ELECTROSTATIC AGITATION IN HYDROMETALLURGICAL SOLVENT EXTRACTION

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ABSTRACT

The use of mechanical agitation in solvent extraction (SX) provides limited capability to control droplet size, droplet size distribution, and droplet motion leading to poor mass transfer, inefficient phase separation, and formation of interfacial precipitates, and thus, a major limitation of the current SX technology. The use electrostatic agitation appears to circumvent these limitations but limited fundamental understanding of the technique, particularly at conditions that are relevant to hydrometallurgical applications, hinder the development of commercial applications of the technique. An attempt to address these issues showed that the nature of the applied field, the properties of the aqueous feed, as well as the properties of the solvent influence phase dispersion, indicating that optimisation of mass transfer in an electrostatically agitated solvent extraction requires a good compromise among these variables.

INTRODUCTION

The use of solvent extraction (SX) in hydrometallurgy is well established, but improvement to the technology and development of new applications remain major research & development interest. SX is particularly attractive as it is applicable to a wide range of metal ions and other dissolved species, it allows simultaneous separation and concentration of these species from both dilute and concentrated solutions, and it can be operated over a wide range of pH values. More importantly, it is the only commercially proven technique that allows complete separation of chemically similar metals, such as nickel and cobalt, hafnium and zirconium, and the rare earths, among others. Given the increasing need to process low-grade and complex ores, often requiring more vigorous leaching conditions and thus, generating highly contaminated pregnant liquor streams (PLS), as well the increasing technological importance of the rare earths, the use of solvent extraction in hydrometallurgy is expected to continually increase and expand.

A major drawback of the current SX technology is the use of mechanical agitation. This, for example, provides limited capability in controlling droplet size and droplet-size distribution, produces high shear mixing, requires high power input, and requires several moving parts. These lead respectively to poor mass transfer and poor phase separation, interfacial precipitation and third phase formation, and high operating and maintenance costs. After more than 40 years of efforts to improve this aspect of the technology, it appears that no work short of a totally new concept could lead to a substantial improvement in the technology.

The use of an electrostatic field to promote phase dispersion and coalescence is well known, but most previous studies have been directed towards coalescence, particularly its application in dewatering of petroleum products, which is now commercially established. A number of studies, however, have shown that electrostatically assisted dispersion could be exploited in solvent extraction (Gu et al. 1990, Yang et al. 1998, Heckley et al. 2002, Collard et al. 2005, and Steffens and Ibana 2005 among others) but certain observations, such as significant differences in the apparent optimal conditions (Usami et al. 1993, Heckley 2002, Steffens 2004) for instance, could not be resolved owing to limited fundamental understanding of the phenomenon, particularly at conditions that are applicable to process metallurgy. These hinder the development of its commercial application.

Theoretically, a distinct feature of electrostatically induced dispersion is that it allows the formation of very small droplets that can be made to move with high velocities leading to high mass transfers. Coupled with electrostatically induced coalescence to promote efficient phase disengagement, this appears to be an ideal alternative to mechanical agitation in solvent extraction. However, other than the limited data that were generated from substantially different experimental conditions, such as, for example, reagents that have significantly different chemical and physical properties to those that are used in hydrometallurgical solvent extraction and reactor configurations that are simply not suitable for hydrometallurgical solvent extraction, no information has been reported that supports this theory.

This paper describes an attempt to develop fundamental understanding of electrostatic dispersion at conditions that are applicable to hydrometallurgical solvent extraction. This includes the effect of the nature of the applied field and the properties of both the aqueous and organic phases on the droplet dispersion. This is part of a work to develop a commercial application of the technique that incorporates the advantages of solvent extraction without the inherent limitations of mechanical agitation.

MATERIALS AND METHODS

Reagents

The following reagents, which were analytical grade unless specified otherwise, were used in this study: calcium chloride (Ajax), calcium sulphate (Ajax), magnesium chloride (Ajax), magnesium sulphate heptahydrate (commercial grade, Faulding), nickel sulphate hexahydrate (Ajax), sodium sulphate (BDH), sodium chloride (BDH), methyl cellulose (98%, Sigma Aldrich), Sucrose (Ajax), Octan-1-ol (Laboratory Reagent, Ajax), Blue Colouring FCF 102 (commercial grade, Queen Colouring), OCTASTAT® 3000 (commercial grade, Octel Corp.), Shellsol® 2046

(commercial grade, Shell Chemicals), Versatic 10 (industrial grade, Resolution Chemicals) and Daelim 2400 (commercial grade, Shell Chemicals). Seawater, with 5% blue food colour to aid visibility of the droplets, was used as the aqueous phase in dispersion tests unless specified otherwise. The pH of the aqueous phase was adjusted to 3 using hydrochloric acid to prevent any mass extraction. The solvent consisted of Versatic 10 (15% v/v) in Shellsol® 2046.

Dispersion Test Cell

A purpose-built all-glass dispersion test cell (Figure 1) was used for all dispersion tests. The column had internal dimensions of $50 \times 50 \times 150$ mm. The electrodes were two pieces of Teflon-coated stainless steel plates ($1 \times 45 \times 90$ mm) bent 65° at 30 mm from the top and mounted at the opposite sides of the top of the column. This configuration allowed a region of low electrostatic field strength where the aqueous phase is fed into the organic phase. A 12-mm diameter hole was drilled at the bottom of the cell and a tap was fitted to allow drainage of the aqueous phase as required. The feed delivery needle was made of stainless steel. This was connected to Norprene® tubing of the peristaltic pump (Cole-Parmer 6404-13) that was used to feed the aqueous phase. The strength and frequency of the applied field were controlled using a variable voltage-variable frequency power supply (California Instruments 801-RP).
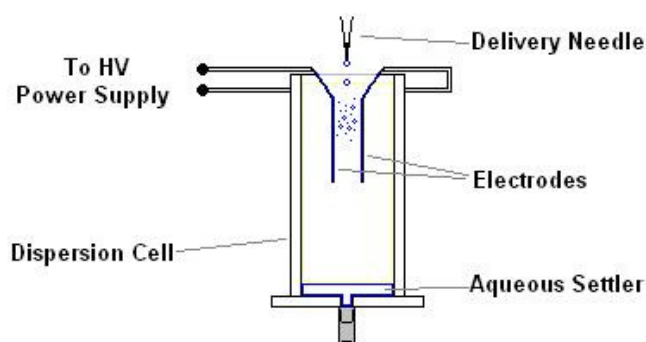

Figure 1. Diagram of the dispersion test cell

Dispersion Test Procedures & Data Analysis

The aqueous phase and the solvent were mutually pre-equilibrated to avoid any mass transfer during the dispersion tests. The cell was then filled with the pre-equilibrated solvent up to approximately 10 mm from the top of the cell. The feed delivery line (including the needle) was flushed for approximately 15 minutes to eliminate any air and wash out any soluble impurity. The dispersion test was started by turning on the variable voltage-variable frequency power supply and then the aqueous feed pump. Once the feed flow rate was apparently stable and thus the dispersion achieved, both the power supply the feed pump were momentarily turned off and photographs of the dispersion were taken using a 5-MP digital camera (Pentax Espio SP) set at 170-mm focal length and 1/250 per second exposure time. Several photographs were taken for each set of experimental conditions and the sharpest photograph with the most appropriate field focus was chosen for analysis. A typical photograph is shown in Figure 2.
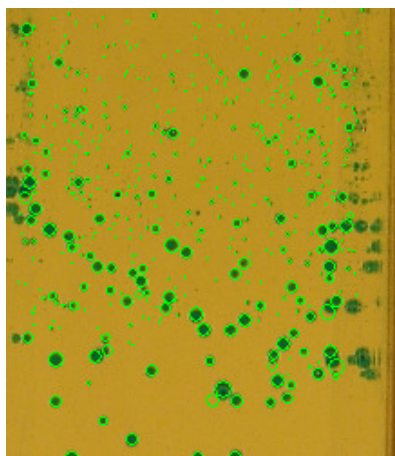

Figure 2. Sample dispersion photograph.

Data analyses involved mainly examination of the photographs of the dispersions and analyses of the droplet size and droplet-size distributions. The latter were carried out by opening the digital image with raster-to-vector conversion software where the individual images of the dispersed droplets were manually defined and the vector image was analyzed using computer-aided design (CAD) software. The resulting data were imported into an Excel® spreadsheet where the droplet size distribution was calculated.

RESULTS AND DISCUSSION

Effect of the Nature of the Applied Field on Aqueous Dispersion

Three different sets of dispersion tests were carried out under comparable conditions except that one was supplied with an alternating current (AC), one with a direct current (DC), and one with a pulsed direct current (PDC). The results showed that only AC sustained a steady dispersion of the aqueous phase fed at a rate that may be useful in hydrometallurgical solvent extraction. DC or PDC could not be made to facilitate useful dispersion because the insulation of the electrodes eventually acted as a capacitor, significantly lowering the strength of the applied electrostatic field. Using bare electrodes will not be practical as it not only poses a significant safety risk but it would also lead to high power consumption, thus negating one of the advantages of electrostatic agitation.

Droplet Size and Droplet-Size Distribution

Previous investigators have pointed out that one the most desirable advantages of electrostatic agitation over mechanical agitation is that it allows the generation of smaller droplets and narrower droplet-size distribution. Until now, however, this claim has been mainly based on theoretical considerations and no actual measurements have been reported. Nonetheless, the results of numerous dispersion tests in the present study gave credence to this claim. Figure 3 is typical of the droplet size and droplet-size distribution obtained. This particular data set was generated using seawater as the aqueous feed.
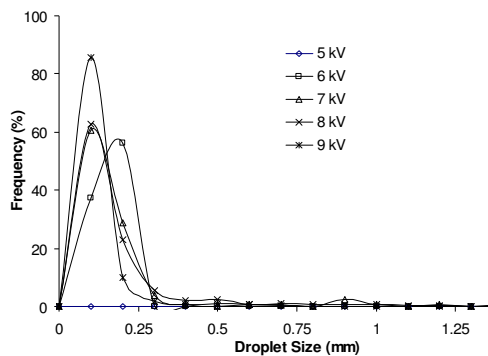

Figure 3. Sample droplet size and droplet-size distribution. The electrodes were positioned 1.5 cm apart.

The plots of similar data obtained for a variety of aqueous feeds including that for purely nitrate, chloride and sulfate media at various concentrations (0.5, 1.0 and 1.5 M each) revealed little differences among them in terms of the range of droplet size (up to approximately 0.30 mm). Clearly, the main variable that affects droplet dispersion was the strength of the applied voltage. In terms of droplet-size distribution, there was a tendency for the higher applied field to produce narrower droplet-size distribution. Another variable that affected the droplet size distribution was the frequency of the applied field. Figure 4 shows that higher frequencies yield narrower droplet-size distribution.
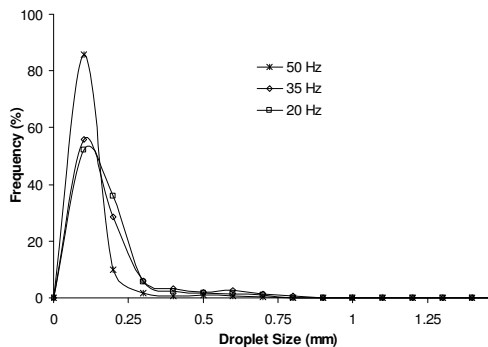

Figure 4.   Effect of the frequency of the applied field on the droplet size and droplet-size distribution. The electrodes were positioned 1.5 cm apart.

Droplet Motion

The motion of the dispersed droplet is an important contributing factor in mass transfer and thus crucial to the design of a solvent-extraction contactor. However, similar to droplet size and droplet-size distribution, no study conducted at conditions applicable to hydrometallurgical solvent extraction has attempted to explore droplet motion in electrostatically generated dispersions. Thus, the present study attempted to determine the factors that influence droplet motion under the influence of electrostatic field.

The photographs in Figure 5 were taken in the same way as those of the dispersion tests described in the dispersion test procedures except that, in these cases, both the power supply and the pump were not momentarily turned off, and longer exposure times were used. Thus, the oscillation (Figure 5a) of an aqueous droplet in the solvent under the influence of electrostatic field and the zigzagging (Figure 5b) of aqueous droplets as they fall through the solvent are evident. Visual observations indicated that, for a given droplet-size, the frequency of the applied field is the main variable that influences droplet motion, both oscillation and zigzagging. For the size of the droplets shown in the previous section, a frequency of 20 Hz provided the optimum droplet motion but for the electrostatic column that is currently being evaluated in this research group, where the droplet sizes were approximately double, a frequency of 40 Hz provided optimum droplet motion. These results indicated that optimizing mass transfer as a function of droplet motion requires a good compromise between the droplet size and the frequency of the applied field.

(a)   (b)
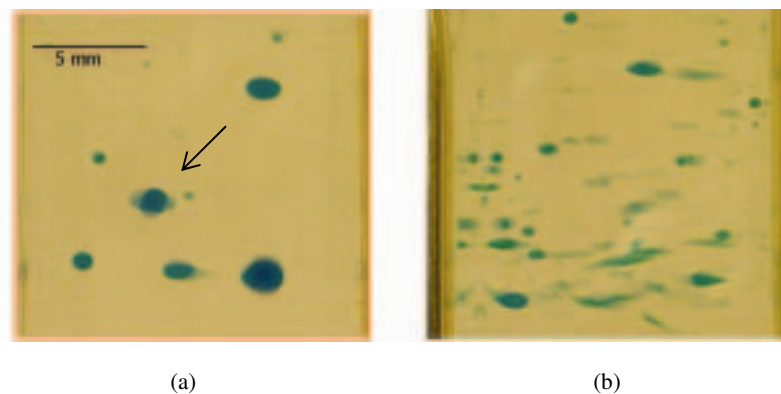
Figure 5.   (a) Oscillation of aqueous droplet under the influence of electrostatic field. (b) Zigzagging motion of aqueous droplets under the influence of electrostatic field.

Effects of the Properties of the Aqueous Phase on its Dispersion

Two properties of the aqueous phase were investigated: ionic strength and viscosity. The aqueous phase used in this part of the study was prepared using distilled water. Its ionic strength was adjusted such that the sulfate to chloride ratio was approximately 0.21. This is typical of the underground waters of the Goldfields in Western Australia, which is the main source of process water for the mining operations in the region. The viscosity of the aqueous phase was adjusted using sucrose.

Systematic variation of each of these properties, while keeping all other variables under comparable conditions, revealed that increases in the ionic strength of the aqueous phase from 0 to 4.8 M resulted in increases in the proportion of fine droplets (< 0.1 mm) and thus, decreases in the average droplet diameter but the population of the larger droplets appeared unaffected. The overall apparent decrease in the average droplet diameter was 19%. The formation of the very fine droplets may be attributed to the shift in the mechanism of dispersion toward jetting. It has been previously proposed that dispersion of droplets of conducting liquids under the influence of electrostatic field could occur in two ways: necking or jetting (Scott 1989). 'Necking' refers to rupture of an elongated droplet from about its centre while 'jetting' refers to the ejection of fine droplets from both ends of an elongated droplet under the influence of an electrostatic field. By nature, the latter leads to much finer droplet dispersion. Given earlier observations that increases in the ionic strength of the aqueous feed resulted in decreases in metal extraction (Collard et al. 2005), it appeared that the fine droplets formed under these conditions may have behaved as rigid spheres.

Increase in the viscosity of the aqueous phase from 1.5 to 3.3 cP had no observable effect on its dispersion.

Effects of the Properties of the Solvent on its Dispersion

Three sets of dispersion tests were carried out under comparable conditions except that, for each set, the viscosity, interfacial tension, and conductivity of the solvent, respectively, were systematically varied. The viscosity, interfacial tension, and conductivity of the solvent were adjusted by adding Daelim 2400, octan-1-ol, and OCTASTAT respectively. The results showed that increases in the viscosity of the solvent from 2.3 to 5.8 cP resulted in increases in the average droplet size diameter from 0.12 to 0.14 mm but a further increase in the viscosity resulted in a significant decrease in the average droplet size. These initial increases in the average droplet size diameter appeared to be due to increases in the hydrodynamic resistance of the continuous phase to droplet dispersion. The decrease in the average droplet diameter with a further increase in the viscosity of the solvent may be due to a shift in the mechanism of droplet

dispersion from necking to jetting because examination of the droplet size distribution revealed that the decrease was largely owing to an increase in the population of ultra-fine droplets while the population of the larger droplets appeared unaffected.

At first glance, the interfacial tension in the range 14.7-18.9 mN/m had little effect on the diameter of the dispersed droplets. However, on closer examination, there was an observable increase in the population of the +0.2 mm droplets. This indicated that increases in the interfacial tension favored necking over jetting as the mechanism by which the droplets dispersed.

The conductivity of the solvent below 80 pS/m had no effect on the droplet dispersion. However, higher conductivities led to substantial decreases in droplet dispersion and at 100 pS/m droplet dispersion completely ceased. Consistent with the theory, this may be attributed to the ease of transfer of charge between the electrodes under these conditions so that no electrostatic field, which a requirement for droplet dispersion, could be maintained.

CONCLUSIONS

Investigation of electrostatically generated dispersions of aqueous solutions in a solvent at experimental conditions that are applicable to hydrometallurgical solvent extraction confirmed theoretical assertions that the technique offers advantages over mechanical agitation in solvent extraction. Specifically, the study found that the technique allows the formation of small and narrowly distributed aqueous droplet sizes that are oscillating and zigzagging as they fall through the cell of continuous organic phase. Among AC, DC and PDC field, only AC provided a sustained dispersion when using insulated electrodes. This has practical advantages as it minimizes power consumption and safety risk. The droplet size of the dispersed phase was largely influenced by the strength of the applied field as well as the physical properties of the aqueous and organic phase while the motion of the dispersed droplets was largely influenced by the frequency of the applied field. These suggest that optimization of mass transfer in the application of the technique in hydrometallurgical solvent extraction depends on a good compromise among these variables.

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