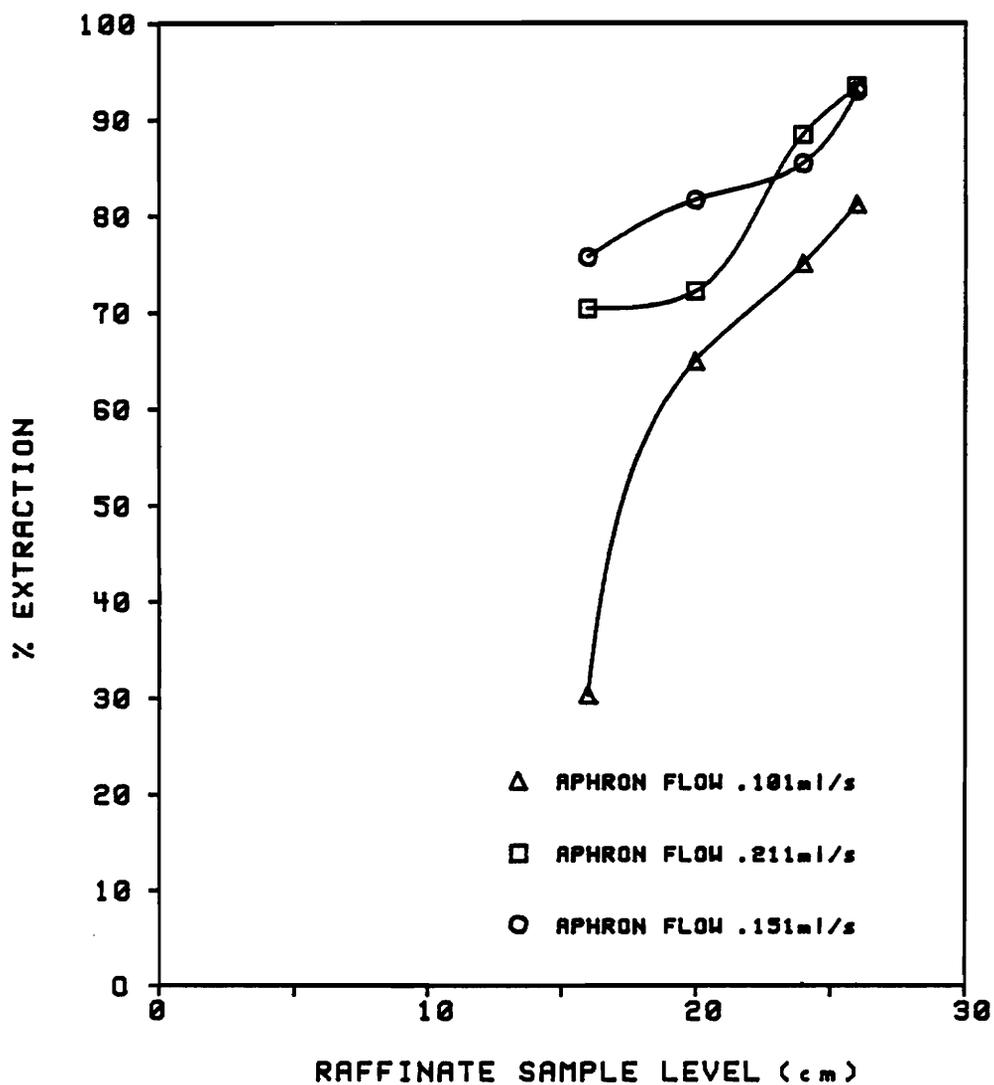
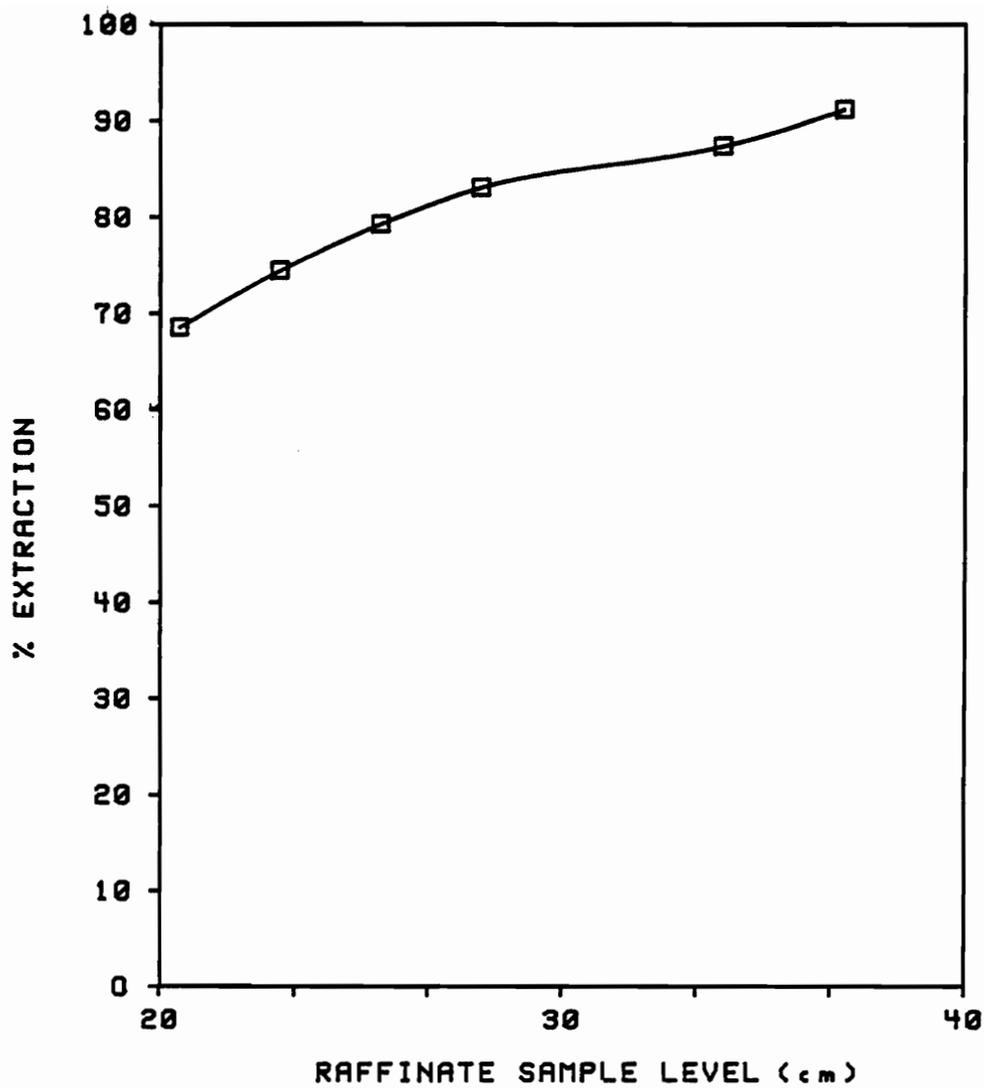


Figure 8. Effect of Raffinate Sampling Level: Copper Extraction, Continuous Flow.



**Figure 9. Effect of Raffinate Sampling Level: Alizarin Yellow Extraction, Continuous Flow.**

efficiency could not be obtained under more favourable conditions. The important fact which emerged but had not previously been demonstrated, is that the path length is important.

It was noted that the solvent layer had a very clearly defined interface with the water, and there was very little foam produced on the top of the solvent. One of the problems being experienced in using conventional solvent extraction in hydrometallurgy is that sometimes a heterogeneity appears in the solvent phase. This is referred to as the third phase and is often difficult to handle. Only once in PDSE was such a formation observed. It occurred when there was a break in the flow of CGA enabling breakdown of the CGA bubbles with the consequence that there were large bubbles in the pipeline. It has been noted that a thin layer of aphrons collects under the solvent layer. These eventually coalesce and merge with the solvent. However, as long as they are in the aqueous phase they remain there as a biliquid foam, as the aphrons are so small that they do not have enough momentum to penetrate the interface into the solvent layer. But, when the large bubbles reach this interface, they have much more energy and so they penetrate into the solvent layer, carrying with them some of the biliquid foam. Once inside the solvent layer, the biliquid foam becomes stabilized, as has also been observed for polyaphrons. This is because the environment has been changed from water to that of the non-polar solvent. This may be one of the ways by which the third phases are formed. If the presence of larger bubbles is avoided this third phase does not appear in PDSE, and this gives it an important practical advantage over conventional solvent extraction.

The second objective of this experiment was to determine the effect of CGA flow rate and the effect of polyaphron flow rate on the percent extraction of copper and alizarin yellow from dilute aqueous solution. To fulfill this objective several tests

were conducted using the same procedure that was previously described, except that this time the CGA flow rate was varied while everything else was maintained constant and afterwards the polyaphron flow rate was varied while all other parameters were kept constant. Results for these experiments are depicted in Figures 10, 11, 12, and 13.

For all these runs the copper feed concentration was  $1 \times 10^{-5}$  mol/l and that of the alizarin yellow was  $3.23 \times 10^{-5}$  mol/l. The data collected for the copper extractions show that as the CGA flowrate increases, the percent extraction also increases at lower flow rates, but it plateaus at the higher flow rates. This is an indication that there exists a critical point for each system after which an increase of CGA flow rate ceases to be effective. The same behaviour is observed when the polyaphron flow rate is varied while everything else is kept constant except that the initial increase in percent extraction is more sharp than that observed for the CGA effect. This is reasonable when one considers the fact that, according to stoichiometry, at low polyaphron flow rates there was not enough solvent to extract all the copper ions. It must be remembered that in PDSE it is the polyaphrons that do the actual extraction while the CGA is just a mechanism that aids the separation of the two phases.

The data obtained from the removal of alizarin yellow from a dilute aqueous solution also follow the general trends described in the previous paragraph, except that the increase in percent extraction is small compared to the increase in flow rates. This extraction presented problems because alizarin yellow complexes with the octanone to form a solid. Furthermore, it was observed that not only do the aphrons disperse themselves spontaneously when introduced into the extraction cell, but also the CGAs produce a large amount of mixing. Since this is specially true of the continuous upright column mode, the solid tended to be mixed vigorously throughout the extraction cell. Therefore, the possibility exists that as the flow rates

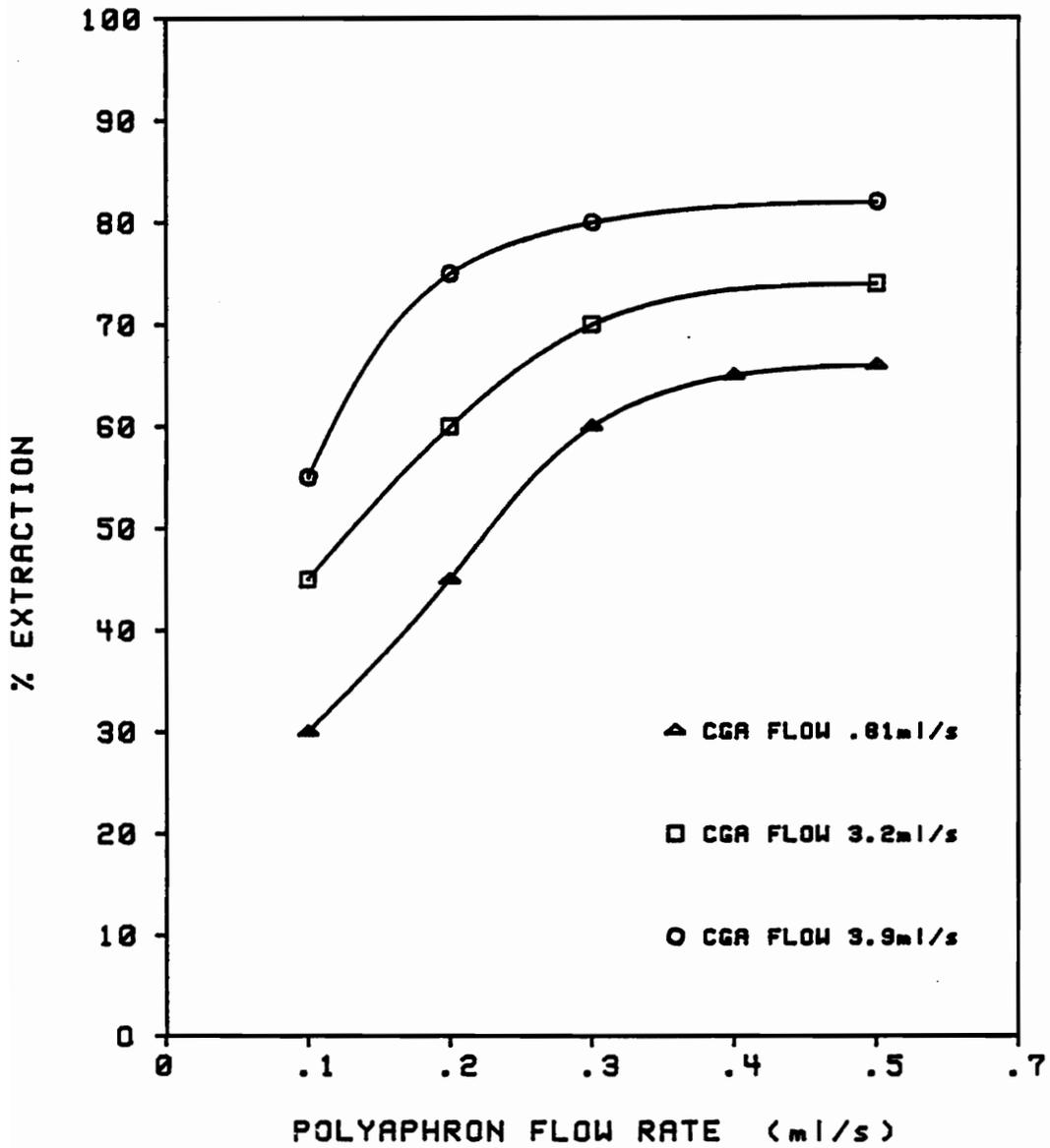


Figure 10. Effect of Polyaphron Flow Rate on Copper Extraction.

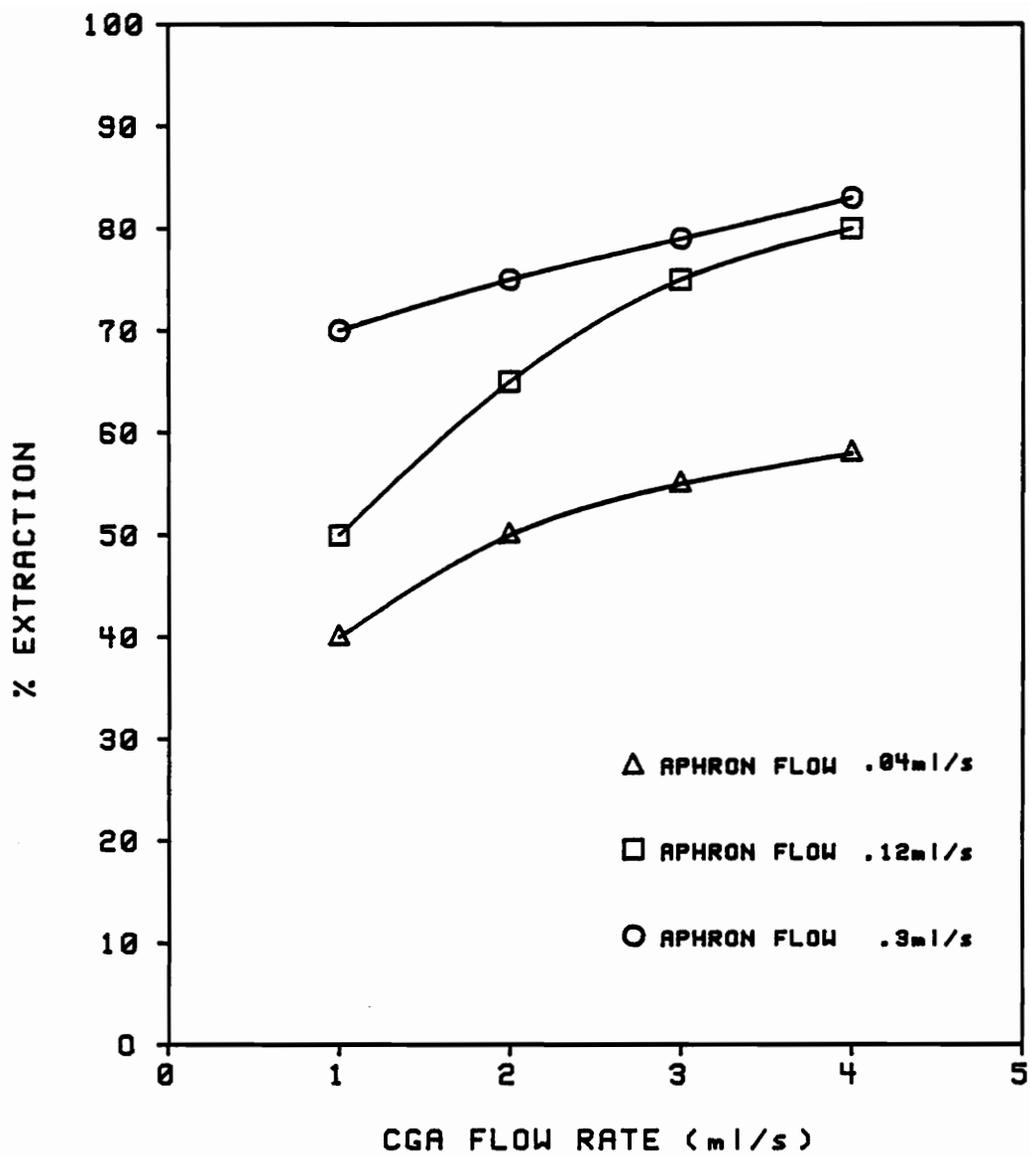


Figure 11. Effect of CGA Flow Rate on Copper Extraction.

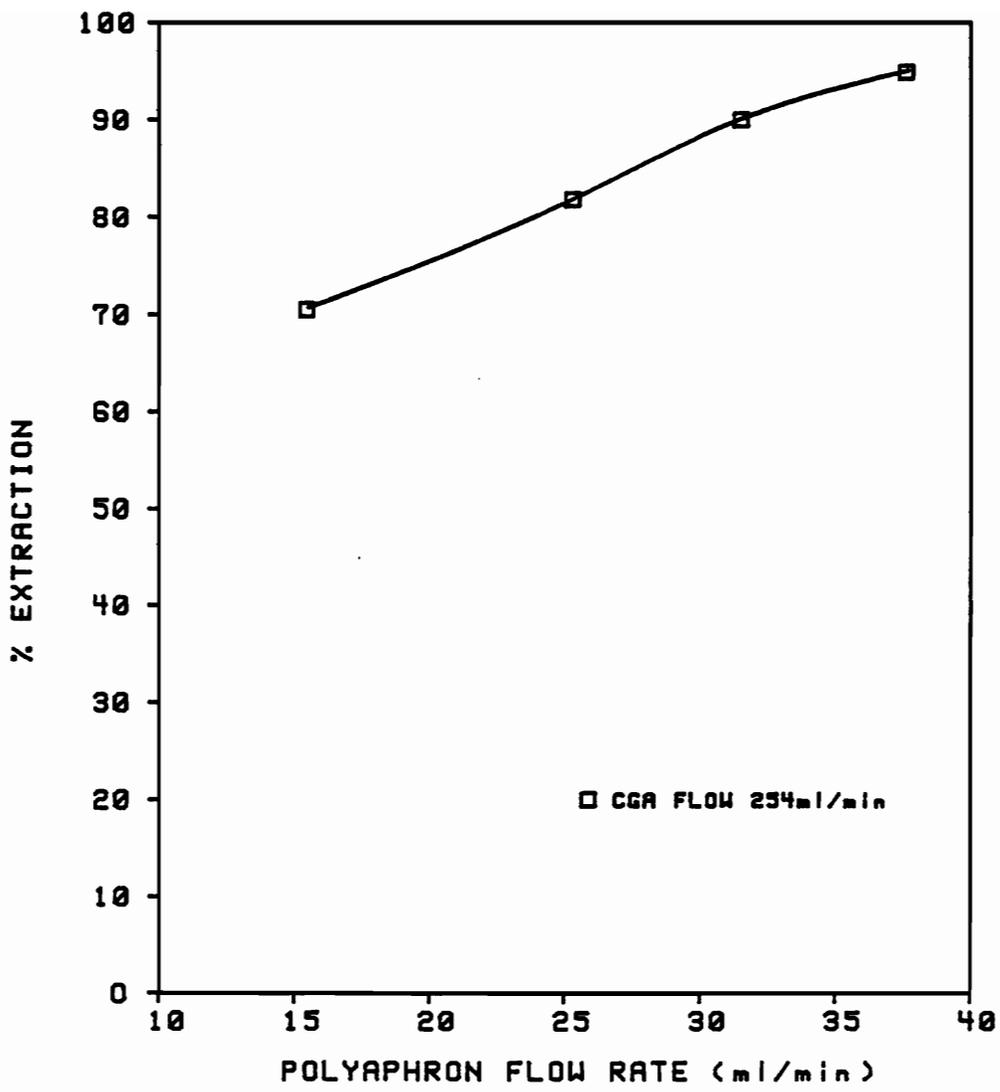


Figure 12. Effect of Polyaphron Flow Rate on Alizarin Yellow Extraction.

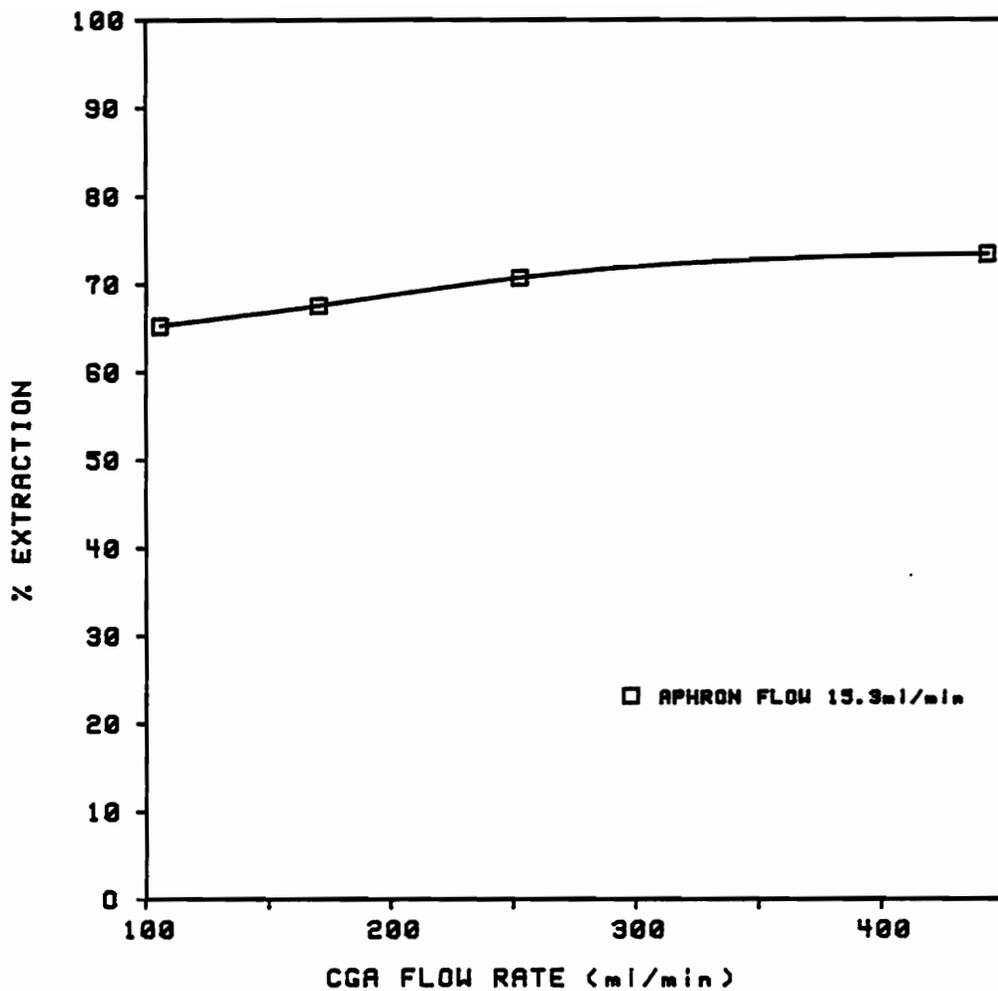


Figure 13. Effect of CGA Flow Rate on Alizarin Yellow Extraction.

were increased, the mixing action became more turbulent and some of the extracted alizarin yellow could have gone back into solution.

#### **4.2.2 Continuous Flow Experiments in a Horizontal Trough**

Tests were performed to gather preliminary data on the continuous extraction of copper ions and alizarin yellow from dilute aqueous solutions in a horizontal trough. The trough was designed based on the results obtained from the experiments performed using the vertical cell. With these experiments it had been determined that the residence time is important; therefore the length of the trough was designed so as to ensure that the length of time the liquid remains in the trough (path length) is long enough. The minimum length necessary was 35 cm since both the copper and the alizarin yellow systems were being considered. It was decided to allow a longer path than appeared to be necessary in the hopes that higher percent extractions would be achieved. The trough was finally built with a length of 2 ft., a height of 1 ft., and a width of 6 in. It has a total capacity of approximately 15 liters. Further description of the trough is given in the apparatus section of this report.

Several tests have been performed in this apparatus and the data has been depicted in Tables 14, 15, 16, and 17.

The concentrations of the feeds were kept the same as those used for the other continuous process, *i.e.*  $1 \times 10^{-5}$  mol/l for the copper feed and  $3.5 \times 10^{-5}$  mol/l for the alizarin yellow feed. All tests were run at a pH between 2 and 3 and all solutions were pumped from one stage to the next using Masterflex peristaltic pumps.

The feed flow rates for the copper system were kept constant at 260 ml/min while the CGA and diluted polyaphron flow rates were varied. The process was allowed to

reach equilibrium before data was recorded. The data for these tests is shown in Figure 14 and 15. The data shows that when the polyaphron rate was kept constant and the CGA rate was varied, the percent extraction increased by 3% while when the CGA rate was kept constant and the polyaphron rate was varied, the extraction increased by only 0.5%. In fact, it was calculated that there would be a theoretical excess of at least 5% LIX-64N in all runs; therefore, the theoretical yield was 100% for all runs. From this data, it is concluded that as long as the LIX is run at a flow rate which maintains an excess, the determining factor in the percentage extraction is the flow rate of the CGA carrier.

The feed flow rate for the alizarin yellow feed solution was kept constant at 250 ml/min. The CGA and polyaphron flowrates were varied one at a time while keeping the other constant. The data for these tests is depicted in Figures 16 and 17. The expected small increase in percent extraction with CGA and polyaphron flow rate increase was observed.

In the continuous extractions, the raffinate always showed a turbidity indicating that all the aphrons were not reaching the solvent layer, but were being removed before they could do so. As the aphrons were not all of uniform size, the smallest ones might not be conveyed to the surface by the CGA. It is possible that if this were to be a problem in an industrial operation, it could be corrected by sending the raffinate to a holding tank before discharge. Another alternative would be to send the raffinate to another cell in which a small amount of aluminum sulfate is added to bring the concentration of aluminum to  $10^{-2}$  M, the pH is adjusted to between 5 and 6 and then a CGA made with 1 g/l NaDBS is added to float an aluminum soap which carries with it the residual oil. This is an application of ion flotation (Sebba, 1962). The froth contains all the residual solvent, leaving a crystal clear raffinate with a negligible

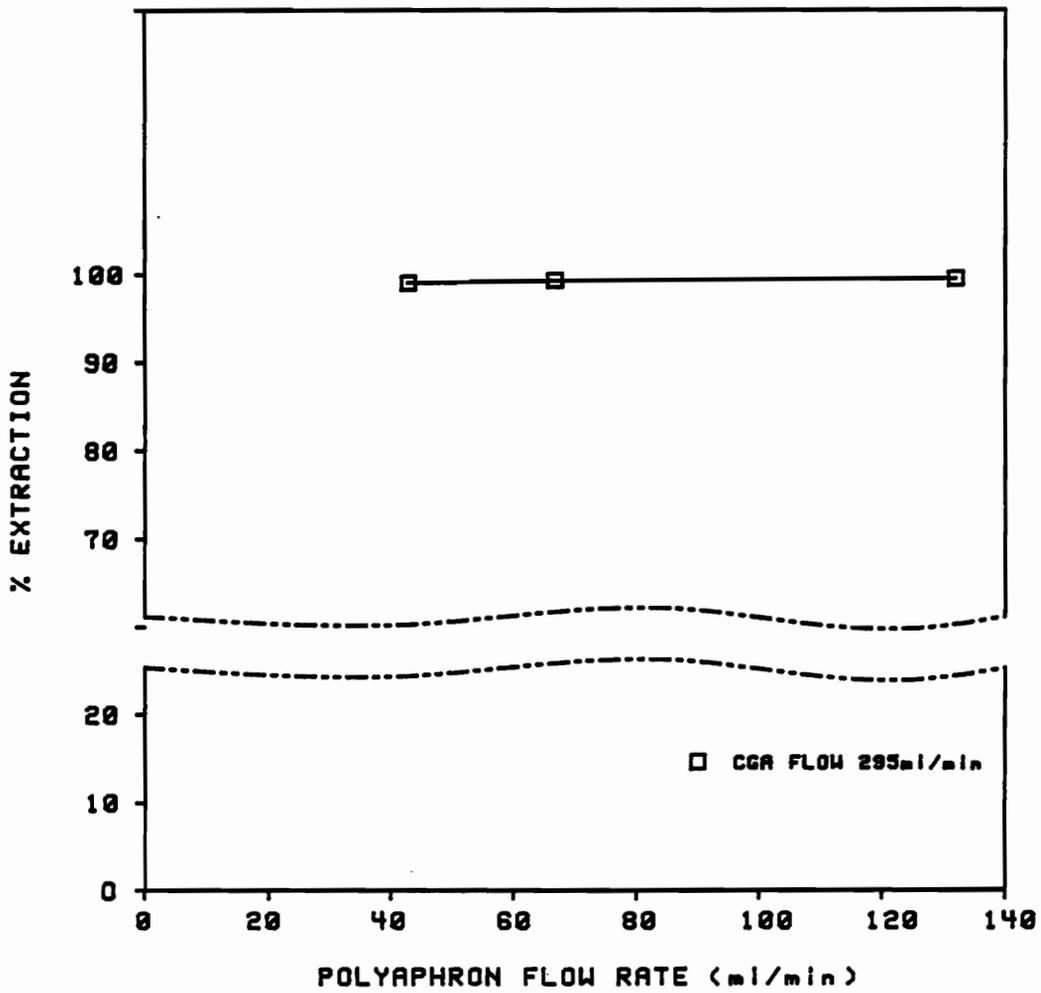


Figure 14. Effect of Polyaphron Flow Rate on Copper Extraction in a Trough.

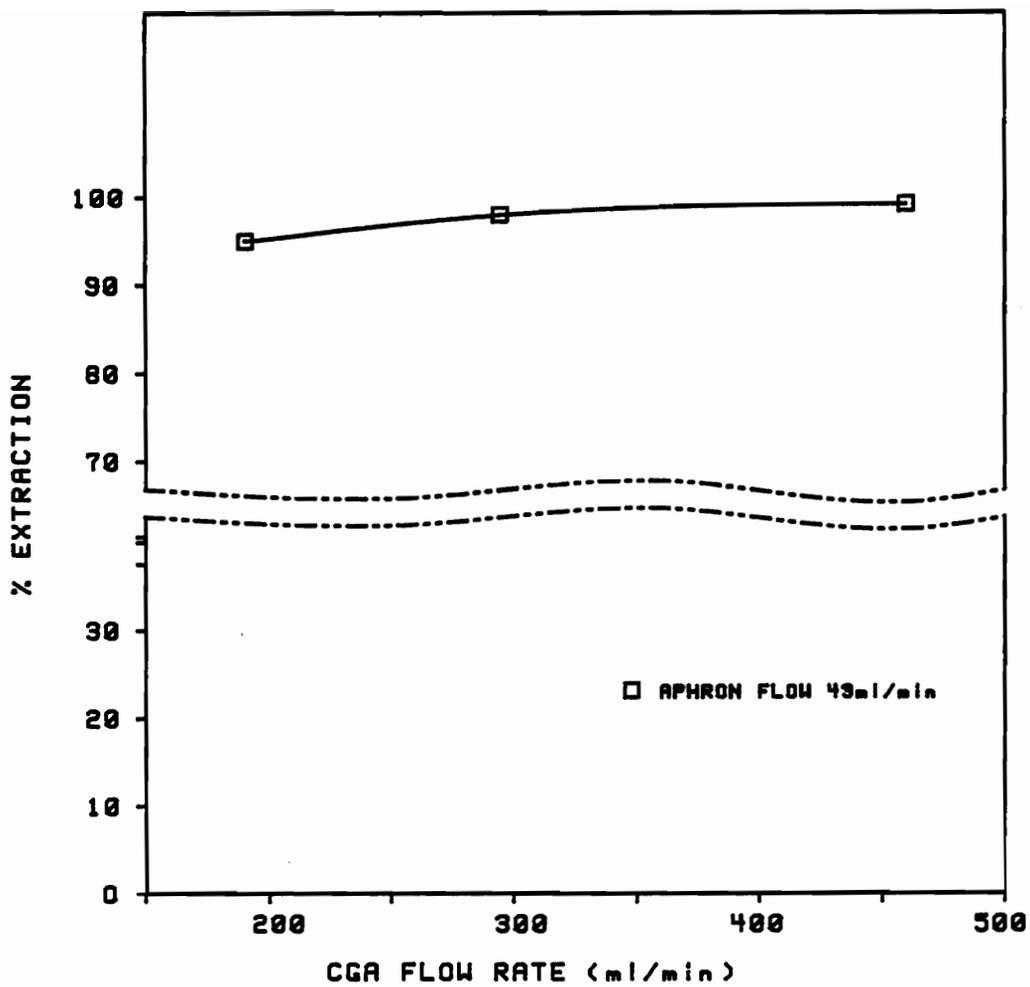


Figure 15. Effect of CGA Flow Rate on Copper Extraction in a Trough.

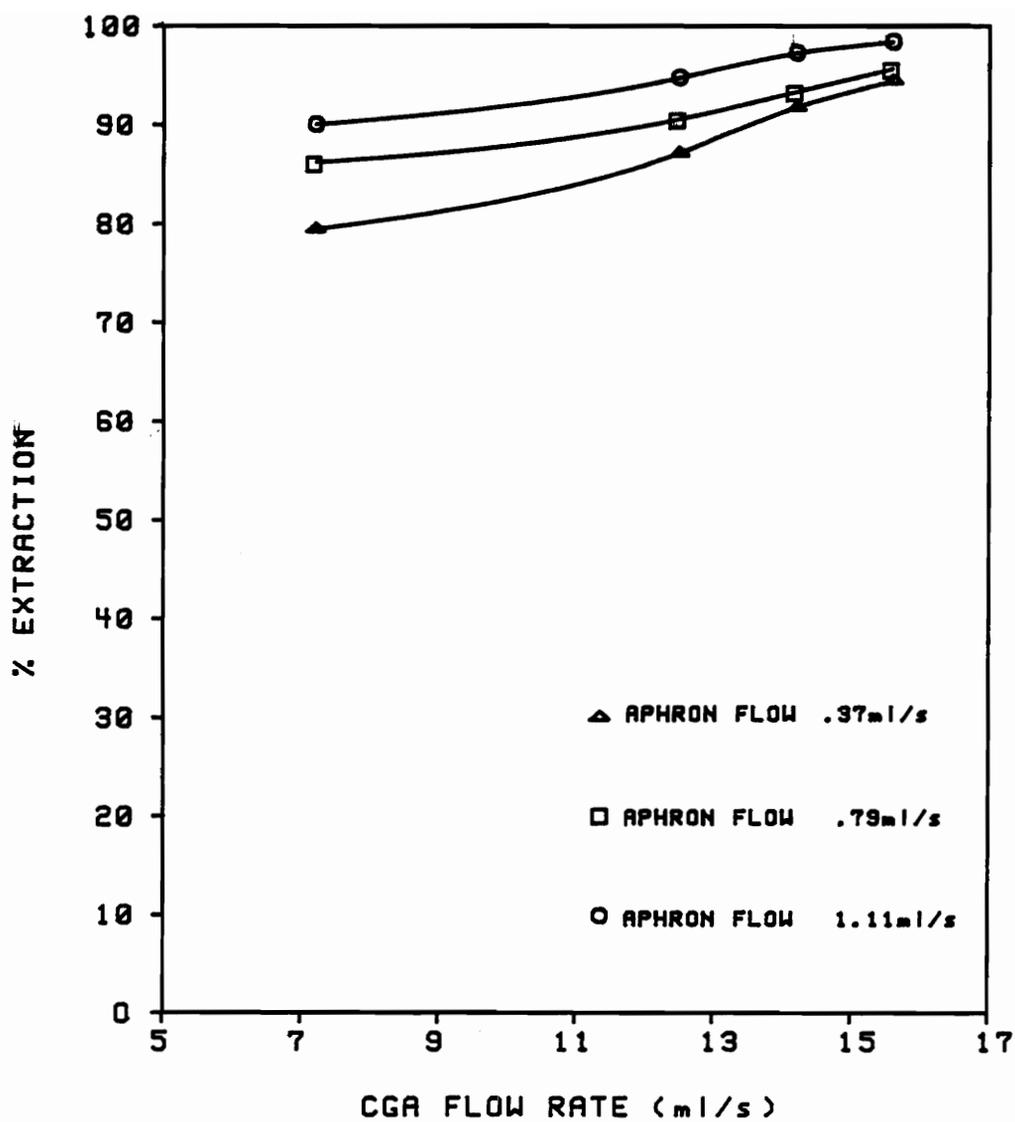


Figure 16. Effect of Polyaphron Flow Rate on Alizarin Yellow Extraction in a Trough.

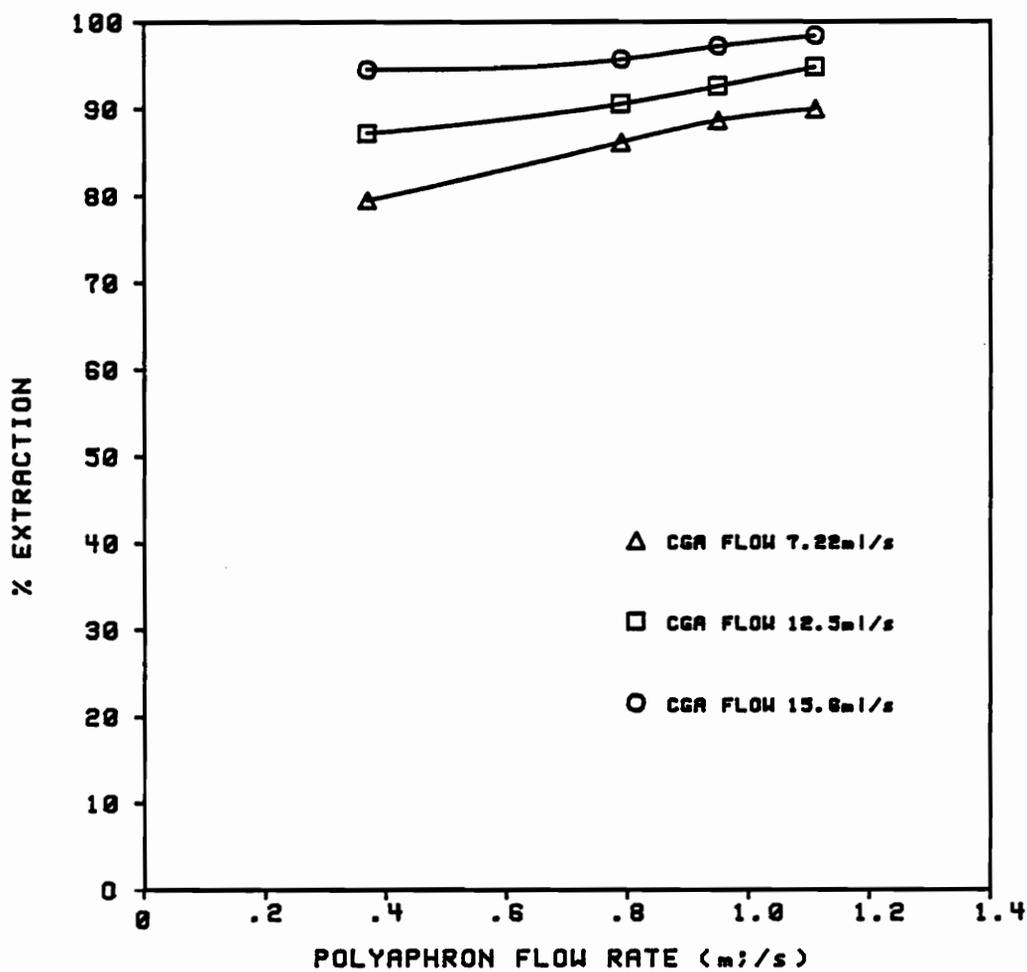


Figure 17. Effect of CGA Flow Rate on Alizarin Yellow Extraction in a Trough.

concentration of copper. However, the loss of solvent in the raffinate may not be such as to justify this procedure.

## 5.0 CONCLUSIONS

Solvent extraction of metal ions can be used for two main purposes. One is the recovery of values. In such a case it is usually necessary to choose a solvent system from which the recovered metal ions can be eluted so that the solvent can be reused. In such cases, provided the losses in the process are kept low, the cost of the collector might be less important than its efficiency for extraction.

In the second case, solvent extraction can be used for removing unwanted metals from waste streams. In such cases what is most important is to find a solvent that can reduce the concentration of ions in the water to a level that is acceptable to the environmental authorities. As the total quantity of metal that needs to be removed is small, and therefore the amount of solvent needed may be small, the cost of reagents may be unimportant compared to the the energy costs for moving large volumes of water. In the first case a batch process may be necessary. In the second case a continuous process should be used. Predispersed solvent extraction seems to be particularly appropriate for the extraction of metal ions such as copper, uranium and chromium from very dilute aqueous solutions.

The experiments have shown that predispersed solvent extraction works very well for the extraction of copper and alizarin yellow in both a batch and two continuous flow systems. It was also shown that the extraction works satisfactorily for the extraction of uranium and chromium in a batch system. The ratio of solvent to pregnant can be very low as compared to what is needed in conventional solvent extraction. The ratio of CGA is also low at about 10%. Further addition of CGA only extracts a minimal additional quantity of solute. Since only 1/3 of the CGA is water,

this means that the amount of surfactant needed for a liter of pregnant solution is of the order of 300 mg. The quantity of surfactant needed for the aphrons is still less, being about 1 mg. The smaller the aphrons the more efficient is the extraction but this is offset by the fact that the smaller aphrons take longer to reach the surface. The extractions performed in the trough gave higher percent extraction than the ones performed in the continuous upright cell process. This is due to the fact that the trough has a higher residence time than the upright cell. The CGA generator worked satisfactorily over long periods. It would appear that there is enough stirring caused by the introduced CGA to suggest that no further stirring device is needed, but this would need to be verified on a larger scale experiment. The diluted solvent aphrons were stable provided they were kept stirred.

In summary, predispersed solvent extraction, PDSE, properly implemented makes possible the removal of metals from aqueous solution down to the parts per billion range.

## **6.0 RECOMMENDATIONS FOR FURTHER STUDY**

The experimental work done so far has demonstrated that predispersed solvent extraction works very well for the extraction of copper, uranium, chromium and alizarin yellow under laboratory conditions. Sufficient preliminary data has been collected and the emphasis should now be directed towards the theoretical aspect of the process. The equations suggested as part of the theory underlying PDSE should be tested and a mathematical model for the system should be developed. If this work is to be carried out, it is suggested that a more sophisticated analytical method such as atomic absorption spectrometry be used since the analytical techniques used in this work presented problems and limitations. Lastly it is recommended that a large-scale pilot plant be built in order to determine whether PDSE can be carried out successfully and still avoiding the use of mechanical stirring in large scale operations.

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## Appendix A. Colloidal Gas Aphrons

Colloidal gas aphrons (CGA), are micron-sized gas bubbles encapsulated by a shell of aqueous soapy film. This film introduces such a strong barrier to coalescence that coalescence never occurs as long as the bubbles are completely immersed in water. The structure of a CGA is illustrated in Figure 18.

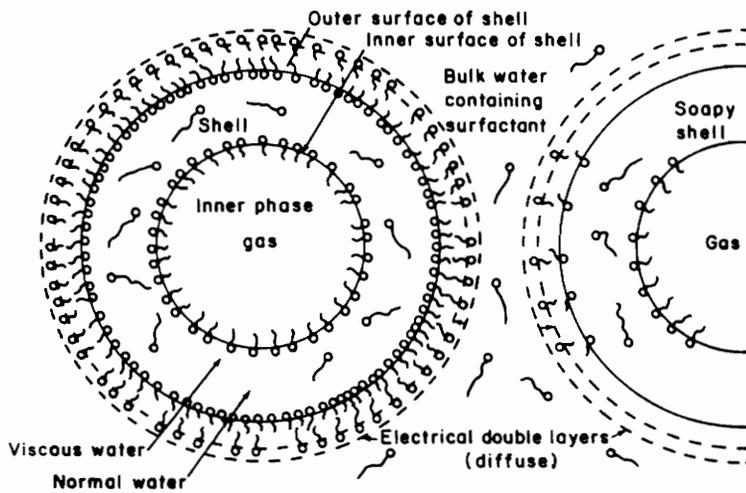
The size of CGAs are in the order of 25 - 50  $\mu\text{m}$  in diameter. CGAs with diameters smaller than 25  $\mu\text{m}$  have never been observed in the laboratory. This might be because the smaller bubbles squeeze out the gas very fast due to the fact that the pressure inside a bubble is inversely proportional to its diameter. Because of the small size of the bubbles, they rise to the surface only very slowly. Therefore, the CGAs have a long enough life-time that they can be generated in one place and pumped to another.

CGAs are made very quickly using a CGA generator (Figure 6), and a dilute surfactant solution. The generator works under the principle that when the disc, fixed to a vertical shaft connected to an electrical motor, is made to rotate at a speed of 4,000 r.p.m. or more; strong waves of surfactant solution are produced at the surface. These waves strike the baffles, mounted vertically around the disc; and on re-entering the water they entrain the gas in the form of very small bubbles. CGAs containing up to 65% of gas in water are very rapidly and easily made.

CGAs have been found useful in many separation processes such as PDSE, ion and precipitate flotation, bubble-entrained floc flotation, and separation of oil from sand (Sebba, 1987). Most of its applications depend upon the following properties:

1. the buoyancy of the encapsulated gas
2. adherence of particles to the encapsulating shell
3. low viscosity of the system
4. large surface area produced by the small size of the bubbles.

Detailed information on CGA properties and applications can be found in *Foams and Biliquid Foams - Aphrons* (Sebba, 1987).



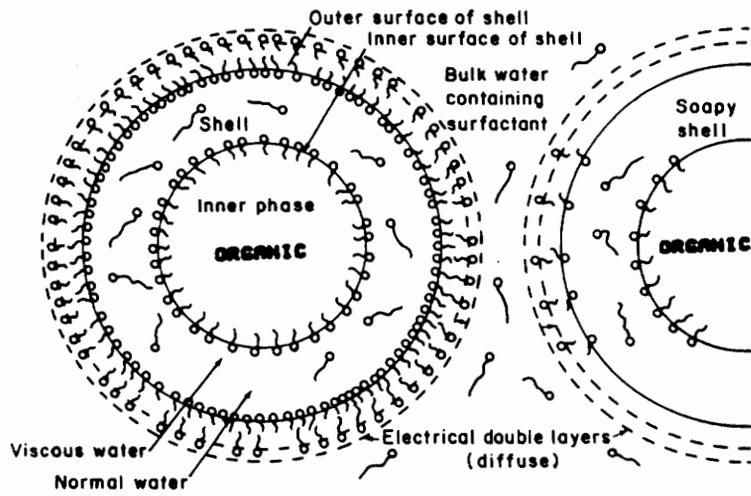
**Figure 18. Structure of a Colloidal Gas Aphron.**

## Appendix B. Polyaphrons

Polyaphrons (oil core aphrons) are a type of biliquid foam which consists of micron-sized oil droplets encapsulated in an aqueous shell (Figure 19). Polyaphrons are made by spreading an oil (internal phase) which contains an oil-soluble surfactant dissolved in it, on the surface of water that has a water-soluble surfactant dissolved in it. As the oil spreads on the water, the oil film becomes so thin that movements of the mixture will allow the water to break through various points of the thin film eventually breaking it up to form minute droplets. When this happens, the water, which has a low contact angle induced by the dissolved surfactant, climbs onto the oil droplets and somehow spreads around it, eventually encapsulating the oil droplet with a soapy shell (Sebba, 1987).

The diameter of polyaphrons will vary from submicrometer to about 100  $\mu\text{m}$ . The size will depend on the type and concentration of surfactants used. The higher the concentration of the surfactant in the oil phase, the smaller the aphrons will be. It has been found useful to describe polyaphrons in terms of the phase volume ratio (PVR). PVR is the volume ratio of the dispersed oil phase to the continuous phase. Therefore, a polyaphron containing 90 parts of kerosene to 10 parts water, has a PVR of 10. Properly made polyaphrons of PVR 5 to 19 are very stable and can be kept for very long periods of time (two years or more).

Polyaphrons can be made by hand or with a continuous polyaphron generator (Figure 7). If made by hand, all that is needed is a stoppered bottle. The aqueous phase is placed in the bottle and the closed bottle is vigorously shaken to form a foam. Small amounts of oil at a time are added to the foam in geometrically



**Figure 19. Structure of an Oil Core Aphron.**

progressive amounts until all the oil has been added. After each addition oil, the bottle is shaken to break up the oil film. The quantity of oil that can be added at a time is limited because the environment of the aphrons that have already been formed must remain aqueous. If not, the aphrons congeal and no longer offer an interface for spreading (Sebba, 1987). Polyaphrons can be made very easily and quickly using the continuous polyaphron generator. The generator must first be seeded with some previously made polyaphrons and then it is just a matter of setting the organic and aqueous phase pumps at the required flow rates. Polyaphrons of PVR 5 to 20 have been made using both techniques.

Polyaphrons, used together with CGA, form the basis for predispersed solvent extraction (PDSE). In conventional solvent extraction mass transfer of the solute across the interface is achieved by vigorous mixing of the aqueous and solvent phases. On the other hand, in PDSE the solvent phase is aphronized before contacting it with the aqueous phase. The small size of the aphrons generates a large amount of surface area, so that when the aphrons are contacted with the aqueous phase, the individual aphrons distribute themselves throughout the aqueous phase, eliminating the need of vigorous mixing.

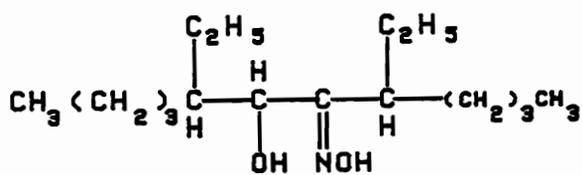
A detailed description of the properties of polyaphrons and its applications can be found in *Foams and Biliquid Foams - Aphrons* (Sebba, 1987).

## Appendix C. Some Facts About LIX 64N and Alamine 336

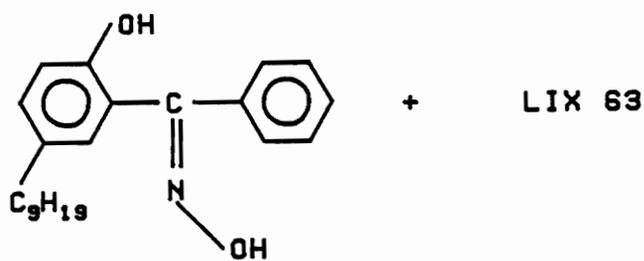
LIX 64N is an alpha-hydroxyoxime designed specifically for the extraction of copper from aqueous solutions. The extractant is a mixture of 2-hydroxy-5-nonylbenzo-phenoneoxime, and 5,8-diethyl-7-hydroxydodecan-6-oxime in kerosene. The extractant and its copper complex are insoluble in water and are characterized by having a solubility of at least 2 weight percent in the hydrocarbon that constitutes the organic phase. Lix reagents are used by numerous commercially successful metal recovery operations around the world. Figure 20 illustrates some molecular structures of some LIX reagents.

Alamine 336, [tri-(C<sub>8</sub>C<sub>10</sub>)amine], also considered a LIX reagent, is a water insoluble, saturated, straight chain, amine. The alkyl groups are a C<sub>8</sub>C<sub>10</sub> mixture, with the C<sub>8</sub> carbon chain predominating about 2 to 1. Alamine 336, a pale yellow liquid, is known to extract, among others, the following metals: uranium, vanadium, iron, cadmium, and chromium. In addition, this reagent extracts both inorganic and organic acids from process and waste streams.

LIX 64N and Alamine 336 are manufactured by Henkel Corporation.



LIX 63



LIX 64

Figure 20. Structure of Some LIX Molecules.

## Appendix D. Selected Results

The following pages contain some of the results obtained for this study.

Table 7 contains data collected for copper from the semi-pilot plant unit. The “Raffinate Sample Level” is the distance from the bottom of the extraction cell to the point where the raffinate sample was removed.

Table 8 contains the results of test performed in the semi-pilot plant unit for the extraction of alizarin yellow. The “Probe Height” is equivalent to the “Raffinate Sample Level” in Table 7.

Tables 9, 10, 11, and 12 have some results obtained to study the effect of polyaphron and CGA flow rates on percent extraction of tests done in the semi-pilot plant unit. All feed flow rates for all tests were 5.09 ml/s. The initial copper feed concentration used for all tests listed in Table 10 was  $1 \times 10^{-5}$  mol/l. The initial alizarin yellow concentration used in the tests listed in Tables 11 and 12 was  $3.23 \times 10^{-5}$  mol/l.

Tables 13, 14, and 15 contain some results obtained from the continuous horizontal trough. For all these tests, the feed concentration was kept at  $1 \times 10^{-5}$  mol/l for copper and  $3.5 \times 10^{-5}$  mol/l for alizarin yellow. The feed flow rates were kept constant at 260 ml/min for copper and 250 ml/min for alizarin yellow.

**Table 7. Results From Continuous Flow Experiments.**

	Raffinate sample level (cm)	Concentration of Cu (g/l)	% extraction
<b>Run A</b>	16	0.00531	75.7
Feed: Cu <sup>2+</sup> 0.24 g/l	20	0.00402	81.6
Solvent level: 32 cm	24	0.00318	85.4
Aphron flow: 0.151 ml/s	26	0.00155	92.9
<b>Run B</b>	16	0.174	70.4
Feed: Cu <sup>2+</sup> 0.66 g/l	20	0.0163	72.2
Aphron flow: 0.211 ml/s	24	0.00680	88.4
	26	0.00390	93.4
<b>Run C</b>	16	0.0161	30.3
Feed: Cu <sup>2+</sup> 0.026 g/l	20	0.00808	65.0
Solvent level: 35 cm	24	0.00575	75.1
Aphron flow: 0.101 ml/s	26	0.00434	81.2

**Table 8. Results for Alizarin Yellow Extractions in Continuous Cell. Effect of Probe Height.**

<b>Probe Height (cm)</b>	<b>Initial Conc. (mol/l)</b>	<b>% Removal</b>
20.5	$3.5 \times 10^{-5}$	68.6
23.0	$3.5 \times 10^{-5}$	74.5
25.5	$3.5 \times 10^{-5}$	79.3
28.0	$3.5 \times 10^{-5}$	83.1
34.0	$3.5 \times 10^{-5}$	87.4
37.0	$3.5 \times 10^{-5}$	91.2

**Table 9. Effect of Polyaphron Flow Rate on the Extraction of Copper**

Test no.	CGA flow rate (ml/sec)	Polyaphron flow rate (ml/sec)	% extraction
1	0.81	0.1	30
2	0.81	0.2	45
3	0.81	0.3	60
4	0.81	0.4	65
5	0.81	0.5	66
6	3.2	0.1	45
7	3.2	0.2	60
8	3.2	0.3	70
9	3.2	0.5	74
10	3.9	0.1	55
11	3.9	0.2	75
12	3.9	0.3	80
13	3.9	0.5	82

Note: Initial feed conc. =  $1 \times 10^{-5}$  mol/l.

**Table 10. Effect of CGA Flow Rate on Copper Extraction.**

Test no.	CGA flow rate (ml/sec)	Polyaphron flow rate (ml/sec)	% extraction
1	0.04	1.0	40
2	0.04	2.0	50
3	0.04	3.0	55
4	0.04	4.0	58
5	0.12	1.0	50
6	0.12	2.0	65
7	0.12	3.0	75
8	0.12	4.0	80
9	0.3	1.0	70
10	0.3	2.0	75
11	0.3	3.0	79
12	0.3	4.0	83

**Table 11. Effect of Polyaphron Flow Rate on Alizarin Yellow Extraction.**

Test no.	Polyaphron flow rate (ml/min)	CGA flow rate (ml/min)	% extraction
1	253	15.3	70.7
2	253	25.4	82.0
3	253	31.6	90.2
4	253	37.7	95.1

**Table 12. Effect of CGA Flow Rates on Alizarin Yellow Extraction.**

Test no.	CGA flow rate (ml/min)	Polyaphron flow rate (ml/min)	% extraction
1	15.3	106	65.2
2	15.3	171	67.5
3	15.3	253	70.7
4	15.3	443	73.4

**Table 13. Effect of Polyaphron Flow Rate on Copper Extraction in a Trough.**

Test no.	Polyaphron flow rate (ml/min)	CGA flow rate (ml/min)	% extraction
1	295	43	99.0
2	295	67	99.3
3	295	132	99.5

Note: Free flow = 260 ml/min.

**Table 14. Effect of CGA Flow Rate on Copper Extraction in a Trough.**

Test no.	CGA flow rate (ml/min)	Polyaphron flow rate (ml/min)	% extraction
1	43	191	95.0
2	43	295	98.0
3	43	460	99.2

**Table 15. Effect of Polyaphrons and CGA Flow Rates in the Extraction of Alizarin Yellow.**

Test no.	Polyaphron flow rate (ml/sec)	CGA flow rate (ml/sec)	% extraction
1	7.22	0.37	79.5
2	7.22	0.79	86.2
3	7.22	0.95	88.7
4	7.22	1.11	90.0
5	12.50	0.37	87.2
6	12.50	0.79	90.6
7	12.50	0.95	92.6
8	12.50	1.11	94.8
9	14.2	0.37	91.8
10	14.2	0.79	93.4
11	14.2	0.95	94.9
12	14.2	1.11	97.3
13	15.6	0.37	94.5
14	15.6	0.79	95.7
15	15.6	0.95	97.2
16	15.6	1.11	98.4

## Vita

**Alma (Isa) Marín Rodarte** was born December 17, 1950 in Tiquisate, Guatemala. She received an Associate of Science degree in Engineering and in Business from Tidewater Community College in Virginia Beach, Virginia in June, 1983. In June, 1985 she received a Bachelor of Science degree in Chemical Engineering from Virginia Polytechnic Institute & State University. In September of that same year she enrolled in the chemical engineering master's program at Virginia Tech. She is currently pursuing a PhD degree in Chemical Engineering at Virginia Tech.

A handwritten signature in black ink that reads "Alma I. Rodarte". The signature is written in a cursive style and is underlined with a single horizontal line.

Alma I. Rodarte