AIR-ASSISTED SOLVENT EXTRACTION

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To my parents

(Beyhan ve İsmet Tarkan'a)

ABSTRACT

Air-Assisted Solvent Extraction (AASX) is a novel concept that uses a solvent-coated bubble to contact the organic and aqueous phases. The advantages over conventional solvent extraction (SX) are high solvent to aqueous contact area with reduced solvent volume and ease of phase separation due to the buoyancy imparted by the air core. This opens the way to treat dilute solutions (<1 g/L), such as effluents.

The novel contribution in this thesis is the production of solvent-coated bubbles by exploiting foaming properties of kerosene-based solvents.

The basic set-up is a chamber to generate foam which is injected through a capillary (orifice diameter 2.5 mm) to produce solvent-coated bubbles (ca. 4.4 mm) which release into the aqueous phase. This generates a solvent specific surface area of ca. 3000 cm^{-1}, equivalent to solvent droplets of ca. 20 μm. Demonstrating the process on dilute Cu solutions (down to 25 mg/L), high aqueous / organic ratios (ca. 75:1) and extractions are achieved. The solvent readily disengages to accumulate at the surface of the aqueous solution.

The LIX family of extractants imparts some foaming to kerosene based solvents but D2EHPA does not. An extensive experimental program determined that 1.5 ppm silicone oil provided the necessary foaming action without affecting extraction or stripping efficiency, greatly expanding the range of solvents that can be used in AASX.

To complement the foam study, films on bubbles blown in solvent were examined by interferometry (film thickness) and infra-red spectroscopy (film composition). A "bound" solvent layer was identified with an initial thickness of ca. 2 – 4 μm, comparable to that determined indirectly (by counting bubbles in an AASX trial and measuring solvent consumption). The film composition appeared to be independent of film thickness as it decreased with time.

As a start to scaling up, the single bubble generation system was adapted by installing up to 8 horizontal capillaries. The bubbles generated were ca. 3.4 mm. Trials showed the multi-bubble set up was a simple replication of the individual bubble case. Preliminary analysis of kinetic data shows a fit to a first-order model.

RÉSUMÉ

L'extraction par solvant assistée par air (AASX) est un nouveau concept utilisant des bulles enduites de solvant afin de contacter les phases organique et aqueuse. Les avantages sur l'extraction par solvant conventionnelle (SX) sont la grande zone de contact solvant-phase aqueuse avec un volume réduit de solvant et une facilité de séparation des phases due à la flottabilité causée par le noyau d'air. Ceci permet de traiter des solutions diluées (<1 g/L), tels des effluents.

La nouvelle contribution de cette thèse est la production de bulles enduites de solvant en exploitant les propriétés moussantes des solvants à base de kérosène.

L'installation de base se compose d'un caisson où est généré la mousse injectée à travers un capillaire (diamètre d'orifice de 2.5 mm) pour produire des bulles enduites de solvant (ca. 4.4 mm) qui sont relâchées dans la phase aqueuse. Ceci génère une aire de surface spécifique du solvant de ca. 3000 cm^{-1} équivalant à des gouttes de solvant de ca. 20 µm. En démontrant le procédé pour des solutions diluées de Cu (jusqu'à 25 mg/L), des ratios phase aqueuse/organique élevés (ca. 75:1) et des extractions sont obtenus. Le solvant se désengage facilement pour s'accumuler à la surface de la solution aqueuse.

La famille d'extractants LIX donne du moussant aux solvants à base de kérosène, ce qui n'est pas le cas du D2EHPA. Un programme expérimental extensif a déterminé que 1.5 ppm d'huile de silicone produisait l'action moussante nécessaire, élargissant grandement la plage de solvants pouvant être utilisés en AASX.

Afin de compléter l'étude de mousse, les films à la surface de bulles soufflées dans le solvant ont été examinés par interférométrie (épaisseur du film) et spectroscopie infra-rouge (composition du film). Une couche de solvant "lié" a été identifiée avec une épaisseur initialle de ca. 2-4 µm, comparable à celle déterminée indirectement (en comptant les bulles lors d'un essai de AASX et en mesurant la consommation de

solvant). La composition du film semble indépendante de l'épaisseur du film qui elle diminue avec le temps.

Afin d'initier une étude à plus grande échelle, le système de génération de bulles simples a été adapté en installant jusqu'à 8 capillaires horizontaux. Les bulles ainsi générées étaient de ca. 3.4 mm. Les essais ont démontré que l'installation multi-bulles était une réplique simple du cas des bulles individuelles. L'analyse préliminaire des données cinétiques démontre un ajustement à un modèle de premier ordre.

CONTRIBUTION OF AUTHORS

This thesis was prepared in accordance with article C of the guidelines Concerning Thesis Preparation of McGill University. This article reads as follows:

1. Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly-duplicated text (not the reprints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprints of published papers can be included in the appendices at the end of the thesis.)

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4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers.

The following are the co-authored manuscripts used in preparation of this thesis. Manuscript 1 comprises Chapter 3, and manuscript 4, 5 and 6 make Chapters 5, 6 and 7, respectively. The manuscripts have been published, accepted for publication or submitted as indicated.

1. **Tarkan H. M., Finch, J. A.,** 2005. Air-assisted solvent extraction: towards a novel extraction process. *Minerals Engineering*, 18, 83-88.

2. **Tarkan H. M., Finch, J. A.,** 2005. Foaming properties of solvents for use in air-assisted solvent extraction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 264, 126-132.

3. **Tarkan, H. M., Gelinas, S., Finch, J. A.,** 2006. Measurement of thickness and composition of a solvent film on a bubble. *Journal of Colloid and Interface Science*, 297, 732-737.

4. **Tarkan H. M., Finch, J. A.,** "Multi-bubble production in the air-assisted solvent extraction process" has been submitted for presentation at XXIII. International Mineral Processing Congress, Istanbul, Turkey, 2006.

All the manuscripts are co-authored by Prof. James A. Finch in his capacity as research supervisor. All the experiments were conducted by the candidate. Manuscript 3 includes Dr. Stephanie Gelinas (Research Associate, Department of Mining, Metals and Materials Engineering, McGill University) recognizing her contribution to measuring the film properties of coated-bubbles using UV-vis and FT-IR. Beyond the noted contributions of

the co-authors all of the work presented in this dissertation was performed by the candidate.

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I would like to express my sincere appreciation to my parents for their years of patience, affection and encouragement.

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CHAPTER 1

Introduction

Solvent extraction can be defined as separation of one or more solutes from a mixture by mass transfer between immiscible phases in which at least one phase is an organic liquid (Ritcey and Ashbrook, 1978). During the first half of the 20th century, solvent extraction found application in organic chemistry to separate or purify substances (Cox and Rydberg, 2004). In these studies, it was found that some organics, e.g. weak acids, could complex metal ions in the aqueous phase, enabling them to transfer to an organic phase.

Uranium extraction in the Manhattan Project during World War II could be cited as the first large scale solvent extraction plant in extractive metallurgy. Later, solvent extraction processes started to be used as a separation and purification process for other metals, notably copper, with the Ranchers Bluebird and Bagdad solvent extraction (SX) plant opening in the late '60s (Sole et al., 2005). Today, 30% of the world's copper is produced using solvent extraction.

Now an established process, solvent extraction, nonetheless, is only applicable to concentrated solutions (> 500 mg/L) (Kentish and Stevens, 2001). Solvent losses, capital cost, phase disengagement difficulties and the large solvent inventory needed are among

the disadvantages of SX when applied to dilute solutions. Also, occasional crud formation at the aqueous/organic interface can be an additional limitation (Kentish and Stevens 2001; Ritcey and Ashbrook, 1978). The interest was to extend SX to dilute streams, such as acid mine drainage which led to the subject at this thesis: Air-Assisted Solvent Extraction.

The Air-Assisted Solvent Extraction (AASX) concept was introduced by Chen et al. (2003). The idea was to take advantage of the thermodynamically favourable spreading of solvent at an air/water interface (i.e., bubble surface) to provide high contact area with reduced organic volume. With the dispersed organic phase having an air core rapid phase disengagement would also be favoured. These properties are favourable to treating dilute solutions

Organic coated-bubbles have been used in other applications in extractive metallurgy, notably to promote collection of hydrophobic particles (such as coal, ink and bitumen). Coated bubbles were created by various methods including vapour deposition and use of an atomizer (Wallwork et al., 2003; Gomez et al., 2001; Peng and Li, 1991). In this thesis a novel coating method based on solvent foaming properties is used.

Foam is encountered in many industrial processes, from cosmetics to oil and mineral recovery. Surface active reagents (surfactants) are required to induce foaming (Bikerman, 1953). A limited number of studies on foaming properties of nonaqueous systems have been reported (Schmidt, 1996; Schramm, 1994; Ross, 1984; Owen et al., 1967). Polymethylsiloxanes were found to be good foam stabilizers. A method to assess foam properties is described based on the Ross and Suzin method (Nishioka et al. 1996).

Since the nature of the coating is a fundamental consideration, thin film measurements are included in the thesis. There are various techniques to determine film thickness such as stylus profilometry, interferometry, ellipsometry, spectrophotometry and X-ray microanalysis. Film thickness measurement with transmitted light interferometry is employed here as introduced to study soap films (Huibers and Shah, 1997).

The subject of this thesis is Air-Assisted Solvent Extraction using kerosene-based solvents. The thesis extends from basic properties of foaming and solvent films to extraction studies (on Cu and Zn) using single and multi-bubble generation units.

1.1. Objectives of Thesis

The thesis aims to introduce fundamental aspects of the Air-Assisted Solvent Extraction (AASX) process, and demonstrate its applicability to metal recovery from dilute streams.

The specific objectives are:

i- To show the applicability of the AASX process to dilute metal solutions using Cu and Zn as examples.

ii- To study foaming properties of kerosene-based solvents.

iii- To apply thin layer thickness measurement techniques to the solvent coating.

iv- To explore some methods to produce swarms of coated bubbles for industrial application of the process.

1.2. Structure of Thesis

The thesis consists of seven chapters. Four of them are in the style of a manuscript so inevitably some repetition occurs.

Chapter 1: The introduction, objectives and the structure of the thesis are given.

Chapter 2: This is a brief literature review providing background information on: acid mine drainage as an example dilute solution, solvent extraction principles, and foaming properties of organic liquids.

Chapter 3: The Air-Assisted Solvent Extraction concept is introduced. This chapter was published as,

"Tarkan H.M., Finch, J. A., 2005. Air-assisted solvent extraction: towards a novel extraction process. Minerals Engineering, 18, 83-88"

Chapter 4: Investigations on foaming properties of kerosene-based solvents are covered. This chapter was published as,

"Tarkan H. M., Finch, J. A., 2005. Foaming properties of solvents for use in air-assisted solvent extraction. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 264, 126-132"

Chapter 5: This discusses the measurement of solvent layer thickness on a bubble. This chapter was published as,

"Tarkan, H. M., Gelinas, S., Finch, J. A., 2006. Measurement of thickness and composition of a solvent film on a bubble. *Journal of Colloid and Interface Science*, 297, 732-737"

Chapter 6: A multi-bubble unit for AASX process is introduced. This chapter entitled "Multi-bubble production in the air-assisted solvent extraction process" by H. M. Tarkan and J. A. Finch, has been submitted for presentation at XXIII International Mineral Processing Congress, Istanbul, Turkey, September 2006.

Chapter 7: Overall conclusions and suggested future work are given.

Appendix A: This is a summary paper on AASX designed to introduce the concept to the "environmental community". It was published in a conference proceedings as,

"Tarkan H.M., Finch, J. A., 2005. Air-assisted solvent extraction: potential application to effluent streams. In: Securing the future, International Conference on Mining and the Environment Metals and Energy Recovery, June 27-July 1, 2005, Skellefteå, Sweden, pp. 937-944"

Appendix B: Structure of some reagents.

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CHAPTER 2

Background Material

In this chapter, some background material is given on a variety of topics pertinent to the thesis and judged of importance to follow the later chapters. The topics introduced are: acid mine drainage and its treatment; general aspects of solvent extraction such as equipment selection and application in waste water treatment; an introduction to the Air-Assisted Solvent Extraction (AASX) concept, and finally a brief review of surface and foam properties relevant to the AASX process.

2.1. Acid Mine Drainage

2.1.1. Origin

Chemical reaction between water, oxygen and sulphur bearing metallic minerals, particularly iron sulphides, produces acid mine drainage (AMD). This oxidation process could occur chemically or biologically. In the latter, Thiobacillus ferrooxidans is the most important bacterium, obtaining its energy for growth from the oxidation of reduced sulphur compounds and ferrous iron (Evangelou, 1995). The effect of bacteria could be direct or indirect. The reactions for both mechanisms are given below (Younger et. al., 2002).

- Direct Mechanism

$$4\,FeS_2 + 15\,O_2 + 2\,H_2O \xrightarrow{\textit{bacteria}} 2\,Fe_2(SO_4)_3 + 2\,H_2SO_4 \qquad (2.1)$$

- Indirect Mechanism

$$4\,FeSO_4 + 15\,O_2 + 2\,H_2SO_4 \xrightarrow{\textit{bacteria}} 2\,Fe_2(SO_4)_3 + 2\,H_2O \qquad (2.2)$$

$$2\,S° + 3\,O_2 + 2\,H_2O \xrightarrow{\textit{bacteria}} 2\,H_2SO_4 \qquad (2.3)$$
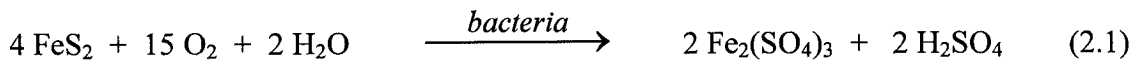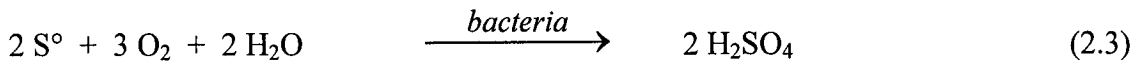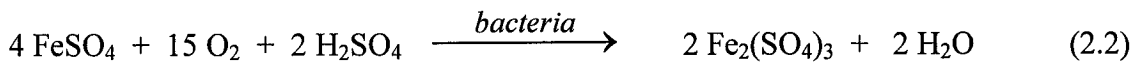
The ferric ions contribute further oxidation, making iron sulphides (especially pyrite and pyrrhotite) particularly important in acid generation. The other sulphide minerals also produce acid drainage, but are less effective, and may better be considered as leached by the acid.

Composition of acid mine drainage depends on the source. Table 2.1 shows some examples.

2.1.2. Treatment Methods

Treatment of AMD can be separated into active and passive. Passive treatment involves wet lands and other naturally occurring systems. Some active treatment methods are given in Table 2.2.

The most commonly applied treatment is neutralization with alkali and precipitation of metal hydroxides. The pH is raised using limestone, lime (calcium hydroxide) or occasionally sodium hydroxide and typically flocculants are added to aid settling. Unrestricted use, however, is limited due to the volume of sludge produced,

which requires disposal and maintenance to avoid pH excursions and resolubilization.

Various engineered options are used (Ritcey, 1989).

Table 2.1. Composition of AMD for selected ore types (mg/L) (Ritcey, 1989)

	Uranium	Gold	Iron	Copper	Cu-Pb-Zn	Cu-Ni	Cu-Mo
pH	2.3	7.6	6.4	3.8	2.0-7.9	7.5	7.7
Aluminum	10	0.6	--	--	--	--	--
Calcium	52	240	--	--	120	--	--
Cobalt	416	--	--	--	--	0.01	0.004
Copper	3.6	0.24	0.1	83	76	0.15	0.02
Iron	30-3,200	3.6	1.3	0.08-48	8.5-3,200	1.2	0.21
Lead	0.7	--	0.1	0.006	0.02-90		0.1
Uranium	67	--	--				
Zinc	11		0.06	0.01-91	0.04-1.600	0.01	0.13

All treatment methods have disadvantages. For example, high-energy requirements (membrane and reverse osmosis), capital cost (electrochemical extraction) and high cost of sorbing agents (sorption and ion-exchange). Many methods of biological / biochemical extraction have been tested at the laboratory scale. Solvent extraction has been suggested (Ritcey, 1989).

Table 2.2. General characteristics of some active treatment processes (Brown et al., 2002)

Treatment Method	Selectivity	Purity of Product	Degree of Neutralization	Nature of Sludge	Complexity of Process
pH Modification	Mostly Non-selective	Not pure	Good	Variable stability and density	Simple to complex
Ion Exchange	Highly selective	Very pure	None	Concentr. solution	Complex
Biology-based treatment	Partially selective	Pure	Reasonable	Sulphide sludge	Simple to complex
Other sorption methods	Partially selective	Not pure	Some	Labile sludge	Simple
Electro-chemical treatment	Highly selective	Pure	None	Concentr. solution	Complex

2.2. Solvent Extraction

2.2.1. General Aspects

Solvent extraction (or liquid-liquid extraction) is one of the most widely used processes for the recovery of metal ions such as copper, uranium and zinc. It is a technique for concentrating metals in aqueous solution by transfer via an organic phase. A principal advantage is selectivity, which results in high purity of target metal.

Solvent extraction is an equilibrium process, which can be described by an equation such as,

$$M + E \rightleftharpoons ME \tag{2.4}$$

where M and E stand for metal and organic, respectively.

A general process flow-sheet is shown in Figure 2.1. When a metal-containing aqueous phase is contacted with an organic phase the metal will distribute between the two phases. Normally, a metal ion exists in aqueous solution as a hydrated ion, with little or no tendency to transfer to an organic phase. In order to achieve the transfer the charge on the metal ion requires neutralization and some or all its water of hydration has to be replaced by another species.

The nature of the metal species to be extracted is, therefore, of fundamental importance and it is logical to classify extraction systems on this basis (Ritcey and Ashbrook, 1978), namely:

(i)   System involving compound formation (chemical reaction between metal ion and component (extractant) of organic phase)

(ii)   System involving ion association (physical attractive force between oppositely charged metal ion and extractant species)

(iii)   System involving solvation of the metal ion (based on the power of oxygen containing extractants to solvate inorganic molecules or complexes into organic phase)

Solvent (organic part) consists of extractant, diluent and modifier. For systems involving compound formation, extractants can be divided into two major groups, acidic extractants and chelating extractants. Among the acidic, organic derivates of phosphoric acids (e.g. D2EHPA) and carboxylic acids are the most important. The LIX, KELEX and ACORGA type extractants are classified as chelating extractants. Extractants involving ion association are limited to amines and quaternary ammonium compounds. Extractants involving solvation are divided into two groups: organic reagents containing oxygen

bonded to carbon (ethers, ketones), and oxygen or sulphur bonded to phosphorus (TBP, TOPO; CYANEX 471). The structures of some extractants are given in Appendix B.
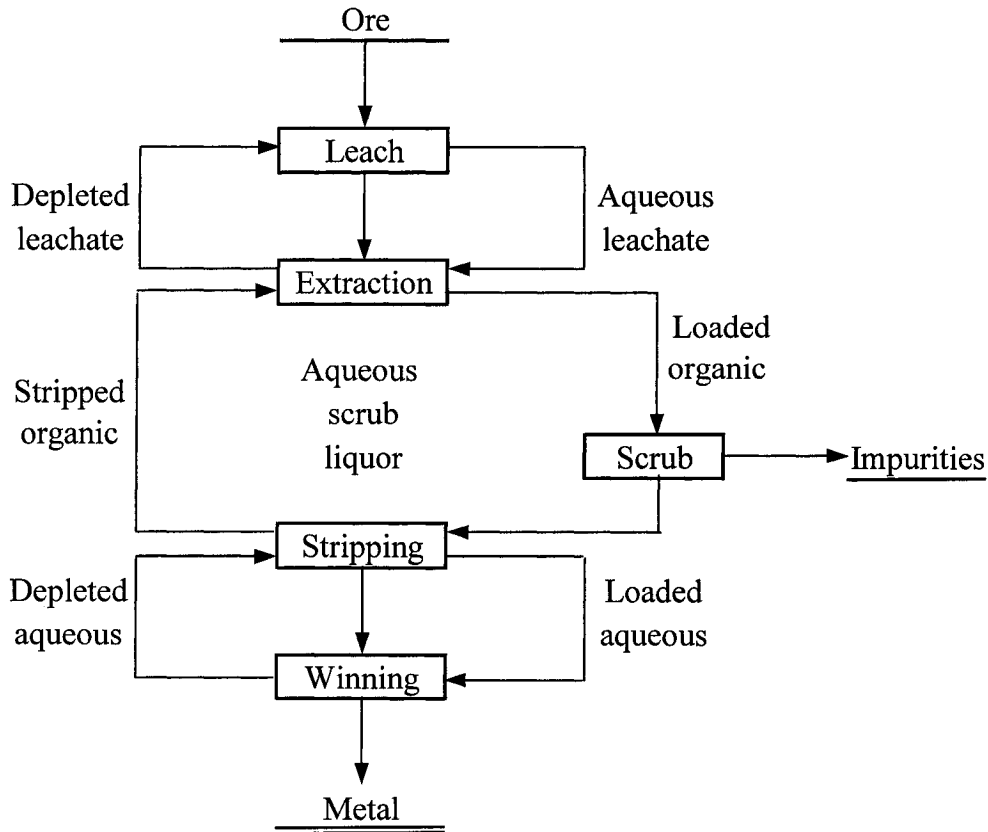
Figure 2.1. General flow sheet of Solvent Extraction/Electrowinning (Godfrey and Slater, 1994)

Diluents are organic liquids in which the extractant and modifier are dissolved to form solvent. They are used to decrease the viscosity of extractant, provide a suitable concentration of extractant and improve dispersion (i.e., control coalescence) properties of the solvent. The selection criteria for diluents are as follows (Ritcey and Ashbrook, 1978):

- Low toxicity

- Environmental applicability

- Low price

- Good rheological properties

- High flash point

- Low vapour pressure

- Low water solubility

Modifiers have several roles: assisting phase disengagement; overcoming formation of a third phase that can occur in some cases; influencing mass transfer; and, reducing entrainment (Ritcey and Ashbrook, 1978).

2.2.2. Equipment

Equipment used for solvent extraction divide into two main groups, column and mixer-settler, the latter being more common. Mixer-settlers for metallurgical applications are classified as horizontal (Figure 2.2) and vertical. They have the disadvantage of requiring agitation energy for solvent dispersion and having a large footprint. In addition, maintenance is difficult when corrosive and particle-laden liquids are processed (Thornton, 1992; Doungdeethaveeratana and Sohn, 1998).
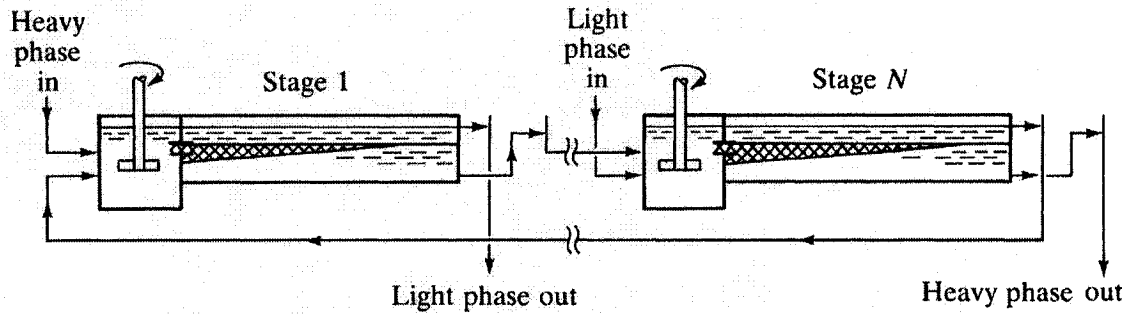
Figure 2.2. Horizontal mixer-settler (Thornton, 1992)

Columns (pulsed and spray (Figure 2.3)) have the simplest construction with few moving parts and have been used in treatment of liquid effluents (Doungdeethaveeratana and Sohn, 1998). The two phases flow countercurrent in a vertical vessel. It has the disadvantage of high backmixing that decreases the extraction efficiency (Godfrey and Slater, 1994; Doungdeethaveeratana and Sohn, 1998).

2.2.3. Solvent Extraction in Waste Water Treatment

The SX process is principally used for large-scale operations where the concentration of contaminants is high. Solute concentration ranges for some separation technologies are given in Figure 2.4. The challenge is to extend solvent extraction to the concentration ranges encountered in effluents such as AMD.
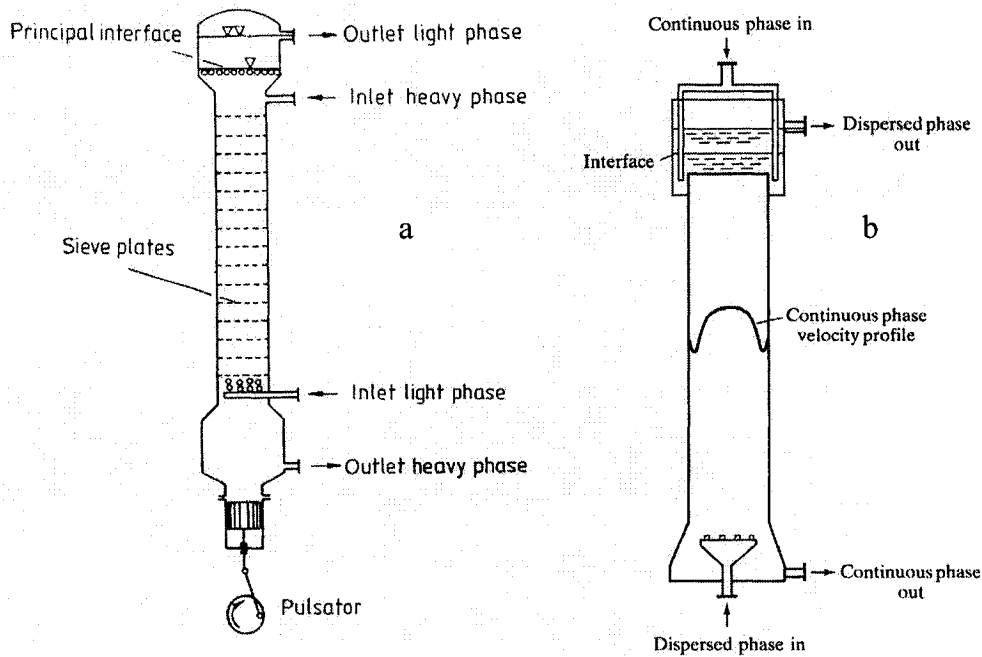
Figure 2.3. (a) Pulsed column (Reprinted with permission from Godfrey and Slater (1994), John Wiley & Sons Limited) **(b)** Spray column (Thornton, 1992)

A factor favouring use of solvent extraction in combination with electrowinning (SX/EW) is the ability to recover metal in saleable form, helping to offset the cost of treatment. On the negative side, the capital outlay for SX equipment can be high and large volumes of organic are required. Loss of reagents, which contaminate effluents, is another drawback of solvent extraction in wastewater treatment (Reed, 1998).

As examples of the use of SX in effluent treatment, Reinhardt (1975) described a process to recover zinc from drainage water by DEHPA and Ortega and Gutierrez (1980) studied the recovery of mercury by solvent extraction from reactor fuels.
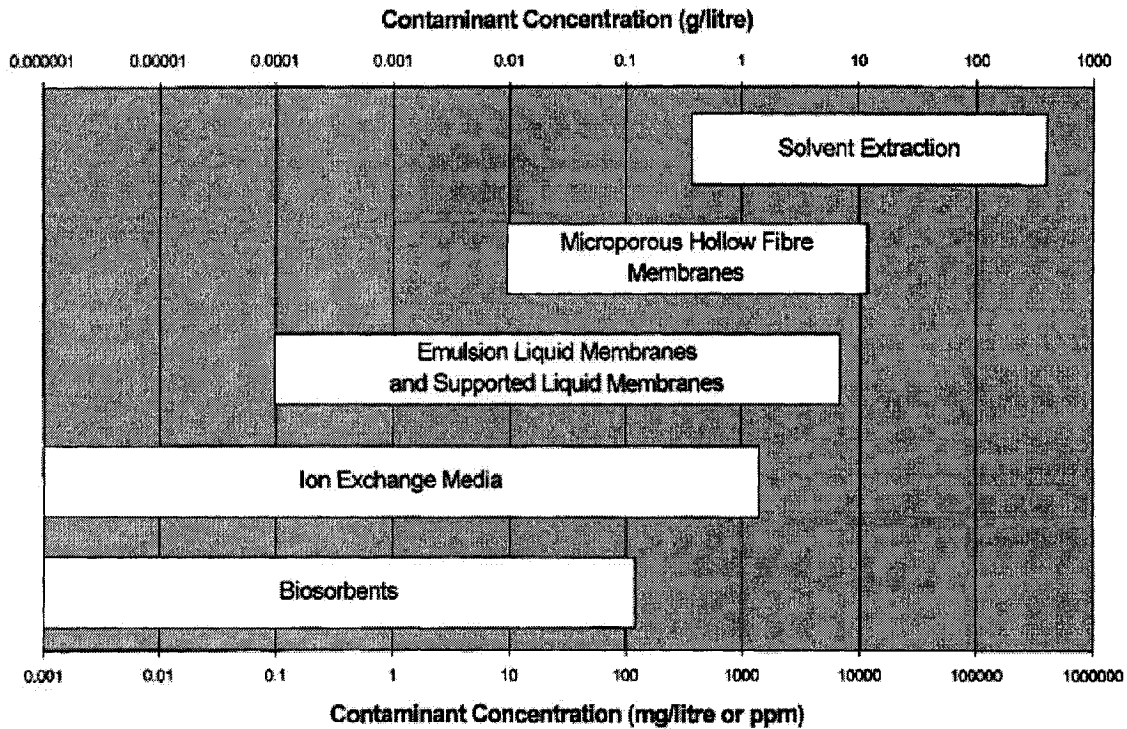
Figure 2.4. Solute concentration ranges for separation techniques (Reprinted with permission from Kentish and Stevens (2001), Elsevier)

In order to use solvent extraction in waste treatment, Ritcey and Ashbrook (1978) suggested the following:

i)   Use of biodegradable extractants

ii)   Minimize entrainment and physical losses

iii)   Development of improved solvent removal and recovery methods

Air-Assisted Solvent Extraction addresses the last two items.

2.3. Air-Assisted Solvent Extraction

The basis of this concept is the use of a solvent-coated bubble. A high specific surface area of organic can be created using little solvent and the buoyancy provided by the air core assists phase separation. When compared to classical solvent extraction processes, the advantages of Air-Assisted Solvent Extraction (AASX) are the small amount of solvent required with consequent lower effluent contamination, and lower capital and operating costs as the mixing and separation stages are combined in a single unit. The idea germinated from the various "oil assisted flotation" processes (Laskowski, 1992).

The use of an organic coated bubble in flotation appears to have been first broached by Taggart (1927). He suggested that an oil film would spread on bubbles and the oil-coated bubbles should act as efficient collectors for hydrophobic particles. This idea was pursued for ultrafine coal flotation by Misra and Anazia (1987). They found that the attachment time for an oil-free bubble on coal of 88 ms was reduced to 5 ms for an oil-encapsulated bubble. Wang et al. (1988) and Peng and Li (1991) studied the approach for selective coal flotation. They found that collector consumption could be reduced without loss of coal recovery. Bitumen particle recovery offers a similar opportunity, as recently demonstrated by Su et al. (2005) and Wallwork et al. (2003). These studies showed, respectively, that oil-coated bubbles reduced induction time and increased recovery.

In de-inking waste paper, Maiolo and Pelton (1998) found enhanced carbon black (i.e., ink particles) removal with bubbles coated with silicone oil. Gomez et al. (2001) confirmed this in continuous testing at a de-inking plant.

In sulphide mineral flotation, Liu et al. (2002) adapted the concept to try to reduce undesired recovery of gangue particles and reduce collector consumption. In this version, a flotation collector was dissolved in kerosene which was mixed with air and passed through a porous frit to produce a "reactive oily bubble".

The oily bubble concept bears some similarity to its proposed use in solvent extraction, the coating now being to extract metal ions not minerals. In this context, the process could be classed as ion flotation (Doyle, 2003). Also, it has some similarities with the solvent sublation technique (proposed by Sebba (1962) as an option for ion flotation (1962)), which is a non-foaming adsorptive bubble separation method for removing organics (i.e., hydrophobic materials) from wastewater by transferring to an oil layer on the water surface (Karger, 1972). The Air-Assisted Solvent Extraction concept was first described by Chen et al. (2003).

2.4. Some Surface Properties Relevant to AASX

Formation of a solvent-coated bubble is an exercise in controlling interfacial properties. Some background therefore is required into the following areas: surface tension, spreading and foaming.

2.4.1. Surface Tension

The force acting on the surface of a liquid tending to minimize its area is the surface tension. The molecules at the surface do not have a uniform environment in all directions; they have a net attraction to molecules in the bulk of the liquid, thus tending to minimize the surface area which gives rise to the force (Figure 2.5). Surface tension of a

liquid can be measured by a variety of techniques (Davies and Rideal, 1963) such as du

Nuoy ring, drop-weight, Wilhelmy plate, sessile drop and capillary rise.
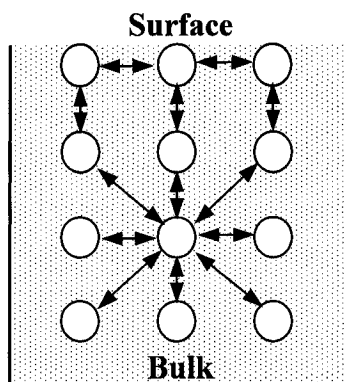
Surface

Bulk

Figure 2.5. Illustration of origin of surface tension: Environment of atoms at surface is different from those in the bulk.

The Wilhelmy plate method is one of the most widely used. When a thin plate is attached to the arm of a balance, the additional pull on the plate when it becomes partly immersed is equal to the product of the perimeter and the surface tension. Given suitable surface characteristics, so that the plate is completely wetted by one liquid, the method may also be used to measure interfacial tension (Adamson, 1990; Davies and Rideal, 1963).

2.4.2. Spreading Coefficient

If a column of a pure liquid is separated to form two surfaces, the energy of cohesion of this liquid, W_C, is converted to surface energy,

$$W_C = \gamma_{lg} dA \qquad (2.5)$$

where, γ_{lg} is surface tension of liquid.

When two different liquids (a and b), insoluble in each other, are separated along an interface, the work of adhesion (W_A) to be overcome in this separation is given by (Dupre 1867):

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \qquad (2.6)$$

where, γ_a and γ_b are surface tension of each liquid and γ_{ab} is interfacial tension between the two liquids.

Harkins (1952) extended this approach to the spreading of one insoluble liquid over another liquid (or solid), introducing a spreading coefficient, defined as:

$$S = W_A - W_C \qquad (2.7)$$

which has to be positive for spontaneous spreading to occur. In the case of two liquids, we can write;

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) \qquad (2.8)$$

If Eq 2.8 is derived for the organic/air/water system, the stability of a thin organic film coating on a bubble is controlled thermodynamically by the spreading coefficient, S_c (Adamson, 1990):

$$S_c = \gamma_{a/w} - (\gamma_{a/o} + \gamma_{o/w})$$ (2.9)

Figure 2.6 shows a practical example of oil spreading on a gas bubble in residual oil extraction.
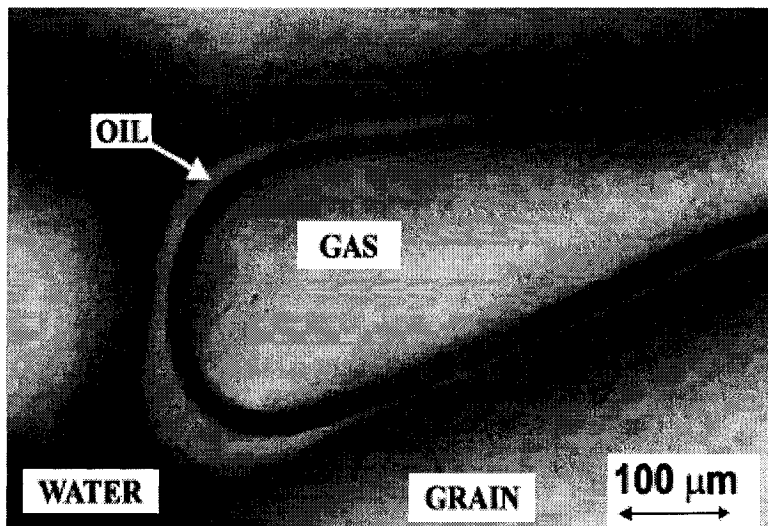
Figure 2.6. Gas (air)-Oil-Water interface showing oil coating a gas bubble (Reprinted with permission from Grattoni et al. (2003), Elsevier).

2.5. Foaming Properties

A foam is a network of gas bubbles separated by thin liquid films (Figure 2.7). Foams occur in a variety of industrial process from personal care products to oil and mineral recovery.

Pure liquids, regardless of surface tension, $\gamma_{a/w}$, tend not to foam. The formation of foam generally requires addition of a foaming agent, i.e., a surface active agent (surfactant). These surfactants adsorb at the air – solvent interface (i.e., bubble surface)

due to their combined lyophilic / lyophobic structure (Figures 2.8)[1]. One consequence is a

reduction in surface tension. However, it is not the decrease in surface tension per se that

matters but the fact that surface tension differences (gradients) can occur, which give rise

to a force (Gibbs-Marangoni effect) opposing film drainage (Schmidt 1996). A second

consequence is that the concentration of surfactant at the surface can also change film

rheological properties, increasing viscosity which impedes drainage (Schramm and

Wassmuth, 1994).
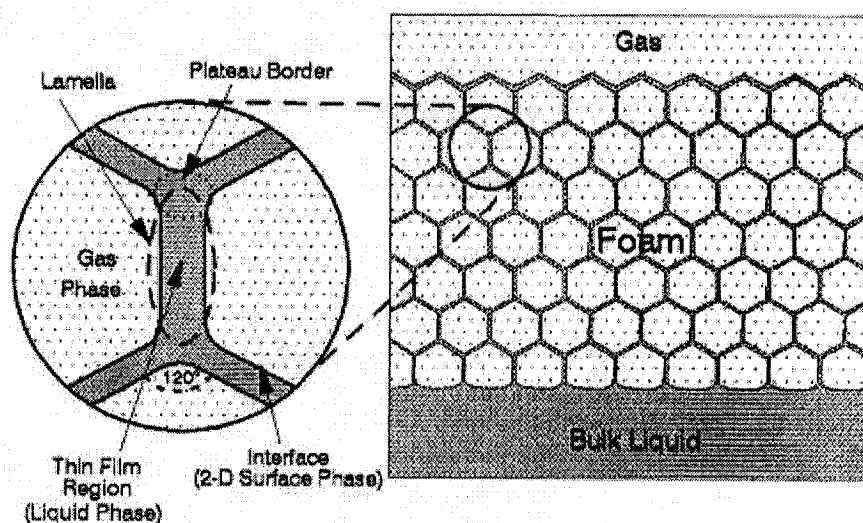
Figure 2.7. Schematic representative of a foam system (Reprinted with permission from

Schramm and Wassmuth (1994), American Chemical Society).

Most literature on foams focuses on aqueous systems (Edwards and Wasan, 1996;

Khristov et al., 1981; Vrij, 1964; Bikerman, 1953). Although there are some differences

between aqueous and nonaqueous systems (such as the surface tension of water being

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[1] In the case of water as solvent the equivalent terms are hydrophilic / hydrophobic.

much higher than for nonaqueous liquids), the same basic foam theories can be applied to both (Schmidt, 1996).

Head group   Hydrocarbon
(lyophilic)   (lyophobic)

Air
Bubble

(a)   (b)
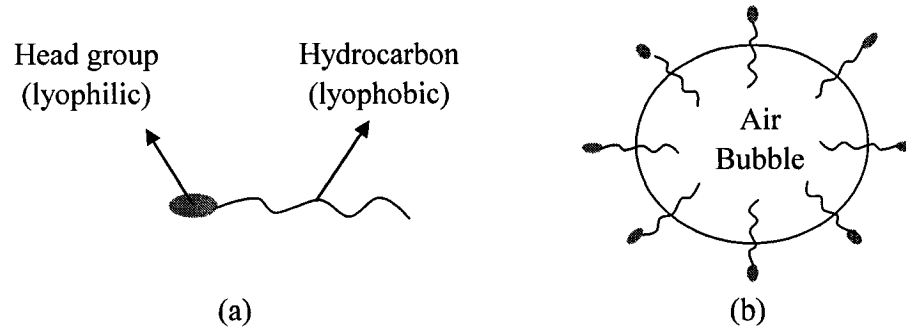
Figure 2.8. General structure of surfactant (a) and orientation at a bubble surface (b)

2.5.1. Foam Stability Measurement

Foam measurements can be divided into two groups: dynamic and static. The former represent the equilibrium point of formation and breaking of foams. In static foams, formation is zero; once foam is produced, the air is shut off and it is allowed to collapse. The latter is usually reserved for highly stable foams (Nishioka, 1996). Just dynamic measurements are considered.

Bikerman (1953), presuming that steady-state foam volume is independent of container shape, suggested a column to measure the foaminess (Σ) defined as,

$$\Sigma = \frac{V}{U}$$ (2.10)

where V is the steady-state volume of foam (cm^3) and U is the air-flow rate (cm^3/min). Later Watkins (1973) found that the shape of container could affect the volume of foam

at steady-state. He defined the loss of air from the top of the foam as kA (cm^3/min), where

A is the area of cylinder and found that the foam volume, V, changes with time, t, according to,

$$V = Udt - kAdt \qquad (2.11)$$

or

$$\frac{dV}{dt} = U - kA \qquad (2.12)$$

At equilibrium, from the definition of dynamic foam stability, there is no change in foam volume ($dV/dt = 0$), therefore;

$$U = kA \qquad (2.13)$$

But, Eq. 2.12 introduces two other possibilities,

- $U > kA$; $V \rightarrow$ infinity

- $U < kA$; $V \rightarrow$ zero

In order to ensure that Eq 2.13 was met, Watkins suggested using a conical shaped apparatus (where the volume and the area of foam change together) to measure the foaminess. The angle of cone was selected as $60°$ based on reproducibility of measurement (Figure 2.9).

As calculated from Figure 2.9, for $60°$ cone,

$$A_f = 1.047(h_f + 1.732r)^2 \qquad (2.14)$$

where h_f is the steady-state height of foam and r is the radius at the base of the truncated cone. At equilibrium,

$$U = kA_f = 1.047k(h_f + 1.732r)^2 \qquad (2.15)$$

The parameter, k, however, is not a characteristic property to evaluate foam properties, such as the Σ, proposed by Bikerman.

Ross and Suzin (1985) determined a way to analyze dynamic foams using the cone-shaped container. The Σ can be written for a conical system as,

$$V = \int_0^\Sigma U dt = U\Sigma \qquad (2.16)$$

Considering the geometry of the apparatus, V can be re-written as,

$$V = \left(\frac{1}{(3\pi)^{1/2}} \right) A_f^{3/2} - \left(\frac{h_0 A_0}{3} \right) \qquad (2.17)$$
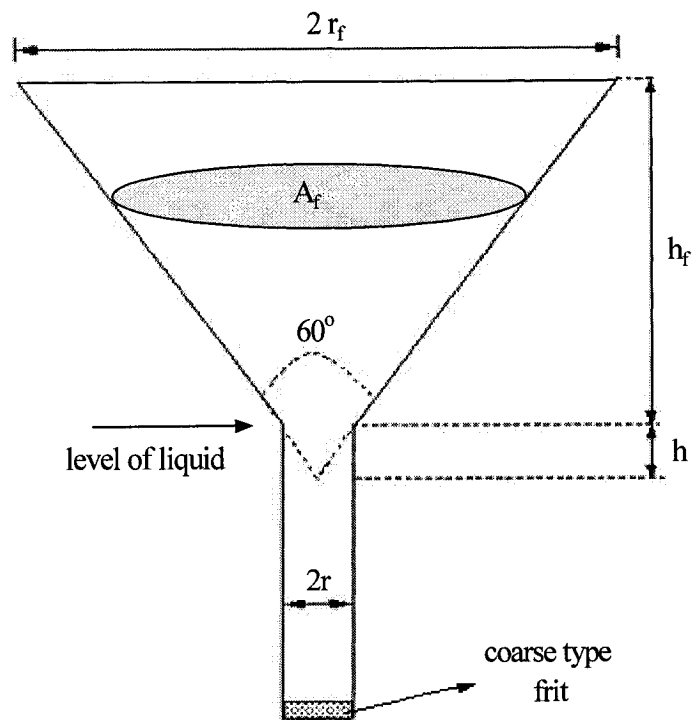
Figure 2.9. The conical foam meter

and, from Eq. 2.16 and 2.17,

$$A_f^{3/2} = mU + c \tag{2.18}$$

where $m = \Sigma(3\pi)^{1/2}$ and $c = h_0 A_0 \left(\dfrac{\pi}{3}\right)^{1/2}$

Ross and Suzin (1985) found that the plot of $A_f^{3/2}$ against U gave two regimes: one linear, i.e., air retention time (bubble life) is independent of flow conditions, and one exponential, where the flow conditions affect the bubble life.

2.5.2. Nonaqueous Foams

Perhaps the most important physical difference between aqueous and nonaqueous systems is the surface tension. Because of hydrogen bonding, water surface tension is high and, therefore, surfactants can easily reduce the surface tension.

The surface tension of nonaqueous systems is already low, and further lowering is difficult. Three groups of surfactants have been found to lower the surface tension: hydrocarbons, fluoroalkyls and polymethylsiloxanes (silicone oils) (Schmidt, 1996).

Some hydrocarbon surfactants can reduce the surface tension of nonaqueous solvents, such as lauryl sulfonic acid in the case of mineral oil, benzene and heptane, and sorbitan monolaurate (Span 20) for mineral oil (Ross, 1984; McBain and Perry, 1940). Most can not produce stable foams in low viscosity nonaqueous liquids due to a weak Gibbs-Marangoni effect, and many hydrocarbon surfactants cannot lower the surface tension of nonaqueous solvents due to moieties being too soluble in organic media.

Fluoroalkyl-type surfactants ($CF_3[CF_2]_n$) can reduce the surface tension of nonaqueous liquids more than any other agents (Jarvis and Zisman, 1959; Sholberg et. al., 1953) and produce very stable foams (Netherly, 1971). The ability to lower surface tension (increase adsorption) increases with an increase in fluorine/hydrogen atomic ratio. Fluorad FC-740, a nonionic fluorocarbon surfactant, can decrease the surface tension of kerosene, diesel fuels and xylene and produce stable foams (Schmidt, 1996).

Siloxane surfactants (silicone oil, for the structure see Appendix B) were first introduced in 1954 for producing polyurethane foams (Snow and Stevens, 1999). Below their solubility limit, they can produce relatively more stable nonaqueous foams than hydrocarbon surfactants. The key properties in producing stable foam using silicone oil

appear to be the Gibbs-Marangoni effect (Owen et. al., 1967), and an increase in viscosity (Schmidt, 1996; Kendrick et. al., 1967).

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CHAPTER 3

The Concept*

3.1. Abstract

The Air-Assisted Solvent Extraction (AASX) concept uses a solvent-coated bubble to contact the organic and aqueous phases. Compared to conventional solvent extraction, a high contact area can be created using less solvent and the natural buoyancy provided by the air core promotes phase separation. A method of producing coated bubbles exploiting foaming properties of kerosene-based solvent is introduced. Coating thickness is estimated at ca. 3 µm on a 4.4 mm diameter bubble giving a specific surface area of ca. 3000 cm^{-1}, equivalent to a solvent droplet of ca. 20 µm. Such a droplet would have very poor phase separation properties. In extraction tests (500 mg/L Cu solution), high aqueous/organic ratios could be used (e.g., 75:1) while phase separation remained excellent. This shows the potential for AASX to treat large volume, low concentration streams such as acid mine drainage.

3.2. Introduction

Large volumes of dilute metal bearing effluents are generated in the metal extraction and processing industries. An important example is acid mine drainage (AMD), produced when sulphide minerals are exposed to oxygen and water in the presence of certain microorganisms (Younger et al., 2002; Kuyucak, 2002; Feng et al., 2000; Demopoulos, 1998; Machemer and Wildeman, 1992). It is one of the major environmental challenges facing the mining industry. In Canada, collection and treatment of existing and potential AMD generating sites as estimated at over $3 billion (Tremblay and Hogan, 2001) and in the US the treatment cost is $1 million/day (Evangelou, 1995).

A variety of treatment options have been proposed (Table 3.1). Lime treatment to neutralize and precipitate metals as hydroxides is the most common. The volume of toxic sludge requiring disposal and maintenance against pH excursions, however, restricts continued use. As with all challenges, the need to treat AMD has driven innovation (Younger et al., 2002; Matis and Lazaridis, 2002; Dibrov, 1998; Gazea et al., 1996). The McGill group has focused on techniques that incorporate metal recovery. Selective precipitation (Rao and Finch, 1992) and adsorption (El-Ammouri et al., 2000; Gelinas et al., 2000) from solution and selective leach/recovery options on sludge (Calzado et al., 2005; Gelinas et al., 2002; Felsher et al., 2000) have been considered. A current innovative approach being explored is a version of solvent extraction, which is the subject of this communication.

Solvent extraction is widely used in primary metal extraction, notably for Cu and U (Rao et al., 2000; Doungdeethaveeratana and Sohn, 1998; Bullock and King, 1975; Flett et al., 1973). Solvent extraction has been included as an option to treat wastewater

(liquid-liquid extraction, Table 3.1). For example, Reinhardt (1975) described a process to recover zinc from drainage water in rayon manufacture and Ortega and Gutierrez (1980) suggested a process to recover mercury from nitric acid wastes. At a growing number of mine sites solvent extraction/electrowinning (SX/EW) is used to recover Cu from drainage waters and pregnant liquor from engineered leach systems. The main difficulties are applying the process to dilute solutions (largely because of the need to keep the aqueous/organic (A/O) ratio $\sim$ 1 to provide satisfactory phase disengagement which offers no concentration enrichment), loss of reagents and the capital outlay (Kentish and Stevens, 2001; Ritcey and Ashbrook, 1978).

The need is to treat large volumes cheaply. In the minerals industry this was solved when flotation was introduced at the turn of the last century. If solvent could be carried as a thin layer on bubbles this could provide a high specific surface area with high A/O ratio while maintaining rapid phase disengagement due to buoyancy provided by the air core. This combination may open the way to adapting solvent extraction to dilute streams. This concept was termed "Air-Assisted Solvent Extraction" (AASX) by Chen et al. (2003).

The concept has its origin in the periodic attempts to use oil to argument flotation ("oil assisted flotation" (Laskowski, 1992)). Of course a connection with oil goes back to the earliest days of flotation (Crabtree and Vincent, 1962) but specifically we are targeting an oil-coated bubble. Taggart (1927) suggested that an oil film spread on a bubble would enhance collection of hydrophobic particles by forming compact gas/oil/solid agglomerates.

Table 3.1. Comparison of active water treatment methods (Reed, 1998)

Process	Chemical/Energy Input	Metal Reclamation	Major Advantages	Major Disadvantages
Chemical precipitation	Precipitant, flocculant, acid base; mixing and fluid handling	Metal sludge	Well established, low effluent concentrations	High chemical dosages, several unit operations
Electrolytic recovery	Electrical power	Solid metal scrap	Well established; direct recovery of solid metal; no chemical consumption	Energy intensive; high capital costs; reduced efficiency at dilute concentrations
Ion-exchange	Regenerated solutions; fluid handling	Concentrated soluble metal stream	Highly selective, effectiveness <100 mg/L	Chemical regeneration requirements, adsorbent expense; prone to fouling in mixed waste streams
Disposable adsorbents	Replacement adsorbent; fluid handling	Metal immobilizes on solid adsorbent	Simple metal remove process; low adsorbent cost; effective <100 mg/L	Selectivity, recurring cost of new adsorbent, disposal cost of spent adsorbent
Membranes	Extractant for liquid-supported membrane; fluid handling	Concentrated soluble metal stream	Selective; continuous concentrated metal solution recycle	Membrane durability, fouling
Liquid-liquid extraction	Organic solvent/water contact: loading and stripping in mixer and settlers	Concentrated soluble metal stream	Selective; continuous concentrated metal solution recycle	Capital costs; solvent emissions to air/water; solvent disposal

This idea was pursued for fine coal flotation by Misra and Anazia (1987) who found the induction time for a bubble was greatly reduced when encapsulated in oil. Wang et al. (1988) and Peng and Li (1991) investigated the approach for selective coal flotation finding that collector consumption could be reduced without loss of recovery. In processing recycled paper, Maiolo and Pelton (1998), found enhanced ink removal with bubbles coated with silicone oil. Gomez et al. (2001) confirmed this in continuous testing

at a de-inking plant. For sulphide mineral flotation, Liu et al. (2002) adapted the concept to try to reduce undesired activation of gangue particles. Flotation collector was mixed with kerosene to produce a "reactive oily bubble".

The application in solvent extraction is to recovery metal ions. Chen et al. (2003) first described the Air-Assisted Solvent Extraction concept. They showed that spreading of a kerosene-based solvent over a bubble was thermodynamically favored. Experimentally, coating was achieved by carefully passing air through a thin plug of solvent replenished from a reservoir.

AASX appears to offer potential for treating large dilute volumes. There is the prospect of obtaining high aqueous/organic ratio without the attendant problem of phase separation (entrainment of organic in the aqueous phase and vice versa), which keeps the recommended ratio close to 1:1. Some aspects of Air-Assisted Solvent Extraction are explored in this communication.

3.3. Materials and Procedure

3.3.1. Materials

Reagent grade $CuSO_4.5H_2O$ was used to prepare aqueous solutions. The solvent comprised the chelating type extractant LIX 973N (Cognis) diluted in kerosene. The chemical composition of the extractant is given in Table 3.2. The density of LIX 973N is 0.950 g/cm^3. All chemicals were used as received. Density and surface tension of example solvents, measured using Wilhelmy Plate Method (Kruss Tensiometer K 12), are given in Table 3.3. A typical LIX/kerosene ratio in conventional SX is 1:9. The surface

tension of kerosene alone given in the literature is 25.22 mN/m and interfacial tension with water is 20.38 mN/m (Chen et al., 2003).

Table 3.2. Chemical composition of extractant (Material Safety Data Sheet of LIX 973N)

Extractant	X (%)	Y (%)	Pet. Distill. (%)	Alcohols (%)	Nonylphenol (%)
LIX 973N	<46	<18	>30	--	<6

X: Benzaldehyde, 2-Hydroxy-5-Nonyl Oxime; **Y**: 5-T-Nonyl-2-Hydroxyacetophenone, Oxime

Table 3.3. Surface tension and density of example solvents

LIX/kerosene Ratio	Surface Tension (mN/m)	Density (g/cm^3)
1:9	26.4	0.815
3:1	27.8	0.912

3.3.2. Procedure

For extraction tests the objective was to inject a single stream of solvent-coated bubbles into a column containing the aqueous phase (Figure 3.1). This was achieved by placing solvent in A and bubbling through air (4 cm^3/min for all experiments) to produce foam. Foaming was easier the higher the LIX/kerosene ratio. The foam passed through the capillary (diameter, 2.5 mm) and bubbles were released at the orifice. In this fashion the bubble carried a thin coating of solvent into the aqueous phase. Fresh solvent input (C) was regulated by an autoburette (radiometer, Copenhagen ABU 91). The air readily disengaged at the surface of the solution to produce a layer of solvent (D). Provided fresh solvent was introduced below the foam no solvent droplets were released.
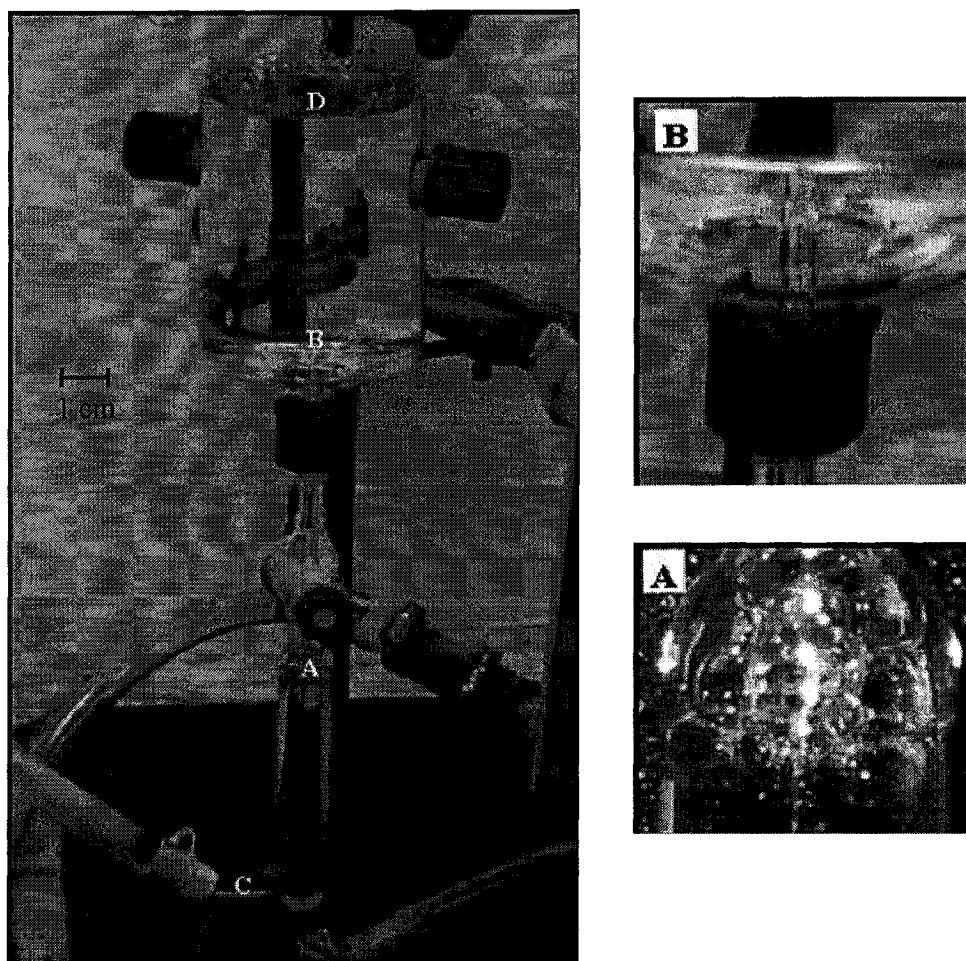
Figure 3.1. Experimental set-up

Solvent extraction is pH sensitive. Trying to keep pH constant (with NaOH to counter the release of H^+ ions) caused local precipitation of copper. Therefore, buffered solutions were prepared from 0.2 M NaOH, 0.04 M acetic acid, 0.04 M phosphoric acid and 0.04 M boric acid (Dean, 1992). All experiments were made at pH 2.10 using 1:1 LIX 973N/kerosene ratio with 150 mL aqueous solution of 500 mg/L Cu. One mL samples of solution were taken by syringe to analyze for Cu using atomic absorption spectroscopy.

3.4. Results and Discussion

3.4.1. Demonstration of Coating

One way to demonstrate coating is to measure the rise velocity compared to air bubbles alone. Velocities were measured in a square cross-section (10 cm x 10 cm) by 150 cm Plexiglas column using a stopwatch over a 1 m rise. In each experiment 625 particles[1] were counted. The results are given in Figure 3.2. The volume equivalent diameter of the coated bubble and air bubble alone, measured by collecting a known number in a graduated cylinder, were 4.4 and 4.6 mm, respectively.
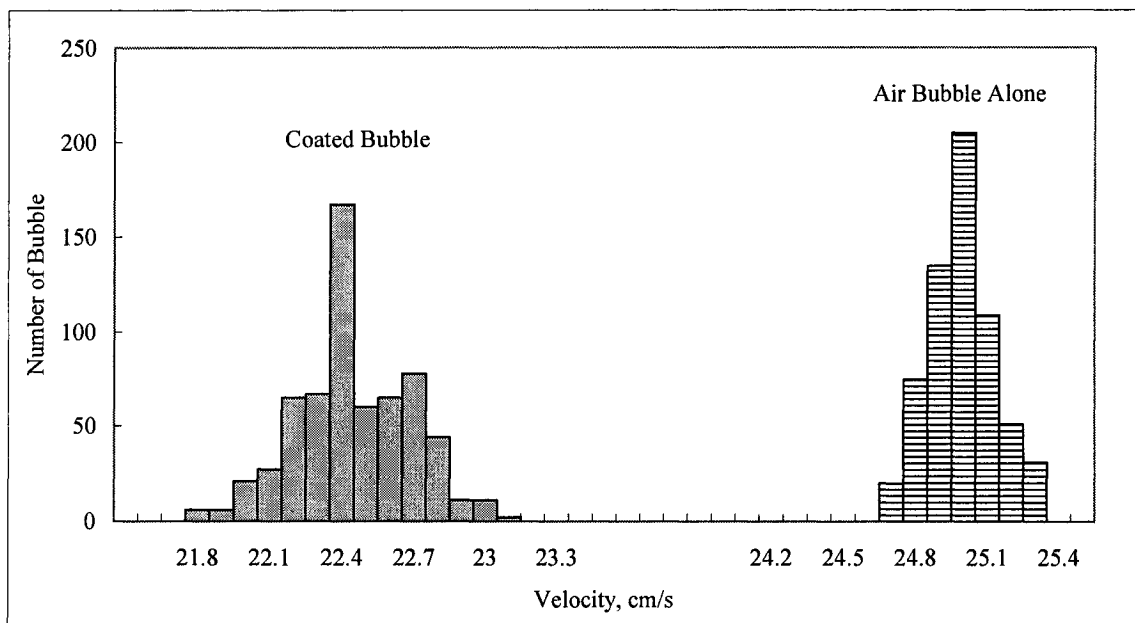
Figure 3.2. Velocity of coated bubbles and air bubbles alone

As evident in Figure 3.2, the coated bubble rises more slowly, reflecting the solvent load. The distribution appears to be wider than for the bubble alone, suggesting a spread in coating thickness. The velocity of the air bubble alone corresponds to the

[1] Particles = bubbles alone, coated bubbles or solvent droplets (all produced from the same capillary).

literature (Clift et al., 1978). For reference, the diameter and the velocity of solvent droplet produced at the same orifice were 0.54 cm and 13 cm/s, respectively.

The stability of a thin organic film on a bubble is governed thermodynamically by the spreading coefficient, S_c (Adamson, 1990). The appropriate form in the AASX case is

$$S_c = \gamma_{a/o} - (\gamma_{a/w} + \gamma_{o/w})$$ (3.1)

where γ is interfacial tension and subscripts a, o, and w refer to air, organic and water.

If $S_c < 0$ coating occurs spontaneously. Using the data in Table 3.3, S_c is found to be negative, which means formation of a stable solvent coating on a bubble is favored. Chen et al. (2003) made the same observation.

3.4.2. Coating Thickness

The average thickness of coating was estimated at ca. 3 μm by measuring solvent consumption for a known number of bubbles. Hughes and Kuipa (1996) estimated the reaction zone thickness around a solvent droplet for a chelating type extractant to be ca. 1.3×10^{-3} μm and Neuman et al. (1993) reported a value between $7\text{-}40 \times 10^{-3}$ μm. The coating thickness achieved on the bubble appears to carry sufficient solvent.

In principle, an estimate of the mass of solvent carried per bubble (hence providing an estimate of average coating thickness) could be made from the decrease in rise velocity (Figure 3.2). In the literature, although there are many velocity equations for rising or settling particles, none correspond to the current situation: no rising particle equation fitted the data.

3.4.3. Comparison with Solvent Droplets

In separate experiments solvent-coated bubbles (AASX) and solvent droplets (4.4 mm and 5.4 mm, respectively) were passed through the 150 mL, 500 mg/L Cu solution. Extraction was compared on the basis of cumulative surface area and volume of solvent. To allow for the difference in retention time (rise velocity of droplet was ca. 13 cm/s; of solvent coated bubble, ca. 22.5 cm/s) columns of different diameters were used giving heights of 7.4 cm (droplet) and 12.8 cm (coated bubble). The AASX tests were done three times and showed good repeatability (Figure 3.3).

In terms of surface area (Figure 3.3a), the degree of extraction by the droplet exceeded that of the solvent-coated bubble. This suggests that some extractant molecules in the bulk of the droplet can be accessed, perhaps exchanging with Cu-loaded molecules at the surface.

Figure 3.3b reveals the significantly higher consumption (volume) in the case of solvent droplets for the same extent of extraction, some 70 mL at ca. 25% extraction compared to ca. 1 mL in the AASX test. That is, an A/O ratio of some 2:1 in the former case and 150:1 in the AASX case. This means the resulting Cu content in the organic phase in the AASX experiment is significantly increased, revealing the concentration enrichment capability.

The comparison is unfair in the sense that the large droplets employed are not the practice. The data do permit calculation of the size of droplet required to equal the specific area of the solvent in the AASX. At the same 25% extraction the surface area of solvent in AASX is ca. 3000 cm^2 thus, knowing the corresponding volume is ca. 1 mL, the specific surface area is ca. 3000 cm^{-1}. To match requires a 20 μm droplet, a size

difficult to generate and obviously one with poor disengagement properties. The
disengagement issue is illustrated next.
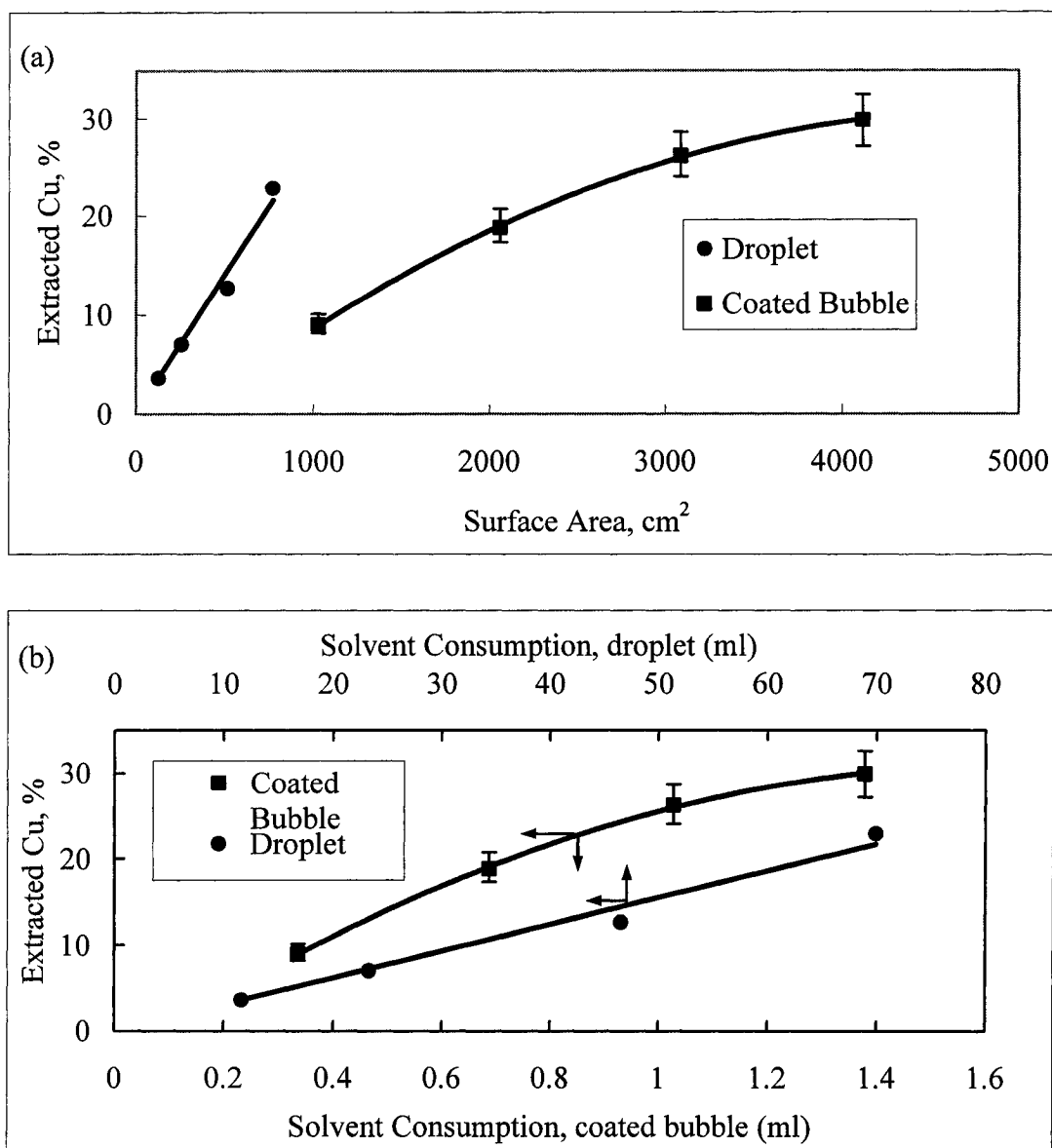
Figure 3.3. Comparison of extraction by solvent droplet and solvent coated bubble
(AASX) on the basis of cumulative surface area (a) and cumulative volume (b). (The bars
represent the range of three experiments)

3.4.4. Disengagement

Air-Assisted Solvent Extraction was compared to a conventional "shaking" test. For both experiments the same A/O ratio, 75:1, was used representing a possible condition for AASX. Figure 3.4 illustrates the two systems: Figure 3.4a) the shaker test after 12 hours of settling still showing entrainment of solvent in the aqueous phase (about 24 hours was needed to complete the disengagement), and Figure 3.4b) the AASX test where excellent phase separation is evident which occurs essentially immediately. Figure 3.4a) illustrates the problem with high A/O ratio in the conventional process: fine droplets form that disengage slowly, exacerbated as they load with Cu (in this case) which drives down the buoyancy force. For dilute aqueous solutions this buoyancy force is already restricted and in the current case the use of a high LIX/kerosene ratio (1:1), by increasing solvent density (Table 3.2), further exacerbates the problem. These concerns do not apply to AASX.
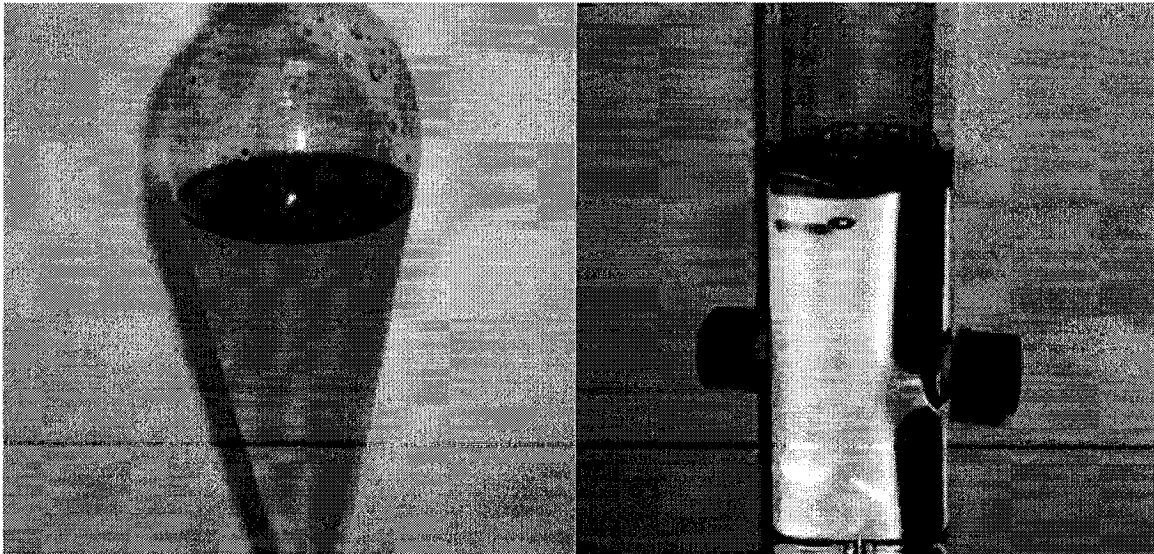
Figure 3.4. (a) Disengagement in conventional SX shake test (after 12 hours)

Figure 3.4. (b) Disengagement in AASX (instantaneous) (Note, object close to solvent layer is a coated bubble.)

The shake test was made for two times, 2.5 and 5 min. The result was extraction of 80.1% and 81.4%, respectively, suggesting the equilibrium distribution had been reached. Extraction in AASX reached 40% by the time 2 mL solvent had been introduced. We can anticipate that the figure may be increased by additional bubble retention time (only ca. 0.5 s in this test).

The results do seem to confirm the potential of AASX to treat low concentration solutions by offering significant concentration enrichment while preserving ease of phase separation. A future paper will focus on its application to dilute solutions (e.g., < 100 mg/L). The key to producing the coated bubble is the foaming of solvents. This property, how to produce and control it, will also be pursued in a subsequent paper.

3.5. Conclusions

1.   Air-Assisted Solvent Extraction (AASX) is proposed to overcome some drawbacks of conventional solvent extraction for treating dilute (e.g., effluent) streams by providing high aqueous/organic (A/O) ratio, and consequently high concentration enrichment, while maintaining ease of phase separation.

2.   The foaming properties of solvents can be used to generate coated bubbles.

3.   Solvent-coated bubbles of diameter 4.4 mm produced a coating thickness of ca. 3μm and a specific surface area of solvent of ca. 3000 cm^{-1}, which would require solvent droplets of ca. 20 μm to match.

4.   Using the same 75:1 A/O ratio, a conventional shake test took some 24 hours for the phases to disengage, while in AASX disengagement was essentially instantaneous.

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CHAPTER 4

Foaming Properties*

4.1. Abstract

The Air-Assisted Solvent Extraction (AASX) concept uses a solvent-coated bubble to contact the organic and aqueous phases. Compared to conventional solvent extraction, a high contact area can be created using less solvent and the buoyancy provided by the air core promotes phase separation. Solvent-coated bubbles are produced by forming a foam. The foam is injected through a capillary and a solvent-coated bubble is produced at the orifice and released into the aqueous solution. To control foam properties, the effect of some surfactant additives is investigated. Silicone oil is found to have a strong foaming action with kerosene-based solvents. The volume of foam produced was increased substantially without affecting extraction or stripping of copper (with LIX reagents) or zinc (with D2EHPA).

4.2. Introduction

Solvent extraction (or liquid-liquid extraction) is widely used to purify metals from pregnant leach solutions (Owusu, 1999; Ritcey and Ashbrook, 1978; Flett, 1973). Air-Assisted Solvent Extraction (AASX) differs from conventional solvent extraction (SX) by introducing the solvent as a thin layer (a few μm) on a bubble (Tarkan and Finch, 2005; Chen et al., 2003). It offers the potential of high aqueous/organic ratio while maintaining excellent phase separation, introducing the possibility of treating dilute solutions (<1 g/L): AASX becomes a concentration process while retaining the purification capability of SX. Tarkan and Finch (2005) found a convenient way to coat bubbles was to produce a solvent foam. Once formed the foam is injected into the aqueous phase through a capillary to produce a stream of coated bubbles. Solvent foam properties are, therefore, of interest.

Foams occur in many industries from mineral flotation to cosmetics production and oil and food processing. They form in a variety of gas-liquid (slurry) systems whenever gas bubbles arrive faster than the liquid between bubbles can drain (Schramm et al., 1994). In pure liquids, this is difficult to achieve, i.e., some additives – surfactants – are required (Bikerman, 1953).

Foam consists of thin lamella films, Plateau borders where three lamella meet, and vertices where four Plateau borders meet. The amount of liquid present in the Plateau and vertex parts of foam is much larger than in the lamella. The amount of liquid in foam has been investigated by a series of researchers (Neethling et al., 2003; Neethling et al., 2000; Malysa, 1999; Lemlich and Shih, 1971; Rubin et al., 1967).

The liquid content in a foam should control solvent coating thickness on the bubble. The height of foam is one of the parameters which controls the liquid content (Malysa, 1999): the greater the height of the foam, the longer the draining time and the drier the foam. The liquid content of the foam affects the shape of bubble: the base of a foam consists of bubbles roughly the size and shape of those entering the foam layer and the foam is "wet", while in the upper part, the foam consists of larger polyhedral bubbles and the foam is "dry".

Most investigations on foam have focused on aqueous rather than the organic foams required in AASX. Theories of foam stability cover similar ground for both aqueous and nonaqueous liquids, stressing factors such as surface tension and surface viscosity. However, there are important differences. For instance, the surface tension of water, 72.8 mN/m at 20°C (Adamson, 1990), is high because of hydrogen bonding between water molecules, and is easily reduced by surface active agents (surfactants). In contrast, the surface tension of typical kerosene-based solvents is already low and it is hard to decrease further. There are three types of surfactants known to decrease the surface tension of organic liquids, which offers a starting point, namely: hydrocarbons, polymethylsiloxanes and fluoroalkyls (Schmidt, 1996).

Some hydrocarbon surfactants can modify surface properties of nonaqueous liquids, e.g., reduce surface tension and produce stable foams (Schmidt, 1996; McBain et al., 1940). Sorbitan monolaurate (Span 20) is known to decrease the surface tension of some nonaqueous solvents (Ross, 1984).

Polymethylsiloxanes (e.g. silicone oil, polydimethylsiloxane) are strong surface active agents in organic media. They are used, for example, in controlling polyurethane

foams, and their properties have mainly been investigated in that area (Hill, 1999; Snow and Stevens, 1999; Kanner and Prokai, 1971). Silicone oil can increase surface viscosity and reduce drainage, thus stabilizing foam (Owen et al., 1967). The equilibrium surface tension is low, about 21 mN/m (at room temperature) (Kendrick et al., 1967). The amount of silicone oil used to increase the foaming properties of organics is important, because above a certain concentration (associated with the solubility limit) they behave as foam breakers (Takamitsu et al., 1999; Kulkarni et al., 1996; Schwarz, 1970).

In AASX a requirement is that bubbles disengage from the organic layer which forms on the surface of the aqueous phase after extraction, i.e., the foam should not be too persistent. Fluoroalkyl type surfactants are very surface active and are reported to produce stable foams (Netherly, 1971); therefore, they were not considered. Mineral flotation frothers, on the other hand, are designed to produce non-persistent foams[1]. Two candidates, (MP-99 and F-100 from Minerec (now Flottec)) were selected based on low solubility in water, suggesting they would be suitable for organics (i.e., solvents).

4.3. Dynamic Foam Stability Measurement

Bikerman (1953) proposed a unit of foaminess, Σ, for dynamic (i.e., gas is flowing) foams as follows:

$$\Sigma = \frac{V}{U} \tag{4.1}$$

where U and V are air flow rate (cm^3/min) and foam volume (cm^3), respectively.

---

[1]In flotation the term froth is generally used: there is some attempt to reserve "froth" for cases where solids are present as in flotation and "foam" for 2-phase only systems (Neethling et al., 2003).

Using this measure, several dynamic foam stability studies have been performed (Ross and Suzin, 1985; Ross and Suzin, 1975; Watkins, 1973). The shape of the container, however, affects the reproducibility and to overcome this problem the use of a conical "foam meter" was recommended (Nishioka et al., 1996; Watkins, 1973).

The technique of Ross and Suzin (1985) is used here (Figure 4.1). Results were evaluated using the foam area produced, A_f.

$$A_f = 1.047(h_f + 1.732r)^2 \qquad\qquad (4.2)$$

Ross and Suzin (1985) used the parameter $A_f^{3/2}$ to give units of volume and noted that $A_f^{3/2}$ vs air flow rate (V) gave two distinct regimes (Figure 4.2): at low flow rates the relationship is linear (region A) indicating gas retention time (bubble life) is independent of V (i.e., the slope is constant); at higher flow rates (region B), bubble life decreases as V increases (although shown as linear the trend is exponential when taken to higher V (Ross and Suzin, 1985)).
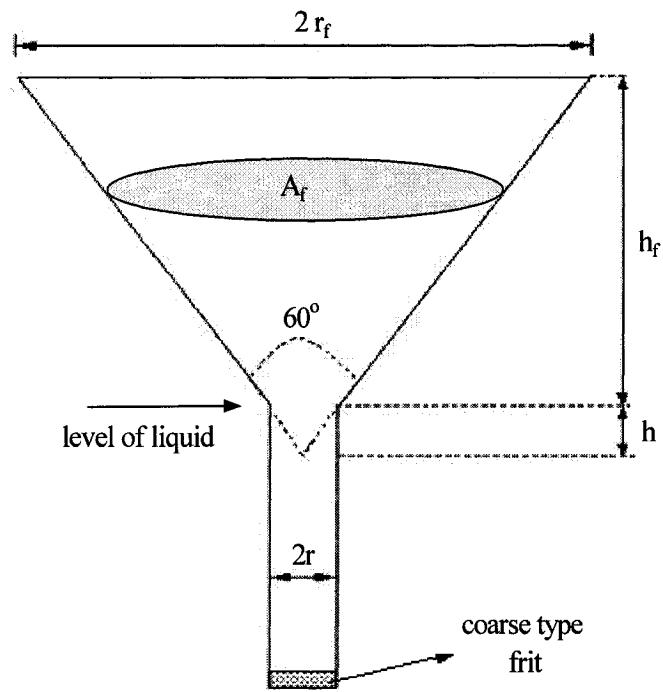
Figure 4.1. The conical foam meter
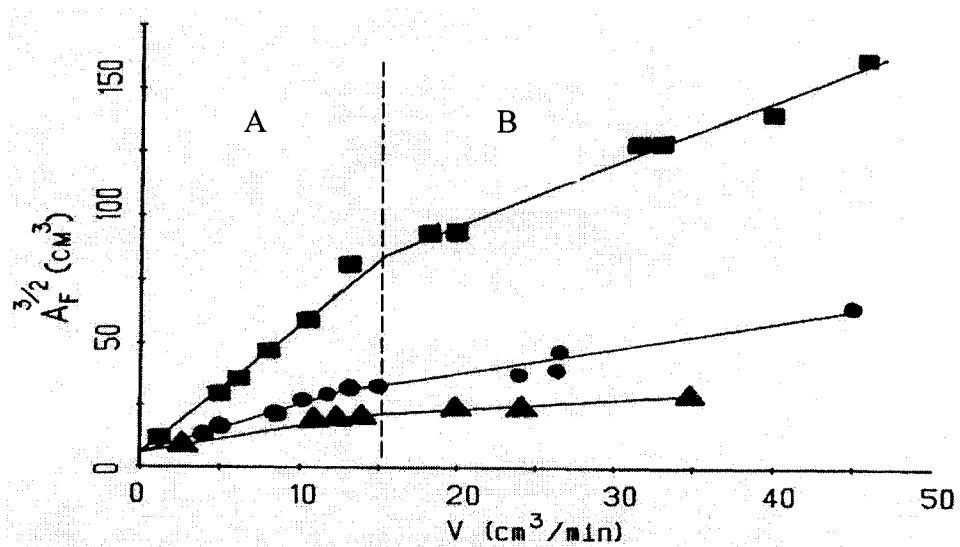
Figure 4.2. The finding of Ross and Suzin (1985) finding (Reprinted with permission from Ross and Suzin (1985), American Chemical Society)

4.4. Experimental

4.4.1. Materials

The solvents were prepared from chelating type extractants, LIX 622, LIX 860, LIX 973N, LIX 984, (received from Cognis) and an acidic extractant, Di (2-Ethylexhyl) phosphate, (D2EHPA, received from SIGMA) diluted in kerosene. Some features of the solvents are given in Tables 4.1 and 4.2. Surface tension was measured using Wilhelmy Plate Method (Kruss Tensiometer K 12). Reagent grade $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ were used to prepare aqueous solutions for extraction experiments. The foaming agents were sorbitan monolaurate (Span 20, SIGMA), silicone oil (SIGMA) and the flotation frothers F-100 and MP-99 (Minerec (now Flottec)). All were used as received.

Table 4.1. Chemical composition of LIX extractants (MSDS)[1]

LIX	X (%)	Y (%)	Pet. Distill. (%)	Alcohols (%)	Nonylphenol (%)
973N	<46	<18	>30	--	<6
984	<33	<30	>31	--	<6
622	<65	--	>11	<20	<4
860	<65	<31	--	--	<4

X: Benzaldehyde, 2-Hydroxy-5-Nonyl Oxime; **Y**: 5-T-Nonyl-2-Hydroxyacetophenone, Oxime
[1]The exact composition is proprietary information.

Table 4.2. Surface tension (mN/m) of selected solvents

Extractant/kerosene Ratio	LIX 622	LIX 973N	LIX 984	LIX 860	D2EHPA
1:9	26.2	26.4	26.3	26.2	25.6
3:1	27.1	27.8	27.5	27.2	26.8

4.4.2. Dynamic Foam Stability

The dynamic foam stability was measured using the foam meter (Figure 4.1) with dimensions: r = 1 cm; r_f = 5 cm; h = 1.7 cm; h_f= 7 cm. In all experiments the same amount of liquid (17.5 mL) at three air flow rates (4, 10, 15 cm^3/min) was used. The height of the foam for each experiment was measured after steady state was reached (~ 5 min), and A_f was calculated (Equation 4.2). From repeat experiments, the pooled estimate of standard deviation on h_f was 0.058 cm.

4.4.3. Conventional and Air-Assisted Solvent Extraction

The surfactants used to increase foaming properties should not change the extraction and stripping properties of the solvents. Therefore complementary conventional (shaking test) and AASX experiments were carried out, using surfactants chosen according to the foaming results.

In the AASX experiments, metal ion concentration (in the aqueous phase) was 500 mg/L. The set-up was a 5 cm diameter column (Figure 4.3), described in detail in a previous study (Tarkan and Finch, 2005). The air flow rate was 4 cm^3/min. First, the foam is produced at location "A", then injected through a 2.5 mm capillary and the coated bubble is produced at orifice "B". Fresh solvent input (C) is regulated by an autoburette (radiometer, Copenhagen ABU 91). The bubbles collect at "D" and break to leave a solvent layer.

Conventional SX experiments, both extraction and stripping, were conducted in a 60 mL separatory funnel with 40 mL solution at 1:1 Aqueous/Organic ratio. The initial metal ion concentration was 4 g/L. The extraction and stripping time was 20 s. The strip

solution was based on standard Cognis quality control tests (Cognis Blue Line Technical Bulletin, 2002). Analysis for copper and zinc was by atomic absorption spectroscopy (Perkin Elmer 3110).

4.5. Foaming Properties

4.5.1. LIX Extractants

4.5.1.1. Solvent Alone

LIX reagents provide some foaming properties. Figure 4.4 shows an increase in LIX/kerosene ratio tends to increase the foam area produced. Drainage rate is a function of the viscosity of the liquid in the foam channels (Neethling et al., 2000; Malysa, 1999): the higher the LIX/kerosene ratio, the more viscous the solvent (Ritcey and Ashbrook, 1978) which probably accounts for the increase in foaming. It is evident that LIX 860 has the poorest foaming properties of the tested reagents and contains no petroleum distillate (Table 4.1), which may be the difference.

The results of experiments carried out on kerosene with and without nonylphenol (Table 4.3) show that foaming properties of LIX reagents are apparently related to the presence of this component. The nonylphenol concentration was 5% (v/v), corresponding to its approximate content in LIX reagents (Table 4.1). The possible foaming effect of petroleum distillate could not be tested readily as the exact composition is not known (proprietary information).
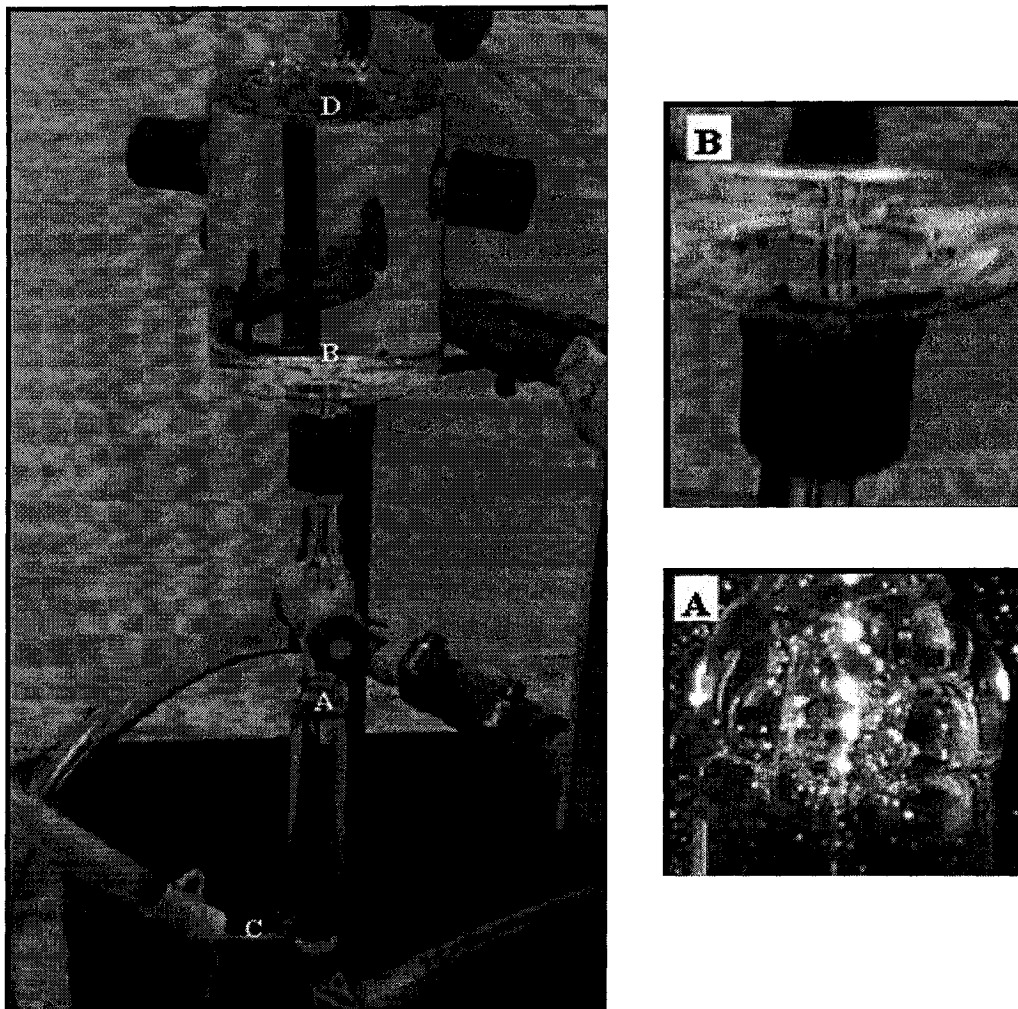
Figure 4.3. AASX experimental column (Tarkan and Finch, 2005)

LIX 973N and LIX 622 were chosen for experiments on the effect of air flow rate. The results (Figure 4.5) show that the higher the air flow rate, the more foam was produced. If the data in Figure 4.5 are evaluated according to Ross and Suzin (1985), they appear to fall in region B, where bubble life is dependent on air-flow rate.
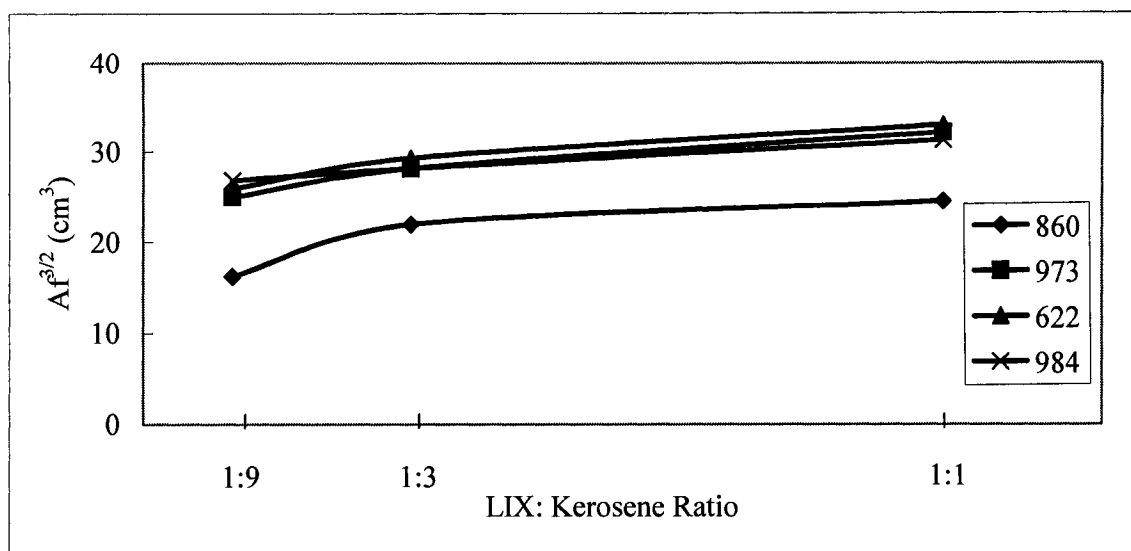
Figure 4.4. Foaming properties of some LIX solvents (air flow rate = 15 cm^3/min)

Table 4.3. Comparison of foaming properties of kerosene with nonylphenol and LIX reagents

Reagent	Air Flow Rate, cm^3/min		
	4	10	15
	$A_f{}^{3/2}$		
Kerosene	6.5	7.5	9.5
Kerosene + Nonylphenol (5%v/v)	16.9	22.9	29.0
Kerosene + LIX[1]	14.4-16.1	19.2-25.9	24.4-33.0

[1]for the range of LIX reagents

4.5.1.2. Solvents with Surfactant

In these experiments LIX 622 and LIX 973N 1:1 with kerosene were the solvents.

a) Flotation Frothers and Span 20

The results for frothers (Figure 4.6) show that while they may function well in water over this range of concentration, they have no effect on foaming properties of the two solvents. Likewise, Table 4.4 shows that Span 20 does not affect the foaming properties of the solvents (if anything foaming is decreased).
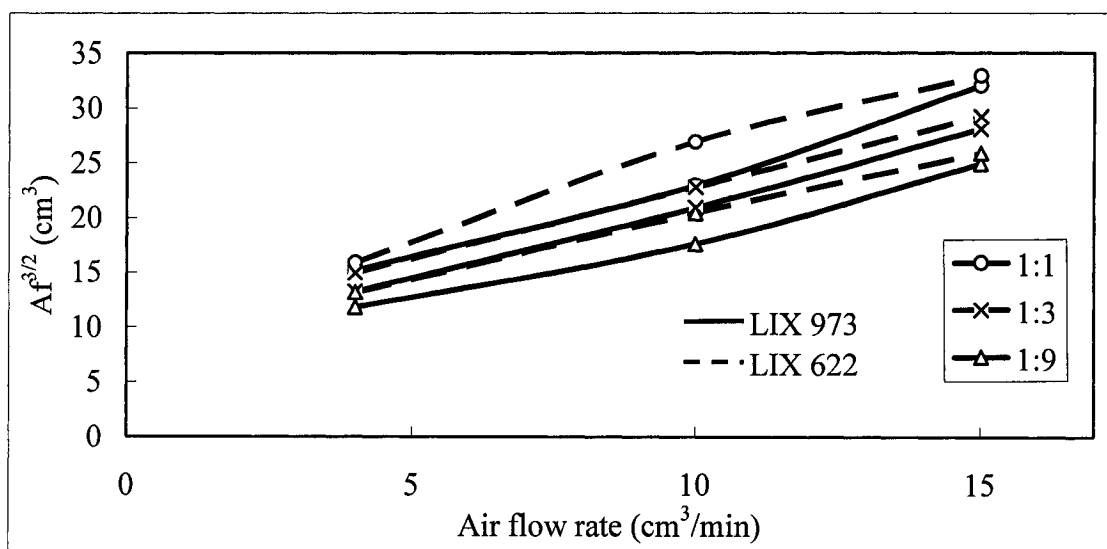
Figure 4.5. Effect of air flow rate on foaming properties for two LIX extractants at three LIX/kerosene ratios

Table 4.4. Effect of Span 20 on foaming properties

Solvent	Air Flow Rate, cm³/min	$Af^{3/2}$, cm³	
		without Span 20	with Span 20
LIX 973N	4	15.2	12.5
	10	22.9	18.8
	15	32.1	27.3
LIX 622	4	15.9	11.9
	10	26.9	18.2
	15	33.0	25.0
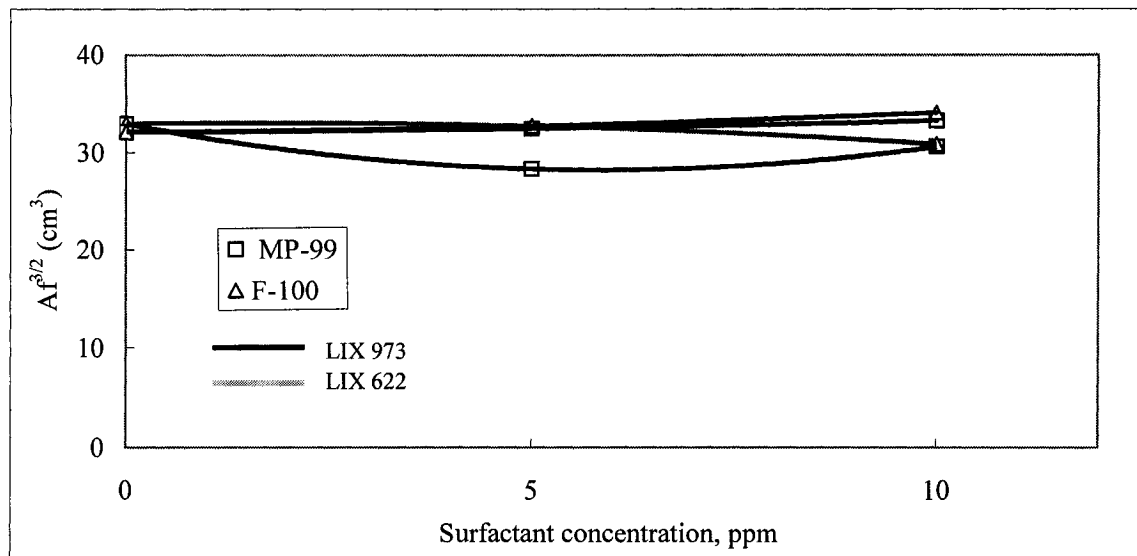
Figure 4.6. Effect of flotation frothers on foaming properties

b) Silicone Oil

The results (Figure 4.7) show the foam area increases significantly for both solvents to a maximum at 3 ppm silicone oil, when foaming starts to decrease. This decrease may correspond to exceeding the solubility limit of silicone oil in kerosene (Schmidt, 1996). The same trend was obtained at 4 and 10 cm^3/min air flow rate.

As a step towards revealing the mechanism, surface tension measurements were carried out. The results (Figure 4.8) show surface tension corresponds to the trend in Figure 4.7: silicone oil initially decreases the surface tension rapidly, but further increases in concentration above ca. 1 ppm have little impact.
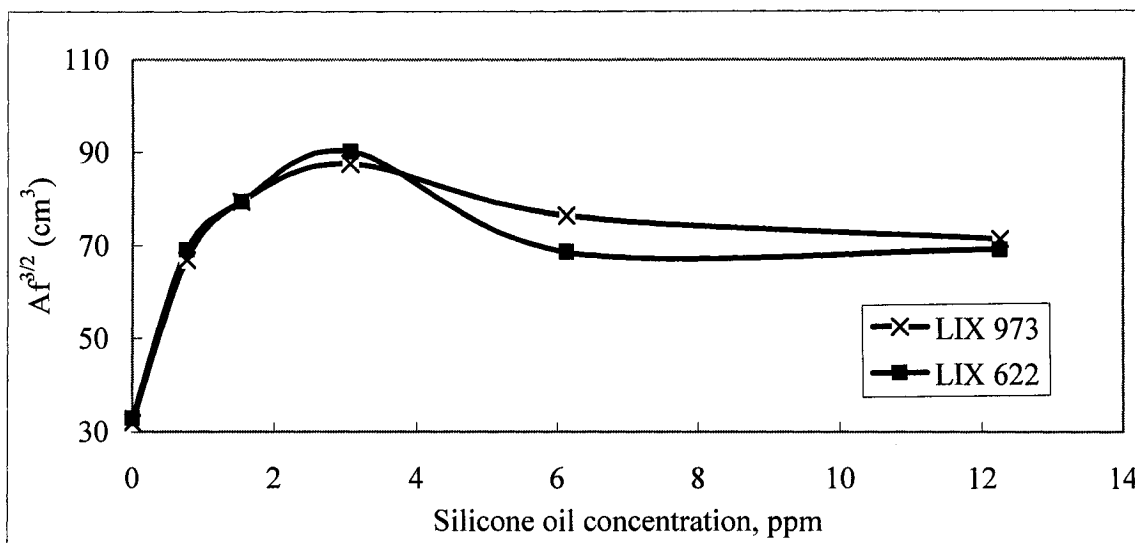
Figure 4.7. Effect of silicone oil on solvent foaming properties (air flow rate = 15 cm³/min)
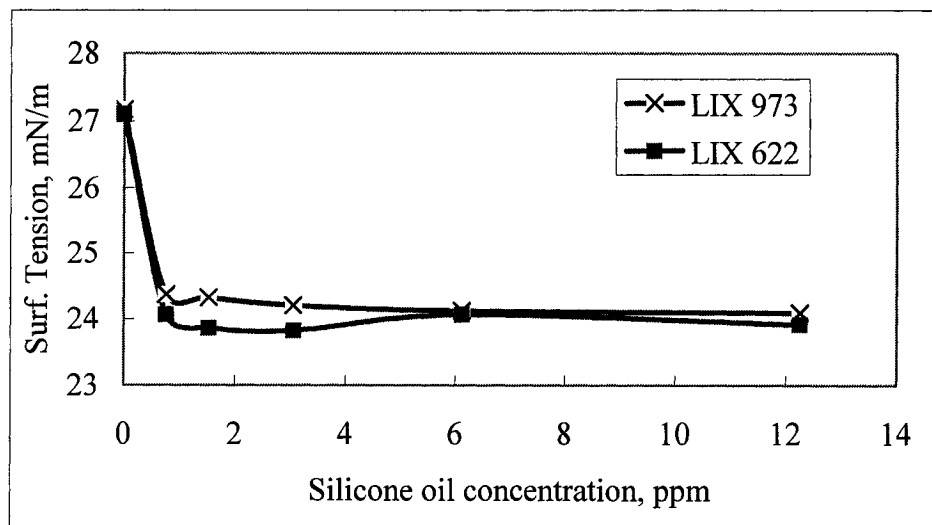
Figure 4.8. Effect of silicone oil on solvent surface tension

4.5.2. D2EHPA Extractant

Silicone oil appears to provide suitable foaming properties. It was tried with D2EHPA/kerosene as this solvent did not have sufficient foaming capacity to support

AASX. The D2EHPA/kerosene ratio was 1:9 and the silicone oil concentration was 1.5 ppm.

The results (Figure 4.9) show the weak foaming property of the solvent alone is significantly increased by the addition of silicone oil.
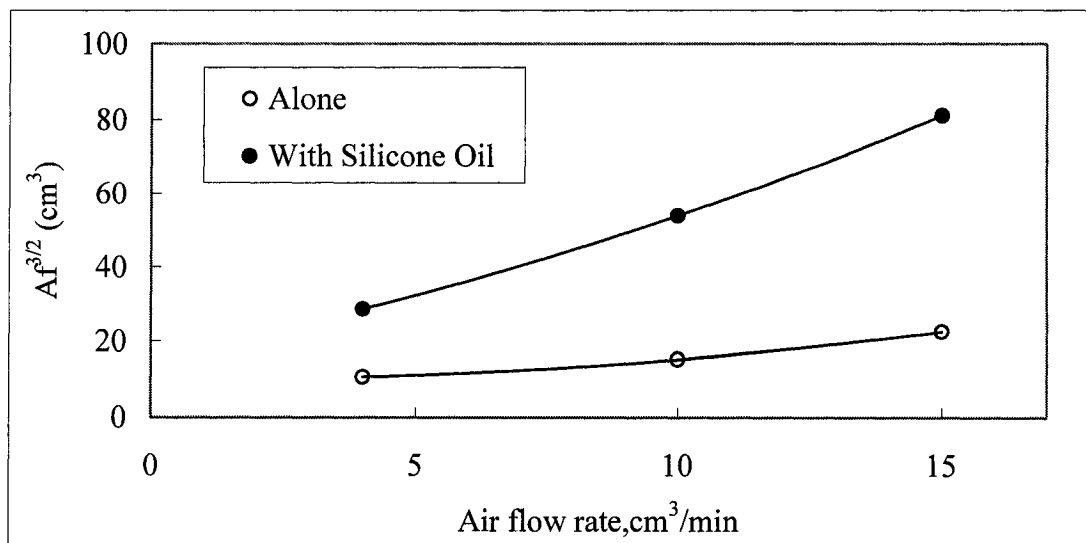
Figure 4.9. Effect of silicone oil on foaming properties of D2EHPA/kerosene solvent.

4.6. Extraction/Stripping

While silicone oil was found to be an effective foaming agent for kerosene-based solvents, it is imperative that the surfactant not degrade the extraction and stripping properties of the solvent. This was assessed using conventional and Air-Assisted Solvent Extraction tests.

4.6.1. LIX Extractants

Using 1:1 LIX/kerosene solvent, conventional (shaking test) solvent extraction experiments were performed with LIX 973N and LIX 622. In each experiment the pH was 2.1. The results are given in Table 4.5. Stripping experiments were carried out with the loaded solvents from the extraction experiments. The results are given in Table 4.6.

Table 4.5. Extraction experiments (initial [Cu] = 4 g/L)

Solvent	Silicone Oil Concentration, ppm			
	0	1.5	3	6
	Remaining Cu in solution, mg/L			
LIX 973N	480	475	470	469
LIX 622	496	513	500	494

Table 4.6. Stripping experiments

Solvent	Silicone Oil Concentration, ppm			
	0	1.5	3	6
	Stripped Cu in solution, mg/L			
LIX 973N	2505	2634	2670	2616
LIX 622	2456	2443	2526	2576

As seen in the Tables, silicone oil did not affect the extraction and stripping performance of either LIX reagent.

AASX experiments, with and without silicone oil (1.5 ppm), were performed with 1:1 LIX 973N/kerosene. Figure 4.10 shows that silicone oil does not affect extraction. It was noted that the height of foam that could be produced in chamber A (Figure 4.3) was greater in presence of silicone oil, and that errant droplet occurrence was reduced.
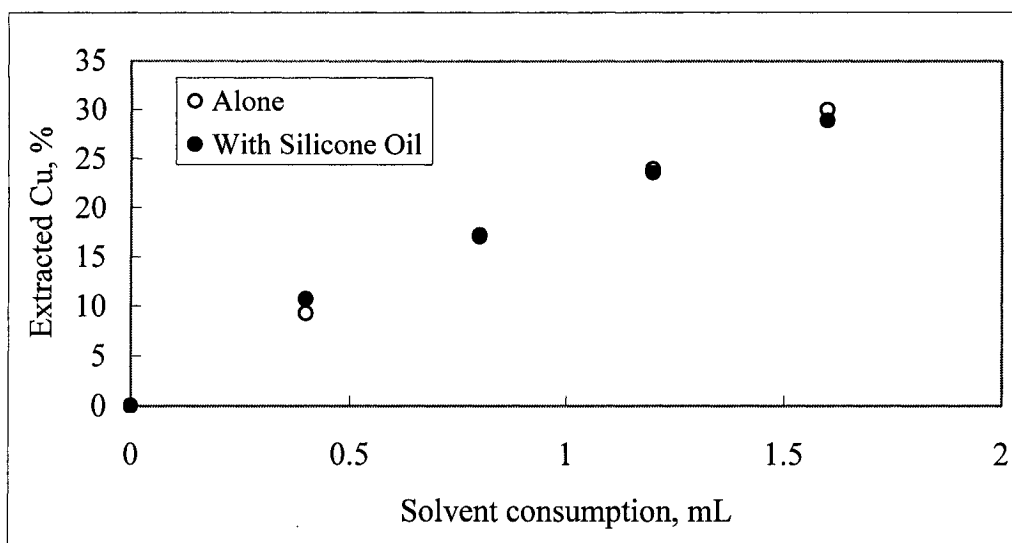
Figure 4.10. Effect of silicone oil on AASX with 1:1 LIX 973N/kerosene ratio

Silicone oil increased the flexibility in the use of LIX/kerosene solvent. Rather than the 1:1 ratio favored to produce adequate foaming with the solvent alone, the use of silicone oil meant any ratio could be used. This increase in range of application of AASX is well illustrated next, in the case of D2EHPA.

4.6.2. D2EHPA Extractant

Experiments with D2EHPA were carried out on zinc, for which this extractant is commonly used (Owusu, 1998; Ritcey and Ashbrook, 1978). Both in conventional SX and AASX, the D2EHPA/kerosene ratio was 1:9, extraction pH was 2.3 and silicone oil concentration was 1.5 ppm. As seen from Table 4.7, silicone oil did not affect the extraction and stripping performance of the solvent.

Table 4.7. Conventional SX (extraction and stripping) experiments with D2EHPA

Solvent	Zn Concentration, mg/L	
	Extracted	Stripped
D2EHPA alone	2374	1958
With silicone oil	2316	1899

AASX results are given in Figure 4.11. It is evident that without silicone oil, there was no extraction as there was no foaming. The silicone oil addition makes D2EHPA/kerosene solvent applicable for the AASX process.
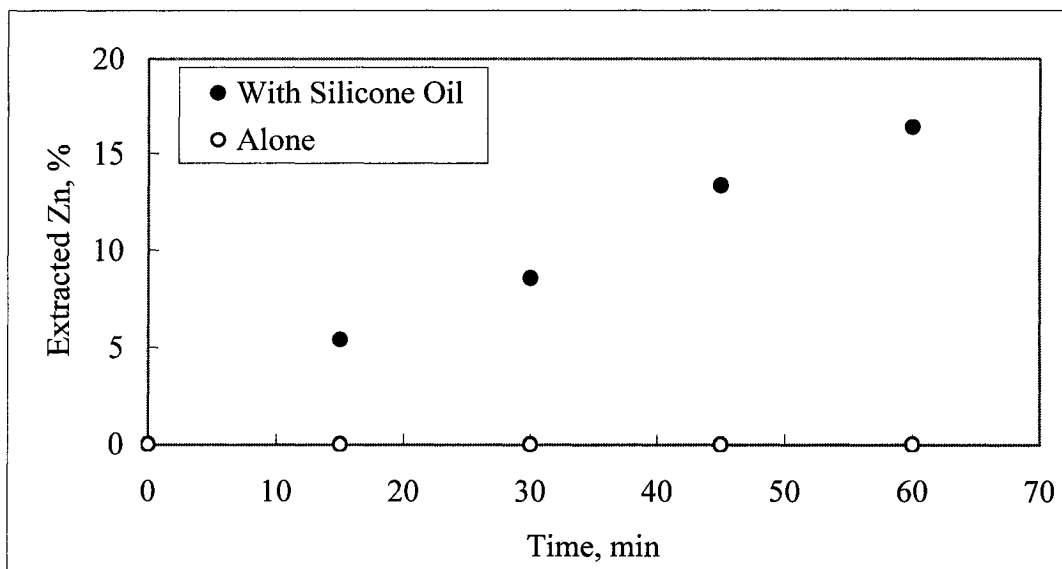
Figure 4.11. Effect of silicone oil on AASX with 1:9 D2EHPA/kerosene ratio (Note: time, rather than consumption is used as there was no solvent consumption without silicone oil)

The evidence indicates that silicone oil renders kerosene-based solvent amenable to AASX. These silicone oil modified solvents will be employed in moving to the next stage: production of "swarms" of solvent-coated bubbles.

4.7. Conclusions

The following itemized conclusions are drawn from this study on controlling foaming properties for the Air-Assisted Solvent Extraction (AASX) process.

1.   Flotation frothers and a hydrocarbon reagent (Span 20) did not influence foaming properties of two solvents, LIX 973N and LIX 622 1:1 with kerosene.

2.   Silicone oil up to 3 ppm did increase foam stability, which correlated with a sharp decrease in solvent surface tension.

3.   D2EHPA/kerosene solvent initially showed insufficient foaming for AASX but addition of silicone oil corrected this.

4.   Silicone oil did not change the extraction/stripping properties of the solvents.

5.   Silicone oil has expanded the range of solvents applicable to AASX.

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CHAPTER 5

Film Properties[*]

5.1. Abstract

Solvent-coated air bubbles in the Air-Assisted Solvent Extraction (AASX) process achieve the dual role of high solvent specific surface area and ease of phase separation. The properties and thickness of the solvent film control the process. As an approach to the study of the layer interferometry (in the UV-vis region) and FT-IR spectroscopy were used to measure the time dependent thickness and chemical composition, respectively, of a film formed by blowing an air bubble in kerosene-based solvents. The film was stabilized by the presence of 1.5 ppm silicone oil, as employed in AASX. The film appears to comprise two layers; an outer layer of almost constant thickness and an inner layer which decreased in thickness with time. The latter is considered relevant to AASX. Generally, the initial thickness was ~ 3 μm which decreased over several minutes to a final rupture thickness of ≤ 500 nm. The initial

thickness is of the order determined indirectly. The chemical composition of the layer did not change with time.

5.2. Introduction

Solvent extraction (SX) is widely used in primary metal extraction, notably for Cu, Ni, Co and U (Ritcey and Ashbrook, 1978; Bullock and King, 1975; Flett et al., 1973). It is included as an option to treat wastewater (Reed, 1998), which typically has low metal concentrations. One difficulty applying SX to dilute solutions (<1 g/L) is the need to keep the aqueous/organic ratio ~ 1 to provide satisfactory phase disengagement which limits concentration enrichment (Kentish and Stevens, 2001; Ritcey and Ashbrook, 1978).

Air-Assisted Solvent Extraction (AASX) differs from conventional solvent extraction by introducing the solvent as a thin layer on a bubble. The concept was first demonstrated in the case of kerosene-based solvent (Tarkan and Finch, 2005a; Chen et al., 2003). It offers the potential of high aqueous/organic ratio while maintaining excellent phase separation, introducing the possibility of treating dilute solutions: AASX becomes a concentration process while retaining the selectivity of SX. Tarkan and Finch (2005a) found a convenient way to coat bubbles was from a solvent foam. Once formed, the foam is injected through a capillary to produce a stream of solvent-coated bubbles. The foam properties of kerosene-based solvents were shown to be readily controlled by silicone oil (Tarkan and Finch 2005b). By measuring solvent consumption for a known number of bubbles of known size, the coating (film) thickness was estimated as 3 μm

(Tarkan and Finch, 2005a). The thickness is an important parameter to control and optimize the process.

The technical application of thin films is increasingly accompanied by development of film characterization techniques (Piegari and Masetti, 1985; Dyson, 1958). Infra-red analysis is used here to investigate film composition and interferometry is used to estimate film thickness.

Film thickness measurement with reflected light interferometry has been well established (Hecht, 2002; Lyklema et al., 1965; Princen and Mason, 1965). More recently, transmission techniques in the UV-visible region have been used specifically for soap bubble films (Sarma and Chattopadhyay, 2001; Chattopadhyay, 1999; Huibers and Shah, 1997) and films formed by blowing air bubbles in frother[1] solutions (Gélinas et al., 2005).

In both, the interference pattern showed a film composed of two layers: an outer "free" water layer and an inner "bound" layer. The outer layer remained roughly constant in thickness over the bubble lifetime, apparently due to a balance of gravity-driven drainage and restoring flow driven by the Marangoni effect. The inner layer reflected structural effects imposed on the water by the polar group(s) of the adsorbed surfactants. The thickness of this layer diminished with time to a critical rupture thickness that defined the film lifetime.

The techniques were adapted to the current application: thickness and composition of the solvent layer on an air bubble blown in kerosene-based solvents.

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[1]Frothers are a class of surfactants, typically alcohols, polyglycols and polyglycol ethers, used in flotation to retard bubble coalescence.

5.3. Experimental Section

5.3.1. Materials

The chelating extractants (LIX 973N and LIX 622 from Cognis) kerosene (Fisher Scientific) and silicone oil (SIGMA) were used to form the solvents investigated. The chemical composition of the extractants is given in Table 5.1. Unless otherwise stated, the solvent contained 1.5 ppm silicone oil, an amount determined previously to maximize solvent foaming properties (Tarkan and Finch, 2005b).

Table 5.1. Chemical composition of LIX extractants (MSDS)

LIX	X (%)	Y (%)	Pet. Distill. (%)	Alcohols (%)	Nonylphenol (%)
973N	<46	<18	>30	--	<6
622	<65	--	>11	<20	<4

X: Benzaldehyde, 2-Hydroxy-5-Nonyl Oxime; **Y**: 5-T-Nonyl-2-Hydroxyacetophenone, Oxime

5.3.2. Methods

a) Bubble cell

A schematic of the spectroscopy cell is shown in Figure 5.1. The custom-made glass cell houses a central bubble pedestal and two sapphire discs ($\varnothing$ 33 mm) mounted on wall ports as transmission windows. Removing the glass lid allows easy access for bubble generation. The accessory is placed inside the sample chamber of either a Bruker FT-IR spectrophotometer (wavenumber range 4500-1500 cm^{-1}) or a Genesys 10 Scanning Thermoelectron UV-Visible spectrophotometer (wavelength range 1100-190 nm) for spectra recording. In the UV-Visible study the wavelength scan speed was approximately

900 nm/min, and the nominal resolution of the IR spectra was 4 cm^{-1}. An empty cell was

used to record background spectra.
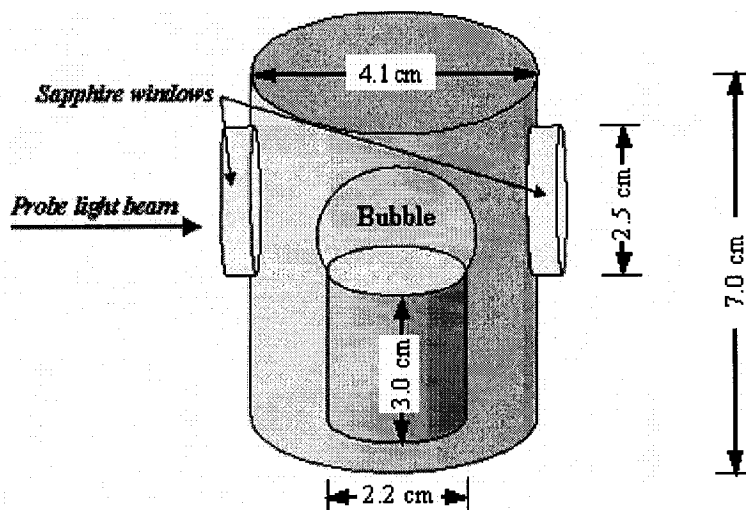
Figure 5.1. Schematic of bubble holder

b) Bubble generation

About 0.5 mL of solvent was placed onto the bubble holder and a single bubble

was blown manually using a disposable plastic pipette. Bubbles of ∅ ~20 mm were

created (for both UV-vis and FT-IR), a size appropriate for the probe beam to travel

through the center of the bubble. The experiments were performed at room temperature

(21-25°C), without humidity control.

c) Layer thickness calculation

The film thickness (*D*) is determined from the interference pattern generated in

the UV-vis region according to Equation 5.1 (Huibers and Shah, 1997),

$$D = (2v)^{-1}$$ (5.1a)

$$v = \left[\frac{n(\lambda_1)}{\lambda_1} - \frac{n(\lambda_2)}{\lambda_2} \right] / N_{cyc}$$ (5.1b)

where N_{cyc} is the number of cycles between wavelengths λ_1 and λ_2, n is the refractive

index of the film material (determined using a Fisher Abbe Model benchtop refractometer

(Fisher Scientific)). To measure the layer thickness, at least a single maximum and a

minimum (half a cycle) in the spectrum are necessary, although theoretically, the

minimum thickness can be measured using a single maximum ($D = \lambda / 4n$) (Huibers and

Shah, 1997).

In the case of kerosene (n = 1.44 (Speight, 2001)), the minimum thickness that

can be measured by the UV-vis instrument used here (where λ_{min} = 190 nm) is,

respectively, 33 and 40 nm for the single maximum and half cycle cases. For the present

study, the thickness calculations used two maxima.

5.4. Results and Discussion

5.4.1. Layer Thickness: UV-visible study

5.4.1.1. Interpreting Interference Patterns

a) Example patterns

Figure 5.2 shows a typical evolution of spectra over a period of 10 minutes.

Initially (ca. 5 s)[2] only a high frequency pattern is seen. At 2 min a lower frequency

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[2] This is the estimated time after bubble formation when the first readings (UV-vis or IR) could be made.

pattern becomes evident which decreases in frequency with time (5, 10 min). The high frequency pattern remains essentially constant.
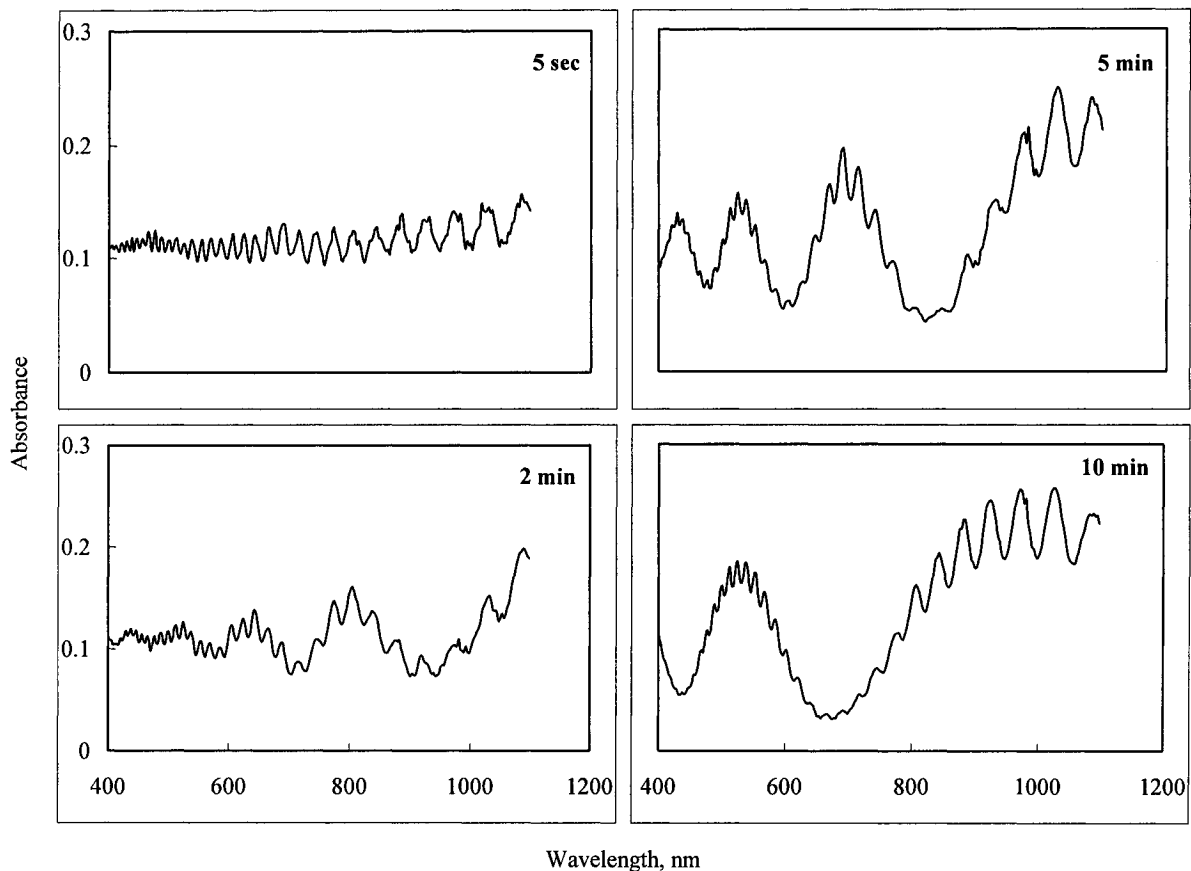
Figure 5.2. Interference pattern for 1:3 LIX973N/kerosene bubble as a function of time after formation

This behavior is similar to that observed for soap and frother bubble films. Interpreting in the same way, the high frequency pattern is associated with an outer "free" layer and the lower frequency pattern with an inner "bound" layer. The free layer remains roughly constant with time (again, attributed to a balance of gravity and Marangoni effect driven flows) with a calculated thickness of 6-8 μm, interestingly similar to that

determined for the soap and frother films (Gelinas et al., 2005; Sarma and Chattopadhyay, 2001).

The outer layer is not considered of direct concern in the present context. The AASX process involves injecting a solvent-coated bubble into water, not air, therefore a free solvent layer is unlikely to form. Consequently attention will focus on the low frequency pattern, i.e., the bound layer.

b) Sample thickness calculations

Figure 5.3 shows how the low frequency pattern is constructed using the result in Figure 5.2 for 5 min. This fitting procedure is suggested by Sarma and Chattopadhyay (2001). The refractive index was determined for each solvent tested with the results given in Table 5.2.
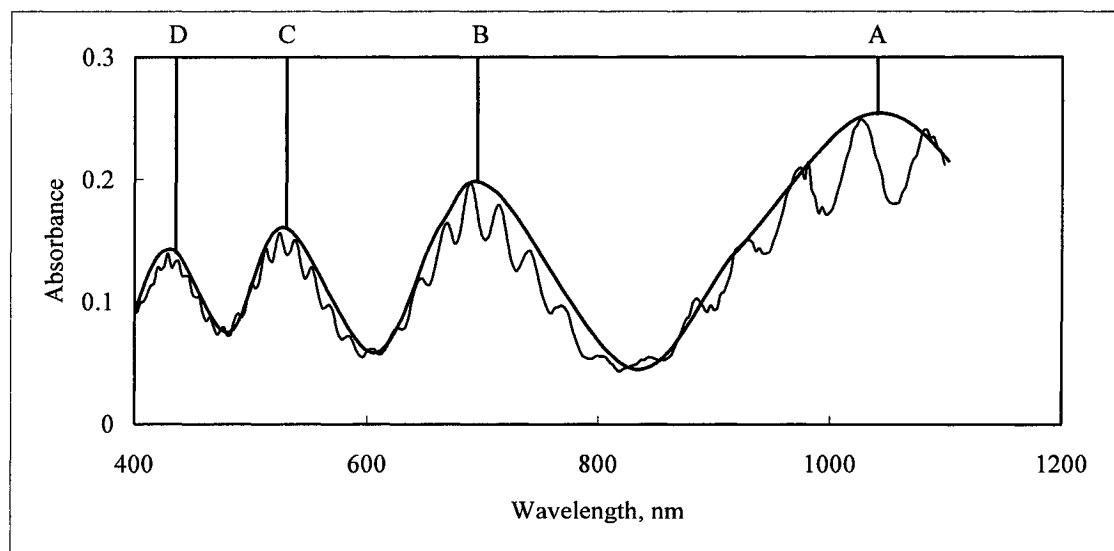

Figure 5.3. Example interference pattern: 1:3 LIX/kerosene at 5 min after bubble generation

Table 5.2. The refractive index of solvents

Solvent	Refractive Index	Solvent	Refractive Index
Water[1]	1.333[1]	Kerosene	1.437
1:9 LIX973N/kerosene	1.443	1:9 LIX622/kerosene	1.442
1:3 LIX973N/kerosene	1.452	1:3 LIX622/kerosene	1.450
1:1 LIX973N/kerosene	1.468	1:1 LIX622/kerosene	1.464

[1]Value corresponds to the literature (Lide, 1994)

Table 5.3 gives the results of selecting a variety of combinations of maxima and corresponding number of cycles. The mean is 761 nm with a standard deviation of 30.7 nm, i.e., a relative standard deviation of ca. 4% which is taken as the measure of precision. Subsequently, thickness calculations used the two maxima-based procedure. Applying this, the thickness of the film in Figure 5.2 is calculated to decline from > 4100 nm at 5 s to 1180 nm at 2 min, 760 nm at 5 min and 450 nm at 10 min.

5.4.1.2. Effect of Variables

a) Silicone oil and extractants

The importance of silicone oil was clearly revealed when trying to compare the layer thickness of kerosene alone and with silicone oil. In the former, a bubble could not be generated but bubbles were readily blown with 1.5 ppm silicone oil present, giving an initial thickness of ca. 2100 nm and lifetimes greater than 5 min.

Previous work had shown that LIX extractants imparted some foaming properties to kerosene (Tarkan and Finch, 2005b). A bubble could be blown using 1:1 LIX 973N/kerosene with no silicone oil, giving an initial thickness of ca. 300 nm and a film

lifetime of ca. 1.5 min. For ratios less than 1:1 without silicone oil the film was too thin to produce two maxima, indicating a thickness less than 150 nm.

Table 5.3. Sample calculations for layer thickness

Cycle*	Number of Cycles, N_{cyc}	λ_1	λ_2	Layer Thickness (D), nm
A-B		690	1029	721
B-C	1	525	690	756
C-D		429	525	807
A-C	2	525	1029	738
B-D		429	690	781
A-D	3	429	1029	760
Mean ± Standard Deviation				761 ± 30.7

* Letters refer to Figure 5.3.

Compared to silicone oil, therefore, the extractants produced limited films, confirming the need for silicone oil. Consequently, from here on all solvents, including reference to "kerosene alone", contain 1.5 ppm silicone oil.

b) Solvent Composition

The effect of solvent composition was investigated using two extractants (LIX 973N and LIX 622) at three LIX/kerosene ratios (1:9, 1:3 and 1:1). The results as a function of time are given in Figure 5.4.
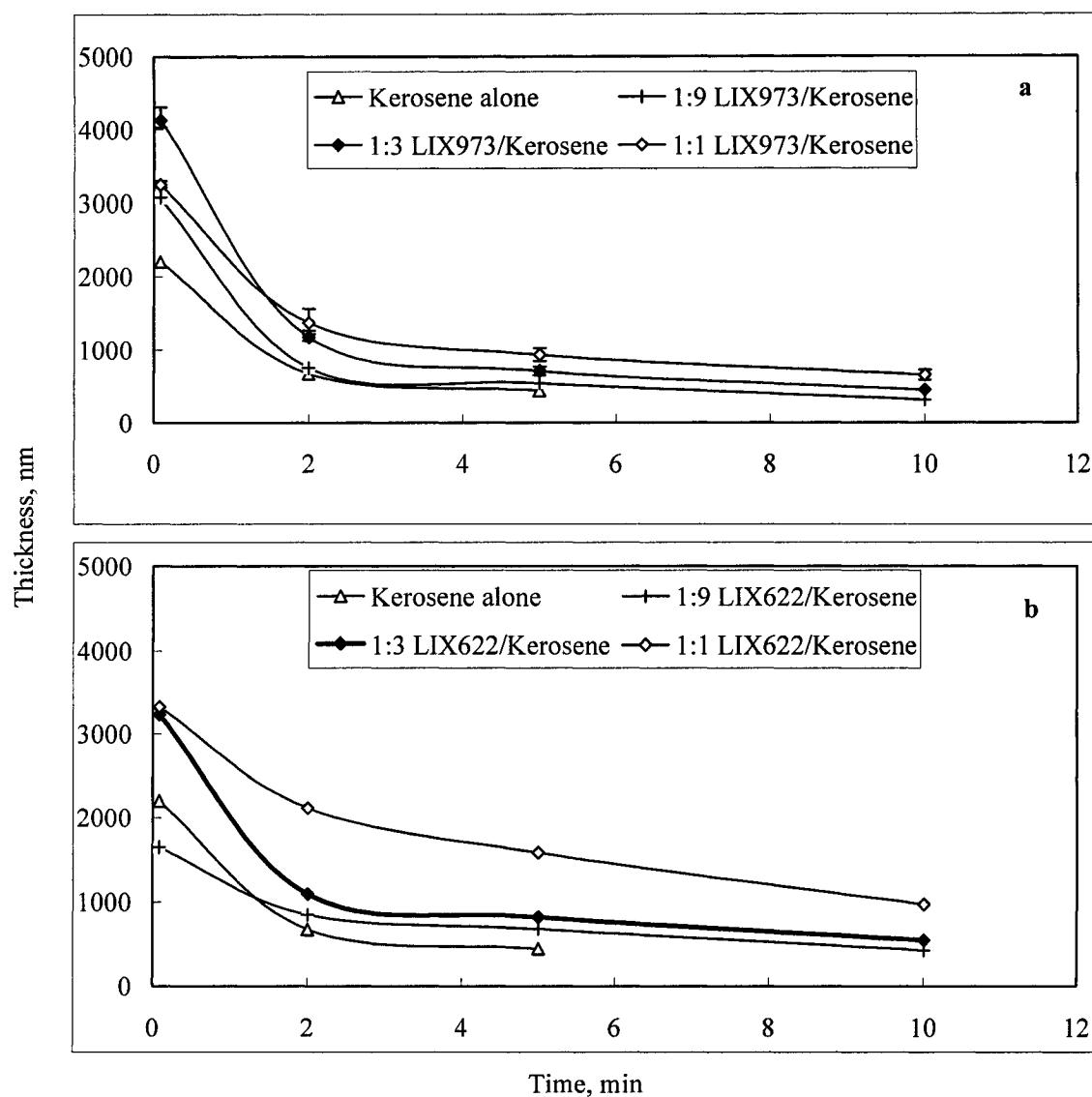
Figure 5.4. Solvent layer thickness with time as a function of solvent composition. (a) LIX973N/kerosene and (b) LIX622/kerosene

The general features show an initial (5 s) solvent thickness ca. 2-4 μm, which decreases sharply over the first 2 minutes and thereafter decreasing slowly. With LIX present the bubbles remained stable up to at least 10 minutes reaching a thickness < 1 μm and in some cases < 500 nm. The result for kerosene alone could be followed only to 5 min as the thickness became too thin to meet the two maxima criteria. The LIX

extractants do therefore enhance the film in addition to the silicone oil. The same observation was made with regard to foaming properties (Tarkan and Finch, 2005b). Compared to bubbles generated in frother solutions (Gelinas et al., 2005) the films here are much more stable.

Comparing the two LIX types, the LIX973N gave higher initial thickness and the LIX 622 a slower rate of decrease, most notable when comparing the two at 1:1 LIX/kerosene. The origin of difference must lie in the chemical composition but for these commercial products, there is some variability (Table 5.1). There is, however, little difference in foaming properties between the two solvents (Tarkan and Finch, 2005b). Future work will use extractants with better defined chemistries.

c) Comparison with indirect estimation of film thickness

An indirect estimate of film thickness had been made previously by counting bubbles of known size (4.4 mm diameter) in an AASX set-up and measuring solvent consumption (Tarkan and Finch, 2005a). For 1:1 LIX973N/kerosene the calculation gave around 3 µm. This corresponds to the initial thickness determined here, despite the differences between the two experimental systems. This lends credence to the present set-up providing a reasonable simulation of the fundamental requirement of AASX, solvent coating of a bubble.

5.4.2. Composition: FT-IR Studies

The study was carried out using 1:1 LIX 622/kerosene, 1:9 and 1:1 LIX973N/kerosene and kerosene alone. The measurements were made as soon as the bubble was generated (~ 5 s) (Figure 5.5) and in the case of 1:1 LIX 973N/kerosene, over time (Figure 5.6).

All solvents show the same peaks, a cluster between 2850 and 2950 cm^{-1}, which corresponds to the CH_2 and CH_3 groups of kerosene (Bellamy, 1978). In the presence of LIX extractants, there is a peak at 3357 cm^{-1} (Figure 5.5).

With time (Figure 5.6) the peak heights diminish. Taking the peak height at 3357 cm^{-1} as indicative of concentration of extractant and the peak at 2923 cm^{-1} as indicative of concentration of kerosene (the CH_2 and CH_3 groups contribution from extractant is negligible) the ratios are roughly constant ((a) 9.0, (b) 9.5, (c) 7.4, and (d) 11.8). This indicates that composition does not change with time. A constant composition is an advantage for the AASX process as the solvent-coated bubble can be expected to perform consistently regardless of film thickness.
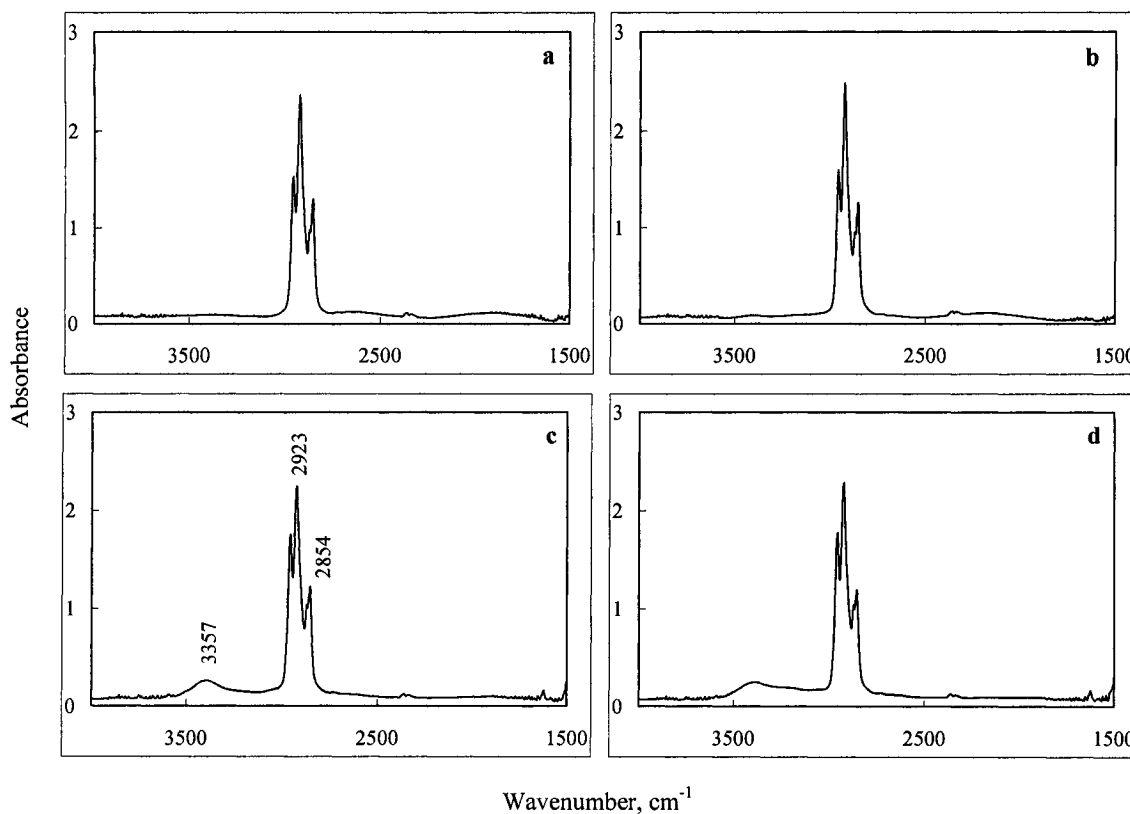
Figure 5.5. FT-IR spectra after ~ 5 s for: (a) kerosene alone, (b) 1:9 LIX973N/kerosene, (c) 1:1 LIX973N/kerosene, (d) 1:1 LIX622/kerosene

Consideration was given to locating silicone oil in the spectra. The combination of low concentration, overlapping of the hydrocarbon groups with those of kerosene and noise in the characteristic range for silicone oil (1500-700 cm^{-1}) (Taranekar et al., 2002) precluded unambiguous identification. Silicone oil probably stabilizes the film by combination of viscosity and surface tension effects, as discussed with regard to its impact on foaming (Tarkan and Finch, 2005b), but the film study throws no new light on the mechanism.
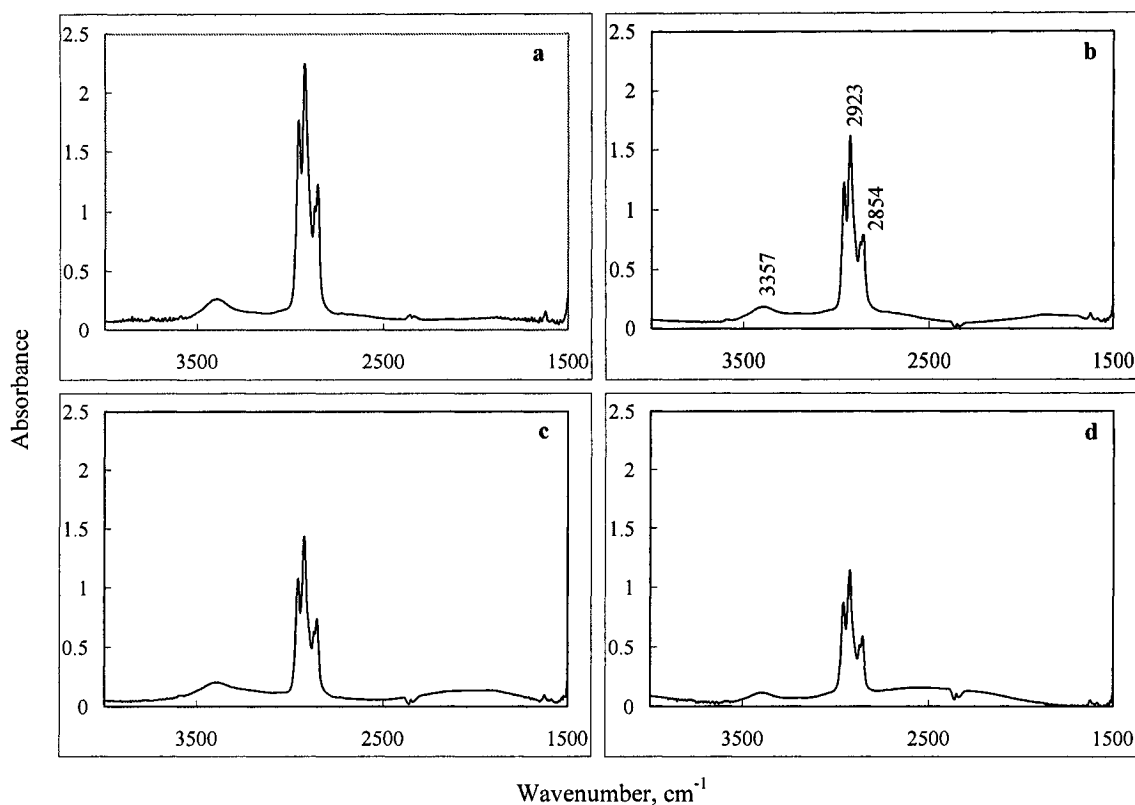
Figure 5.6. FT-IR spectra as a function of time for 1:1 LIX973N/kerosene (a=1 min, b=3 min, c=4 min, d=6 min after bubble generation)

5.5. Conclusions

Bubbles were formed in LIX/kerosene solvents to study film thickness by interferometry and film composition by infra-red spectroscopy. The work was conducted to explore aspects of the Air-Assisted Solvent Extraction (AASX) process which employs solvent-coated bubbles. The following observations were made.

1.   Stable bubble films were formed only in the presence of silicone oil (1.5 ppm), as required to promote solvent foams in the AASX process.

2.   The film comprises two layers, an outer layer, which remains constant in thickness and an inner layer, which decreases in thickness with time. The inner layer is considered relevant to the AASX process.

3.   For LIX/kerosene solvents, the thickness was initially ca. 2-4 μm decreasing over 10 minutes to << 1 μm. The initial thickness corresponds to prior indirect estimates of the coating thickness.

4.   The chemical composition was invariant with time.

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CHAPTER 6

Scaling Up[*]

6.1. Abstract

The Air-Assisted Solvent Extraction (AASX) concept uses a solvent-coated bubble to contact the organic and aqueous phases. Compared to conventional solvent extraction, a high contact area can be created using less solvent and the buoyancy provided by the air core promotes phase separation. A solvent-coated bubble is generated by forming a foam which is extruded through an orifice. As steps towards generating bubble swarms, orifice properties (material, diameter and orientation) were explored. Preliminary results for a multi-bubble unit based on the findings are given.

6.2. Introduction

Solvent extraction is widely used in primary metal extraction, notably for Cu and U (Ritcey and Ashbrook, 1978; Bullock and King, 1975; Flett et al., 1973). Solvent extraction has been included as an option to treat wastewater (Reed, 1998), where metal

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[*] This chapter has been submitted for presentation at XXIII International Mineral Processing Congress, September 2006, as: "Tarkan, H. M., Finch, J. A., Multi-bubble production in the air-assisted solvent extraction process"

concentrations are relatively low. A major limitation applying the process to dilute solutions is the need to keep the aqueous/organic (A/O) ratio ~ 1 to provide satisfactory phase disengagement. Other factors include loss of organic and the capital outlay (Kentish and Stevens, 2001; Ritcey and Ashbrook, 1978).

Air-Assisted Solvent Extraction (AASX) differs from conventional solvent extraction (SX) by introducing the solvent as a thin layer (ca. 2-4 μm) on a bubble. The concept was first demonstrated in the case of kerosene-based solvent (Tarkan and Finch, 2005a; Chen et al., 2003). It offers the potential of high A/O ratio (>>1:1) while maintaining excellent phase separation (Tarkan and Finch, 2005a). AASX introduces the possibility of treating dilute solutions (<1 g/L).

Tarkan and Finch (2005a) found one way to coat bubbles consistently was from a solvent foam. Once formed, the foam is injected through a capillary to produce a stream of coated bubbles. To control the foaming properties a range of additives was tried (Tarkan and Finch, 2005b). Silicone oil was identified as suited to controlling the foaming properties of kerosene-based solvents without affecting their extraction and stripping properties. The optimum silicone oil concentration was 1.5 ppm. This role of silicone oil was further demonstrated in thin film studies on bubbles blown in solvent (Tarkan et al., 2005)

The set-up to date, shown in Figure 6.1, produces a single stream of bubbles. The aqueous solution is held in column "A", inside diameter 5 cm. Solvent foam is produced in chamber "B" connected to "A" by capillary "C", internal (orifice) diameter 2.5 mm and external diameter 7.5 mm. Air (typically 4 mL/min) is introduced via "D" to form the foam which passes through the capillary. The bubbles generated are ca. 4.4 mm in

diameter, and the solvent coating, from a combination of direct (Tarkan et al., 2005) and indirect (Tarkan and Finch, 2005a) measurements, is ca. 2-4 μm thick. The solvent is replenished via "E". The obvious need is to scale-up to bubble swarms.
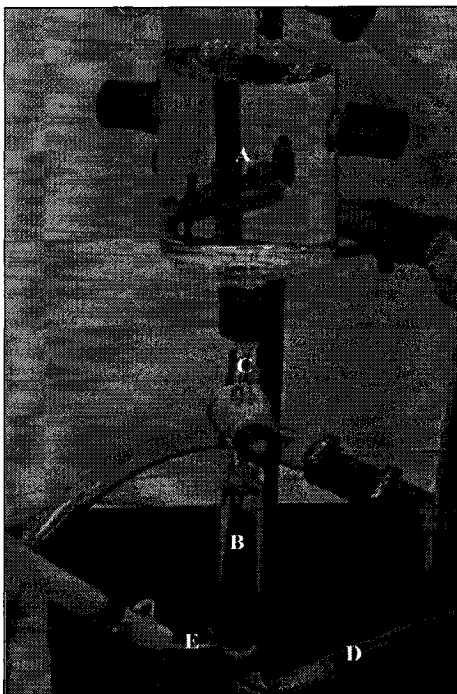

Figure 6.1. AASX experimental column producing a single stream of solvent-coated bubbles (Tarkan and Finch, 2005a)

In the literature, there are some reports on generating oil-coated bubble swarms including using a glass frit (Liu et al., 2002), an atomizer (Gomez et al., 2001; Maiolo and Pelton, 1998; Misra and Anazia, 1987) and vapour deposition (Wallwork et al., 2003; Peng and Li, 1991).

Some trials using glass frit were conducted but it was difficult to conclude that bubbles were consistently coated and difficult to prevent errant solvent droplet formation. Similar difficulties were envisaged using the other techniques. As a first step, therefore, a

design based on replicating the successful single bubble generator was considered; referred to as a "multi-bubble unit". As part of this exercise, orifice dimensions, material (glass vs. Teflon) and orientation (capillary vertical to horizontal) were examined. The findings are outlined under "Exploratory Tests". Based on these findings a multi-bubble unit was constructed and tested on dilute (50 – 500 mg/L) copper sulphate solutions.

6.3. Exploratory Tests

6.3.1. Orifice Size

The 2.5 mm orifice (of the single bubble generator) in vertical capillary orientation produces bubbles ca. 4.4 mm and a solvent specific surface area of ca. 3000 cm^{-1} (Tarkan and Finch, 2005a). Smaller bubbles would give potentially higher solvent specific surface area. It became apparent that to control coated bubble production free of errant droplets, the orifice size of capillary "C" had to be changed in tandem with the chamber "B" diameter. The balance is approximately as follows: to control bubble production and avoid solvent droplet formation, the line velocity in "C" should be less than ca. 1.4 cm/s, and to produce foam (in chamber "B") the superficial air velocity should be greater than 0.033 cm/s. The design of "B" and "C" must respect these criteria. Rather than pursue these aspects, the current dimensions were retained.

6.3.2. Material

The material of construction is of interest to commercialize AASX. Specifically in the case of capillary "C", two materials, Teflon and glass, were tested to give a wide

range in critical surface tension of wetting, γ_c (γ_c for glass = 170 mN/m and for Teflon = 18 mN/m) (Zisman, 1964).

Despite the large difference between water surface tension, 72.8 mN/m (i.e., as exerted by the solvent-free bubble) and solvent surface tension, ca. 26 mN/m (Tarkan and Finch, 2005a) (i.e., as exerted by the solvent-coated bubble), it was evident that both free and solvent-coated bubbles spread easily over the Teflon surface (Figure 6.2) producing large bubbles while in the case of glass they did not. A tentative conclusion is that for the capillary a material with a high critical surface tension of wetting (and probably a knife edge) is required. This will be pursued in later studies. For the current work, glass was again used.

Figure 6.2. Spreading of solvent-coated bubble on Teflon capillary set at 10° to the horizontal to show the spreading effect (inside and outside diameter of orifice 1 and 7 mm, respectively)

6.3.3. Orifice Orientation

The size of bubble at low air flow rate is determined by a balance of buoyancy and capillary (attachment) forces (Park et al., 1977). As the orientation of the capillary is changed, the attachment forces will be effective on only part of the perimeter and the buoyancy force needed to detach the bubble will be lower (Datta et al., 1950). Therefore, the bubble diameter will be smaller.

Two identical glass capillaries, one vertical and one horizontal, were compared. The volume equivalent diameters of bubble, measured by collecting a known number in a graduated cylinder, were 4.4 and 3.4 mm, respectively. The horizontal capillary arrangement otherwise performed the same; errant droplets were avoided and control of bubble frequency could still be exercised. The horizontal arrangement also opened the way for a compact, multi-bubble unit.

6.4. Design of Multi-Bubble Unit

Using the above findings, a custom-made glass multi-bubble unit was constructed. As seen from Figure 6.3a, the capillaries were inserted horizontally around the perimeter of column "A". This made for a more compact geometry than attempting multiple vertical injection sites from the bottom. The set-up otherwise is basically a replication of the single bubble unit. Units with up to eight injection site units have been built (Figure 6.3b).

The column "A" is 5.6 cm diameter by 33 cm high. In the 4-capillary case (Figure 6.3a), the capillaries are situated 2 cm above the column base and project 2 cm in from the wall. By operating one or two opposing capillaries, 1- and 2-unit cases are included.

In the 8-capillary case (Figure 6.3b), a second array of 4 capillaries is set 3.5 cm above

the base of the column at an angle to the first set and projecting 1 cm in from the column

wall. All the capillaries are identical, 2.5 mm inside and 7.5 mm outside diameter. The

air-flow rate to each chamber, where foam is produced ("B" in Figure 6.3a), is controlled

by individual air-flow meters. Coated bubble generation is identical to the single bubble
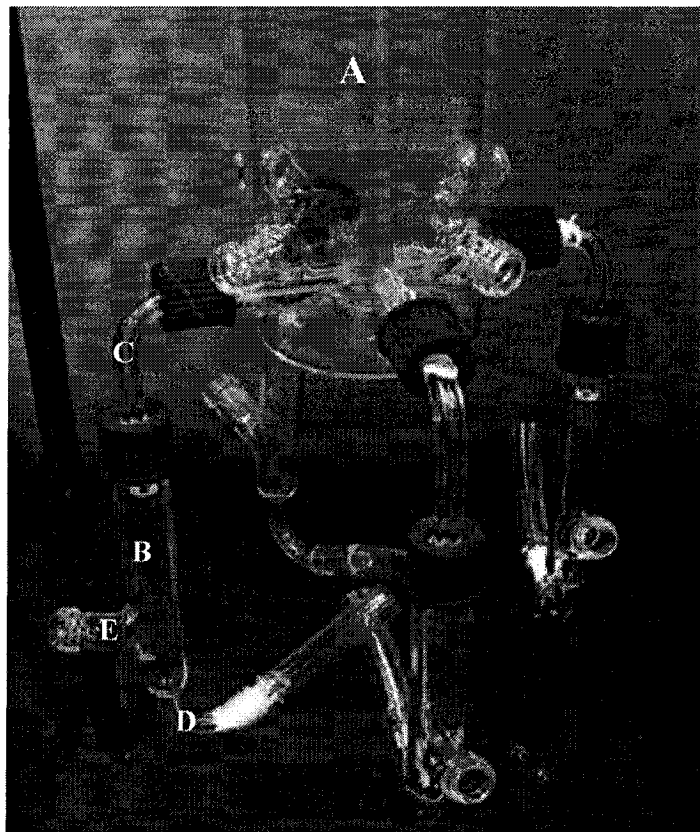
case.

Figure 6.3. (a) A 4-injection site multi-bubble unit (general view)

Compared to the previous attempts to produce coated-bubble swarms mentioned

in the "introduction", the advantage here is that the bubbles are created in a controlled

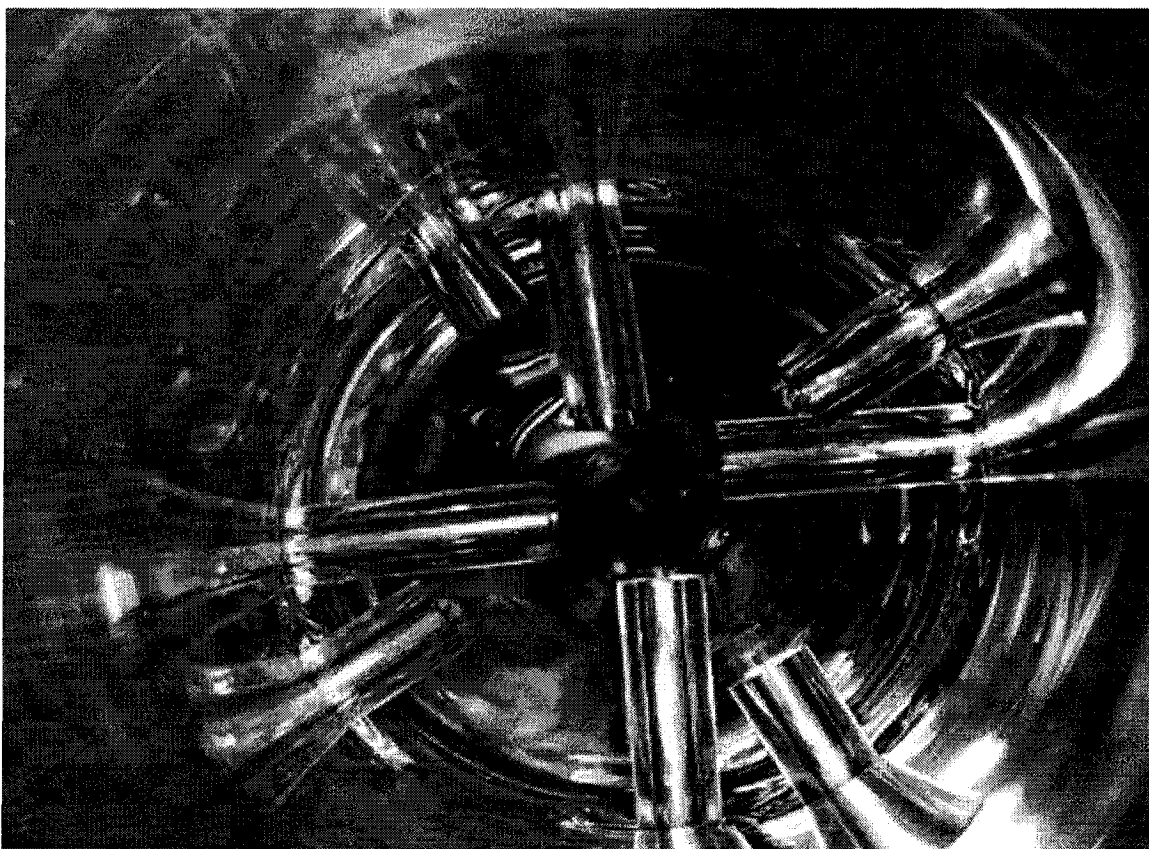manner at a known rate and size, with reproducible coatings.

Figure 6.3. (b) An 8-injection site multi-bubble unit (top view)

6.5. Demonstration Tests

6.5.1. Reagents and Procedure

Solvent was prepared from a chelating type extractant, LIX 973N (received from Cognis), diluted in kerosene. Reagent grade $CuSO_4.5H_2O$ (Fischer) was used to prepare the aqueous solutions. The foaming agent was 1.5 ppm silicone oil (SIGMA) and was used in all solvents prepared. The reagents were used as received.

Analysis for copper was by atomic absorption spectroscopy (Perkin Elmer Model 3110). Aqueous solutions were prepared by buffering at pH 2.1 with 0.2 M NaOH, 0.04 M acetic acid, 0.04 M phosphoric acid and 0.04 M boric acid (Dean, 1992). In each

experiment, the solution volume was 500 mL, and the air-flow rate 4 mL/min to each generator.

6.5.2. Effect of Number of Orifices

One, 2, 4 and 8 orifices were tested using a 1:4 LIX/kerosene solvent and an initial Cu concentration of 100 mg/L. The results are given in Figure 6.4.

As seen, Cu extraction for a given time increased with increase in number of orifices. This reflects the increase in total solvent consumption, which for the 1, 2, 4 and 8 orifices at 30 min was 0.9, 2, 3.4 and 7.1 mL, respectively. The corresponding aqueous to organic ratios (A/O), included in the Figure, decrease by approximately half for each consecutive case. This supports that the multi-bubble unit is functioning as a simple multiple of the single bubble case.
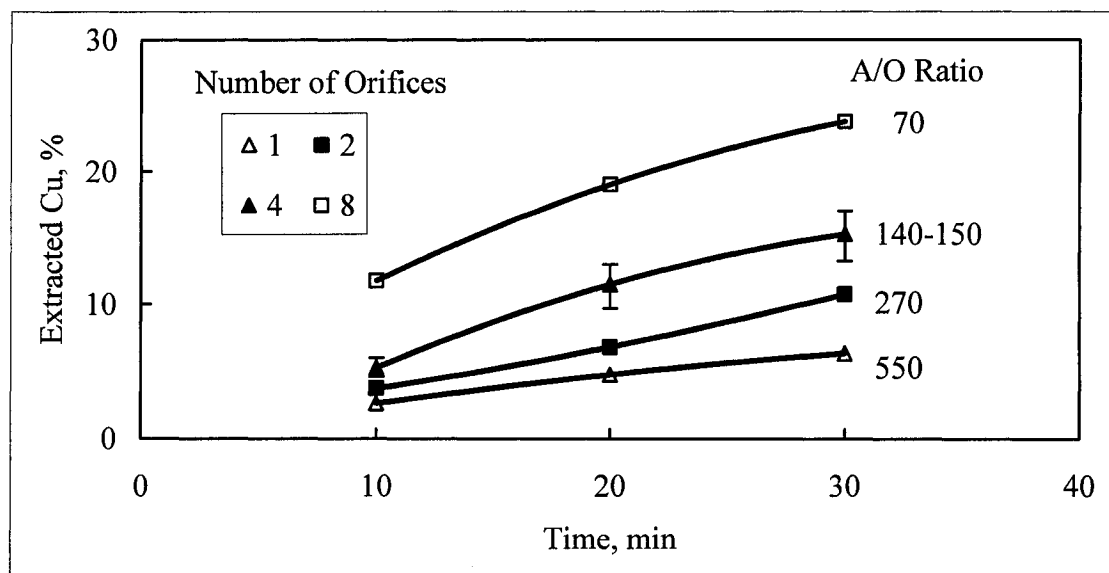

Figure 6.4. Effect of number of orifices on extraction of Cu ("Error bar" is the range of 3 replicates at each time for the 4-capillary case.)

6.5.3. Kinetic Analysis

The first order kinetic model (Equation 6.1) was used to analyze the results in Figure 6.4,

$$[M_t] = [M_0] \, exp \, (-kt) \tag{6.1}$$

where t is time, M_0 the initial copper concentration, M_t the copper concentration at time t and k is the reaction rate constant. The linear regression fit for each number of orifices is given in Figure 6.5.
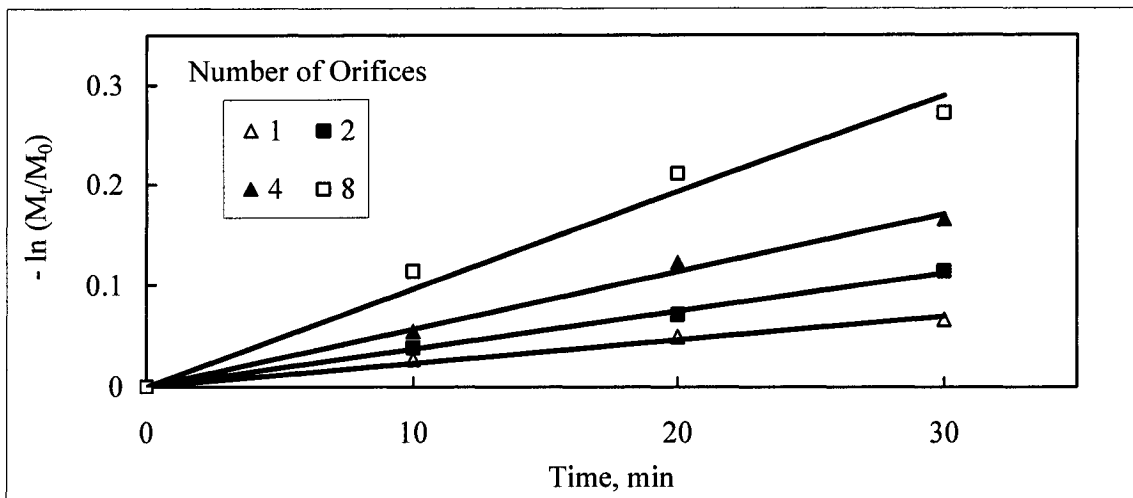

Figure 6.5. First-order kinetic model applied to multi-bubble unit data in Figure 6.4

The first order kinetic model fits the AASX data well, at least up to the 4-capillary case. The manual 8-capillary experiments were taxing, which may account for the poorer fit. However, there is also a significant change in concentration over the 30 min in this case and therefore potentially a change in rate controlling step.

Figure 6.6 shows the experimental relationship between k and number of orifices. The linear trend again supports that the multi-bubble unit is a successful replication of the single bubble unit. This type of analysis will be needed in scaling up the AASX process.
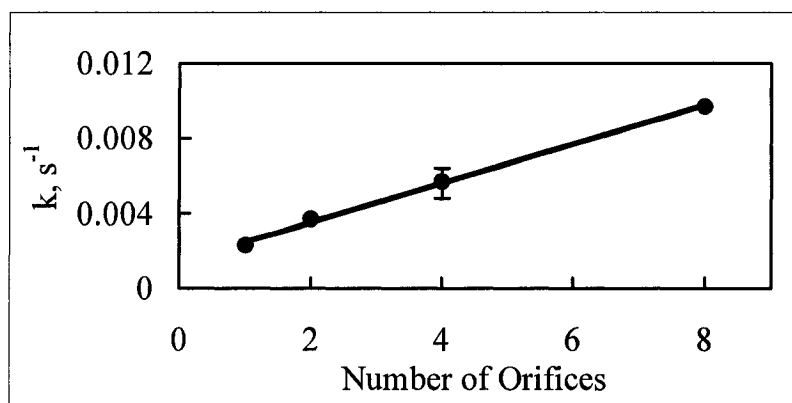

Figure 6.6. Effect of number of orifices on kinetic rate constant

6.5.4. Organic and Aqueous Phase Properties

The multi-bubble unit was also used to re-explore some properties of the system. Using this set-up shortens the test period, permitting variables – LIX/kerosene ratio and initial Cu concentration in this case – to be explored more conveniently.

6.5.4.1. LIX/kerosene Ratio

Previous extraction tests using LIX had been limited to 1:1 ratio with kerosene (Tarkan and Finch, 2005a) but use of silicone oil has extended the range. This is illustrated in Figure 6.7, where two LIX/kerosene ratios (1:1 and 1:4) were tested using the 4-orifice set-up. The initial Cu concentrations were 100 and 500 mg/L.
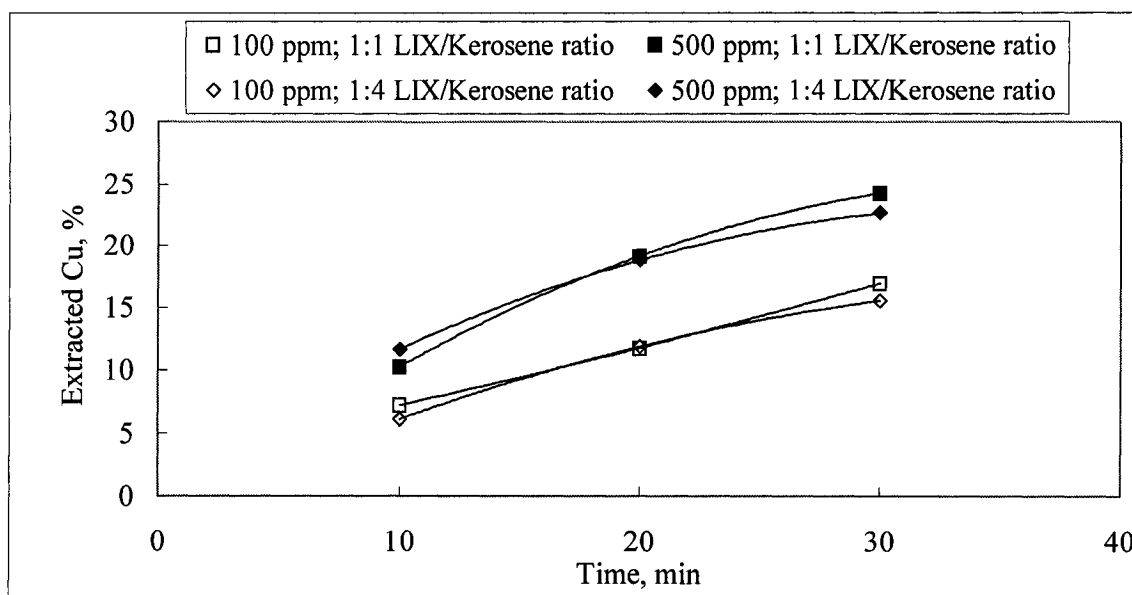
Figure 6.7. Effect of LIX/kerosene ratio on Cu extraction.

The solvent type did not have an effect. This probably reflects the short retention time of the bubble (< 1s) in the current set-up which prevents taking advantage of higher LIX concentrations. A re-designed column "A" to increase bubble retention time may enable full loading of the solvent to be approached and permit exploitation of high LIX/kerosene ratio. There is a practical constraint, however; while the high viscosity of 1:1 LIX/kerosene ratio is not a factor in AASX, it does pose an issue in stripping.

6.5.4.2. Initial Cu Concentration

Using the 4-orifice design and LIX/kerosene ratio 1:4, the effect of initial Cu concentration (50, 100, 250 and 500 mg/L) was investigated.
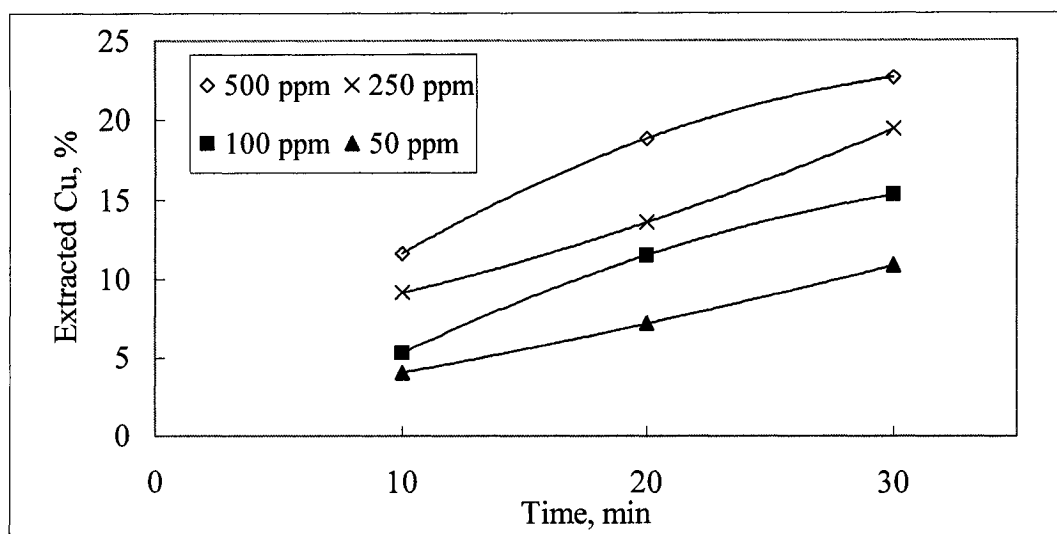
Figure 6.8. Effect of initial Cu concentration

The results indicated that the higher the Cu concentration, the higher the extraction (Figure 6.8). This means that the process is not truly first-order at least over this dilute concentration range. The observation needs to be pursued to select design parameters for scale-up. A future communication will address kinetic and mass transfer studies.

6.6. Conclusions

1. A multi-bubble unit was designed for the Air-Assisted Solvent Extraction (AASX) process by replicating the single bubble unit.

2. A compact multi-bubble set-up was made possible by employing horizontal capillaries. Units comprising up to 8 capillaries were built. With an orifice of 2.5 mm diameter, the horizontal capillary gave bubbles 3.4 mm diameter, smaller than the vertical arrangement (4.4 mm).

3.   Demonstration tests showed that the multi-bubble unit functioned as a simple multiple of the single bubble case.

4.   The multi-bubble unit is a step towards scaling up the AASX process. In the meantime, it provides a more convenient set-up to explore design and operating variables than the single bubble version.

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CHAPTER 7

Conclusions, Contributions, and Future Work

7.1. Conclusions

7.1.1. The Concept

Air-Assisted Solvent Extraction (AASX) is proposed to overcome some drawbacks of conventional solvent extraction for treating dilute streams by providing for high aqueous/organic ratios (A/O) (up to 75:1 was used), and consequently high concentration enrichment, while maintaining ease of phase separation (essentially instantaneous). The foaming properties of solvents can be used to generate coated bubbles. Solvent-coated bubbles of diameter 4.4 mm produced a calculated coating thickness of ca. 3 μm and a specific surface area of solvent of ca. 3000 cm^{-1}, which would require solvent droplets of ca. 20 μm to match.

7.1.2. Foaming Properties

Two flotation frothers (MP-99 and F-100 from Flottec) and a hydrocarbon reagent (Span 20) did not influence foaming properties of LIX 973N and LIX 622 1:1 with kerosene. Silicone oil up to 3 ppm did increase foam stability, which correlated with a sharp decrease in solvent surface tension.

D2EHPA/kerosene solvent initially showed insufficient foaming for AASX but addition of silicone oil corrected this. Silicone oil did not change the extraction/stripping properties of the solvents. Therefore, silicone oil has expanded the range of solvents applicable to AASX.

7.1.3. Film Properties

Bubbles were formed in LIX/kerosene solvents to study film thickness by interferometry and film composition by infra-red spectroscopy. The work was conducted to explore fundamental aspects of the Air-Assisted Solvent Extraction (AASX) process. Stable bubble films were formed only in the presence of silicone oil (1.5 ppm), as required to promote solvent foams. The film comprised two layers, an outer layer, which remained constant in thickness, and an inner layer, which decreased in thickness with time. The inner layer is considered relevant to the AASX process. For LIX/kerosene solvents, the thickness was initially ca. 2-4 μm decreasing over 10 minutes to << 1 μm. The initial thickness corresponded to the prior indirect estimates of the coating thickness (ca. 3 μm). The chemical composition was invariant with time.

7.1.4. Scaling Up

A multi-bubble unit was designed for the Air-Assisted Solvent Extraction (AASX) process by replicating the single bubble unit. A compact set-up was made possible by employing horizontal capillaries. With an orifice of 2.5 mm diameter, these gave smaller bubbles (3.4 mm diameter) than the vertical arrangement (4.4 mm). Demonstration tests showed that the multi-bubble unit did function as a simple multiple of the single bubble

case. The multi-bubble unit provides a more convenient set-up to explore design and operating variables than the single bubble version. It may provide a route to scaling up the AASX process.

7.2. Contributions to Knowledge

1. The Air-Assisted Solvent Extraction concept was expanded by the novel suggestion to exploit the foaming properties of solvents, considered a safer method than some proposed oil-coating techniques, such as vapour deposition.

2. Silicone oil was identified as a promising modifier to produce foam with kerosene-based solvents without affecting extraction or stripping properties.

3. The layer thickness measurement by interferometry was applied for the first time to a non-aqueous system.

4. A design of a multi-bubble unit based on replication of the single bubble version was successfully tested.

7.3. Suggestions for Future Work

1. In this study, kerosene, which is an aliphatic reagent, was used as diluent. The Air-Assisted Solvent Extraction (AASX) process was prompted as a means to treat dilute solutions such as acid mine drainage, which might contain bacteria that can degrade kerosene. Therefore, aromatic diluents should be investigated for use in AASX.

2. To further explore the mechanism of foaming and the properties of the thin film, a solvent with a well defined composition should be investigated.

3.   The advantage of producing solvent-coated bubbles from foam should be considered for other process, such as the flotation of naturally hydrophobic particles, e.g. ink, bitumen, coal.

4.   The single and multi-bubble units could serve as a basis for kinetic and mass transfer studies. No such studies relevant to a coating of reactive material on an air core were found in the literature.

APPENDIX A

AASX: Potential Application to Effluent Streams[*]

A.1. Abstract

Solvent extraction is one of the most widely used processes for the selective recovery of metal ions such as copper, uranium and zinc in hydrometallurgical applications. The main technical drawbacks are the energy to disperse the organic and create high contact area, time for phase separation, limitation to quite concentrated solutions (>1 g/L) and loss of reagents (which can pose environmental risk). The air-assisted solvent extraction (AASX) concept uses a solvent-coated bubble to contact the organic and aqueous phases. Compared to conventional solvent extraction, a high contact area can be created using less solvent and the buoyancy provided by the air core promotes phase separation. The intended application is for large volume, low concentration streams such as acid mine drainage to recover valuable metal ions. Solvent-coated bubbles are produced by first forming a foam. In these proof-of-concept experiments, the foam is injected through a capillary and a stream of solvent-coated

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bubbles is produced at the orifice and released into the aqueous solution. To control foam properties, silicone oil is found to be suitable for kerosene-based solvents. On a bubble size of 4.4 mm the coating thickness is estimated at 3 μm, equivalent to a solvent specific surface area of ca 3000 cm^{-1}, corresponding to solvent droplets of ca. 20 μm. Phase separation is sharp, and the air disengages easily to leave a solvent layer. Extraction tests on dilute Cu and Zn solutions illustrate the process.

A.2. Introduction

Large volumes of dilute metal bearing effluents are generated in the metal extraction and processing industries. An important example is acid mine drainage (AMD), produced when sulphide minerals are exposed to oxygen and water in the presence of certain microorganisms (Younger et al., 2002; Kuyucak, 2002; Feng et al., 2000; Demopoulos, 1998; Machemer and Wildeman, 1992). It is one of the major environmental challenges facing the mining industry. In Canada, collection and treatment of existing and potential AMD generating sites is estimated at over $(C) 3 billion (Tremblay and Hogan, 2001). The McGill group has focused on treatment techniques that incorporate metal recovery. Selective precipitation (Rao and Finch, 1992) and adsorption (El-Ammouri et al., 2000; Gelinas et al., 2000) from solution and selective leach/recovery options on sludge (Calzado et al., 2005; Gelinas et al., 2002; Felsher et al., 2000) have been considered.

Solvent extraction is widely used in primary metal extraction, notably for Cu and U (Rao et al., 2000; Ritcey and Ashbrook, 1978; Bullock and King, 1975; Flett et al., 1973). Solvent extraction has been included as an option to treat wastewater (Reed,

1998). The main difficulties in this application are: the need to keep the aqueous/organic (A/O) ratio ~ 1 to provide satisfactory phase disengagement (which means high solvent volumes and limited concentration enrichment), loss of reagents (also a potential environment concern) and the capital outlay (Kentish and Stevens, 2001; Ritcey and Ashbrook, 1978).

Air-Assisted Solvent Extraction (AASX) differs from conventional solvent extraction (SX) by introducing the solvent as a thin layer (a few μm) on a bubble. The concept was demonstrated in the case of kerosene-based solvent (Tarkan and Finch, 2005a; Chen et al., 2003). It offers the potential of high A/O ratio – up to 75:1 (Tarkan and Finch, 2005a) – while maintaining excellent phase separation. AASX becomes a concentration process introducing the possibility of treating dilute solutions (<1 g/L).

Tarkan and Finch (2005a and b) found a convenient way to coat bubbles was from a solvent foam. Once formed the foam is injected through a capillary to produce a stream of coated bubbles. To control the foaming properties a range of additives was tried (Tarkan and Finch, 2005b). Polymethylsiloxanes (e.g., silicone oil, polydimethylsiloxane) are strong surface active agents in organic media. They are used, for example, in controlling polyurethane foams (Hill, 1999; Snow and Stevens, 1999; Kanner and Prokai, 1971). Silicone oil was identified as being suitable in the case of kerosene-based solvent. The foaming action increases with silicone oil to a certain concentration (associated with the solubility limit) above which it behaves as a foam breaker (Kulkarni et al., 1996; Schwarz, 1970). In the present case, optimum concentration was ca. 1.5 ppm.

In this paper, the AASX concept is described and some operational parameters are investigated in the case of extraction of Cu with LIX 973N and Zn with D2EHPA.

A.3. Experimental Part

A.3.1. Materials

The solvents were prepared from a chelating type extractant, LIX 973N, (received from Cognis) and an acidic extractant, Di (2-Ethylexhyl) phosphate, (D2EHPA, received from SIGMA) diluted in kerosene. Reagent grade $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ (Fischer) were used to prepare aqueous solutions for extraction experiments. The foaming agent was silicone oil (SIGMA). All reagents were used as received.

A.3.2. Foaming Properties

Dynamic foam stability was measured using the Ross and Suzin (1985) "foam meter" method (Figure A.1) with dimensions: r = 1 cm; r_f= 5 cm; h = 1.7 cm; h_f= 7 cm. In all experiments the same amount of liquid (17.5 mL) at three air flow rates (4, 10, 15 cm^3/min) was used. The height of the foam for each experiment was measured after steady state was reached (~ 5 min), and the foam area, A_f was calculated (Equation A.1).

$$A_f = 1.047(h_f + 1.732r)^2$$ (A.1)

A.3.3. Extraction (AASX)

The set-up is shown in Figure A.2. The aqueous solution (150 mL) was held in the 5 cm diameter by 30 cm high column "A" (unless otherwise stated). Solvent foam was produced in column "B" (1.5 by 7.5 cm) situated below and connected to "A" by capillary "C", internal (orifice) diameter 2.5 mm and external diameter 7.5 mm. Air (4 cm^3/min) was introduced via "D" to form the foam which passed through the capillary.

The bubbles produced, roughly 124/min, were ca. 4.4 mm. The solvent were replenished via "E" regulated by an autoburette (radiometer, Copenhagen ABU 91). Analysis for copper and zinc was by atomic absorption spectroscopy (Perkin Elmer 3110).

A.4. Results and Discussion

A.4.1. Foaming Properties

The foam area produced by LIX 973N/kerosene (1:1) and D2EHPA/kerosene (1:9) alone and with silicone oil (1.5 ppm) is given Figure A.3. The results show the foam area increases significantly when using silicone oil.

A.4.2. Extraction

A.4.2.1. Effect of Silicone Oil

Extraction experiments were performed on solutions of 500 mg/L copper using LIX 973N and of 500 mg/L zinc using D2EHPA.

In the case of copper, the experiments were performed with 1:1 LIX 973N/kerosene ratio at pH = 2.10. Figure A.4 shows that silicone oil did not affect the extraction properties.

At the end of the experiment ca. 1.6 mL had been used, i.e., the A/O ratio is ~90:1. This would not be achievable in a conventional mixer settler due to poor phase separation. Knowing the consumption and counting the number of 4.4 mm bubbles involved an average coating thickness of ~ 3 μm was estimated. The corresponding specific surface area of solvent is ca. 3000 cm^{-1}. The size of solvent droplet required to

equal this specific surface area is ca. 20 μm, a size difficult to generate and one with poor
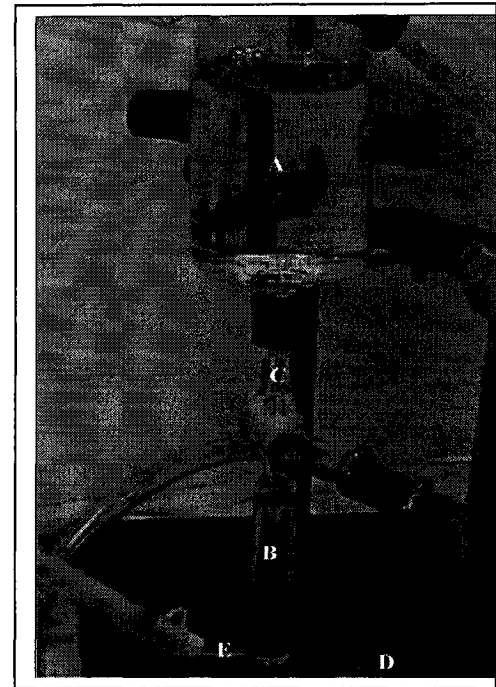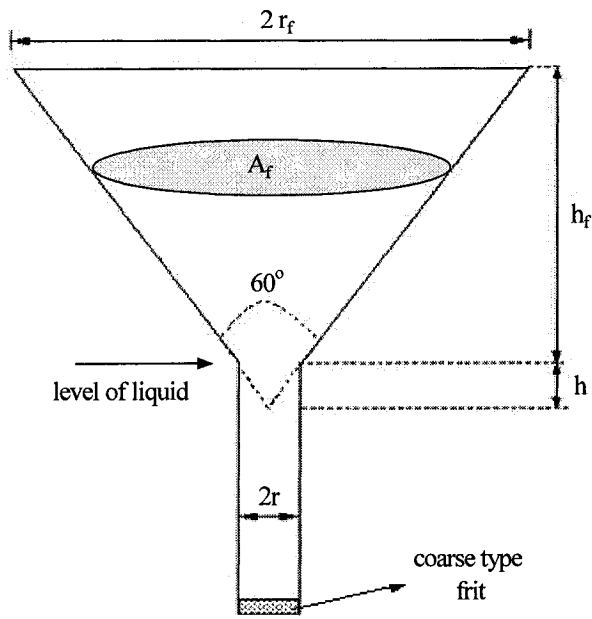
disengagement properties.

Figure A.1. The foam meter (based on Ross and Suzin (1985))

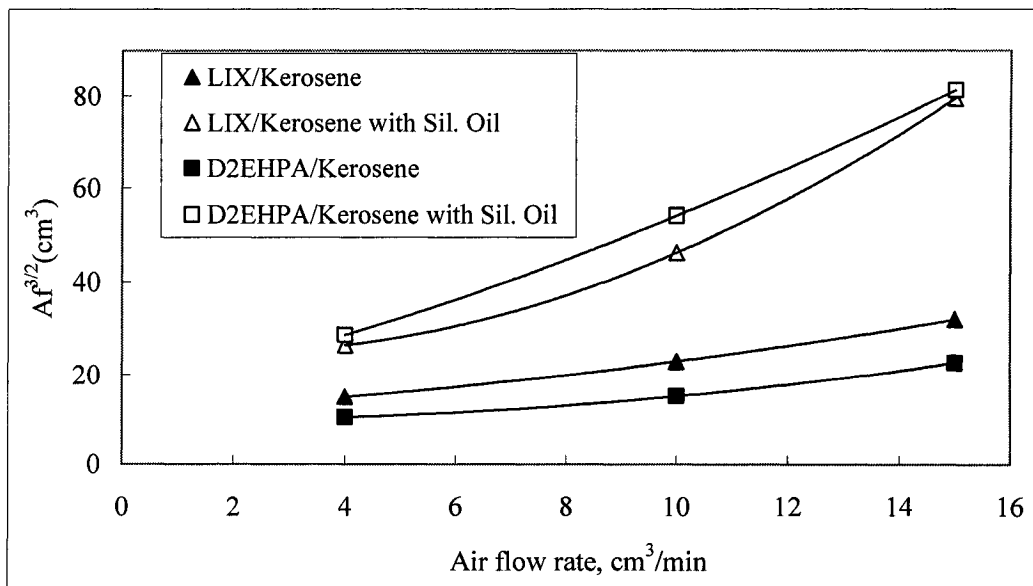**Figure A.2.** AASX experimental column (Tarkan and Finch, 2005). Bubble diameter is 4.4 mm.

Figure A.3. Effect of silicone oil (1.5 ppm) on foam area for the two solvents

For the experiments on zinc, the D2EHPA/kerosene ratio was 1:9, and the extraction pH was 2.3. It is evident (Figure A.5) that without silicone oil, there was no extraction because foaming was insufficient to generate a coated bubble. The silicone oil addition to D2EHPA/kerosene makes this extractant applicable to the AASX process.

In general, silicone oil extends the range in extractant/kerosene ratio and type of extractant amenable to AASX.
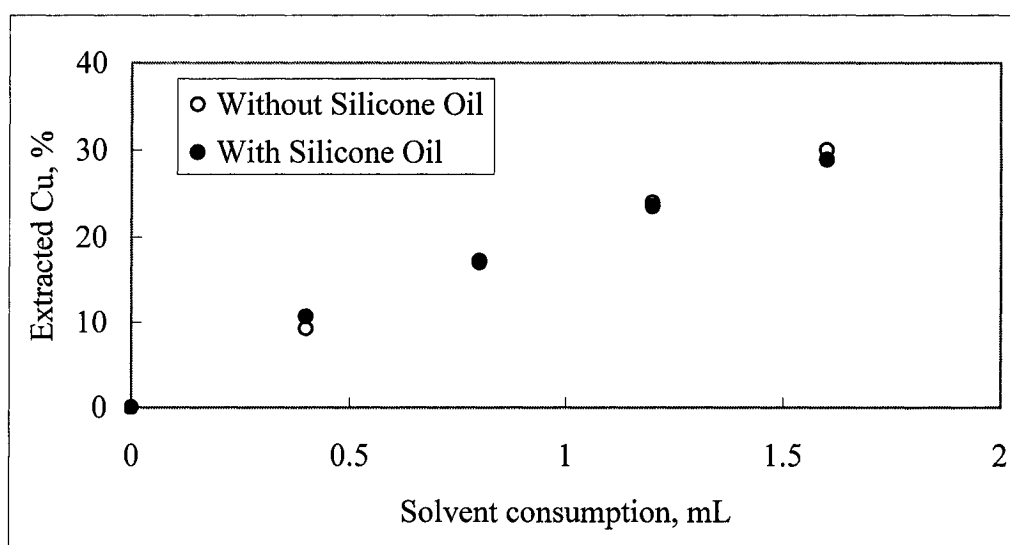
Figure A.4. Effect of silicone oil (1.5 ppm) on AASX with LIX973N

A.4.2.2. Effect of Solution Height and Initial Metal Concentration

To study the effect of solution height (or retention time of coated bubble), experiments using the same volume of aqueous solution (150 mL) were carried out in three different columns with diameters of 5, 3.1 and 2.2 cm, giving heights of 7.5, 19.8 and 39.5 cm, respectively. The coated bubble mean rise velocity was measured at 22.5 cm/s (Tarkan and Finch, 2005a) and, accordingly, the bubble retention times were

calculated. The organic was 1:1 LIX973N/kerosene with 1.5 ppm silicone oil. The initial

concentrations of aqueous solution were 500, 100, 50 and 25 mg/L Cu.
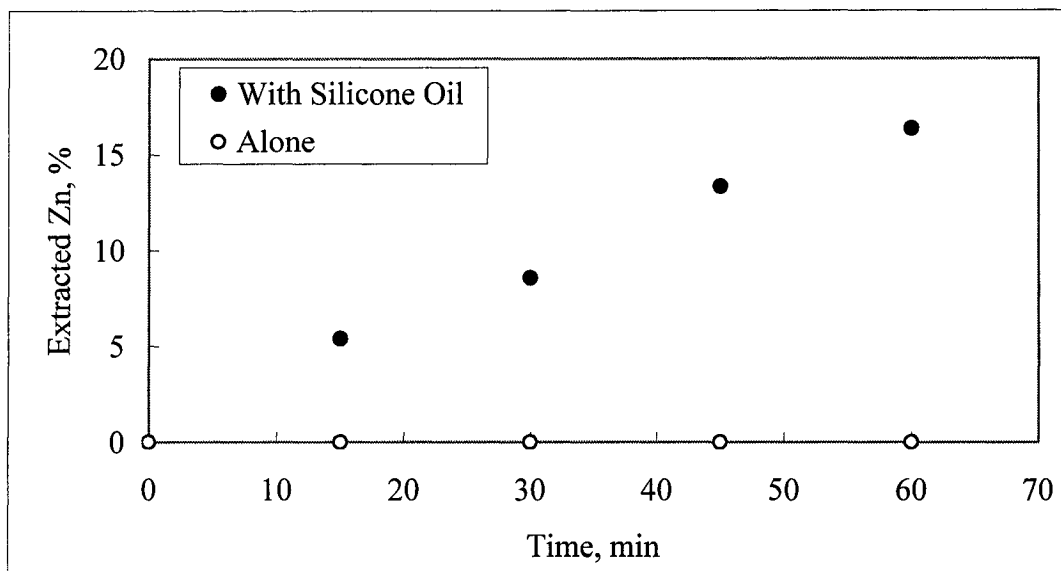

Figure A.5. Effect of silicone oil (1.5 ppm) on AASX with D2EHPA (Time, rather than consumption is used as there was no solvent consumption, i.e., process was inoperable, without silicone oil)

As seen in Figure A.6 the height of solution is important for the lower

concentrations. At the highest initial copper concentration (500 mg/L), the solvent layer

appears to load quickly (< 0.5 s); for the other cases the layer needs more time to load.

The extraction remains limited (max. ca 30%) not so much by solution height as

number of bubbles (this is a single stream) and level of agitation. A design for multiple

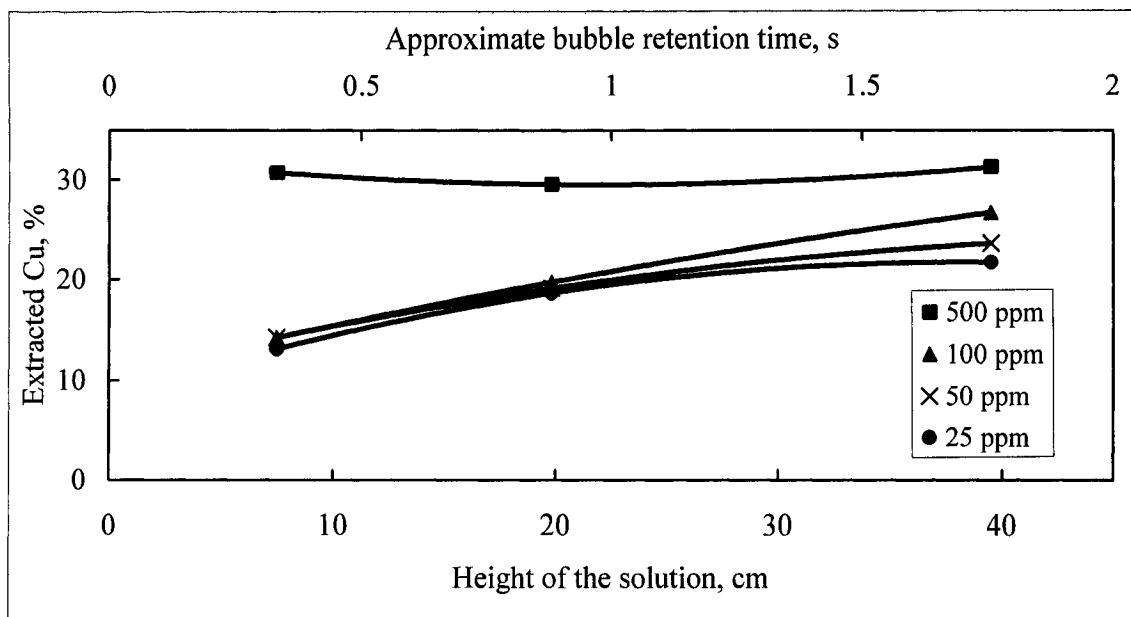bubble injection is being developed which addresses both limitations.

Figure A.6. Effect of solution height (bubble retention time) on AASX

A.5. Conclusions

1. Air-Assisted Solvent Extraction (AASX) is introduced as a possible process to recover metal from dilute streams by providing for high aqueous/organic ratio (A/O up to 75:1) while maintaining ease of phase separation.

2. Silicone oil promotes foaming and has expanded the range of extractants that can be used in AASX.

3. The solvent-coating thickness was estimated as 3 μm.

4. The bubble retention time and the initial metal ion concentration are important design parameters for AASX.

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APPENDIX B

Structure of Some Reagents
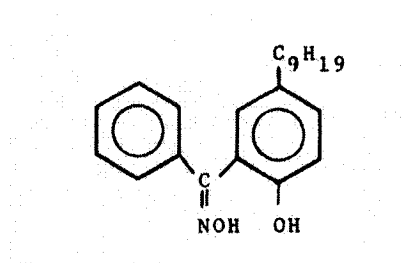
Figure B.1. Structure of LIX 65N
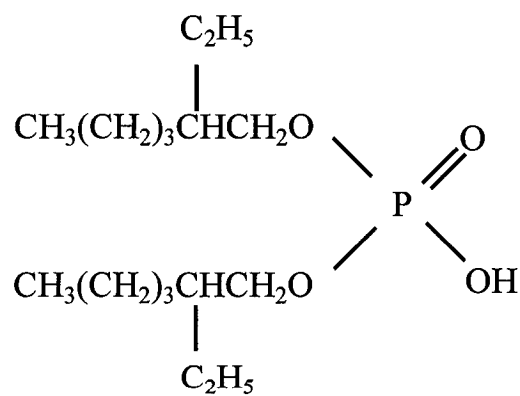
Figure B.2. Structure of D2EHPA
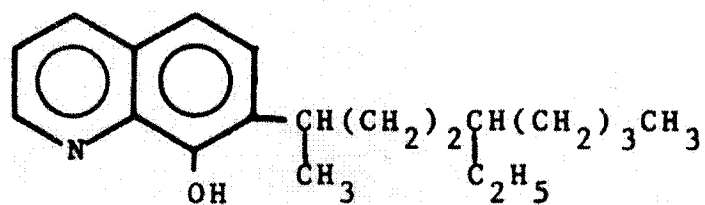
Figure B.3. Structure of Kelex 100
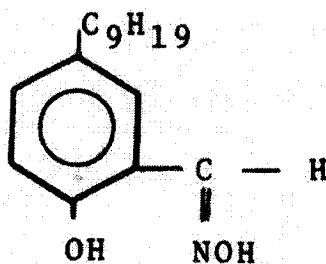
Figure B.4. Structure of Acorga P50
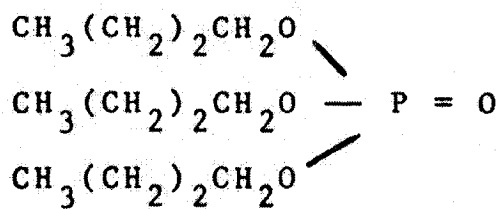
Figure B.5. Structure of tri-n-butyl phosphate (TBP)

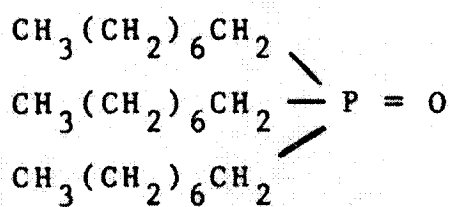$$CH_3(CH_2)_6CH_2$$
$$CH_3(CH_2)_6CH_2 - P = O$$
$$CH_3(CH_2)_6CH_2$$

Figure B.6. Structure of tri-octyl phosphine sulphide (TOPO)

$$CH_3CHCH_2$$
$$|$$
$$CH_3$$

$$CH_3CHCH_2 \longrightarrow P = S$$
$$|$$
$$CH_3$$

$$CH_3CHCH_2$$
$$|$$
$$CH_3$$
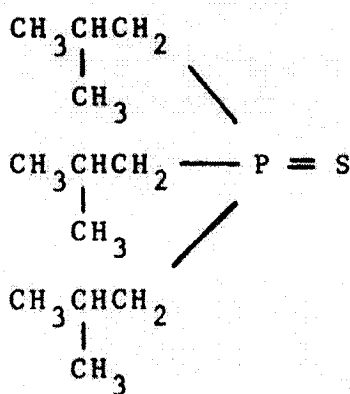
Figure B.7. Structure of Cyanex 471

$$H_3C-Si-O \left[Si-O \right]_n Si-CH_3$$

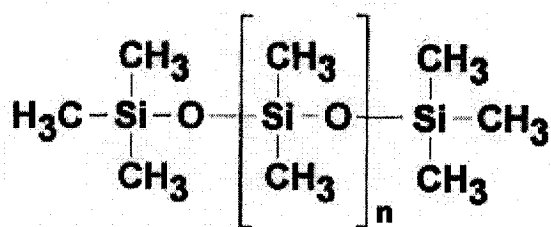with CH_3 groups on the silicon atoms

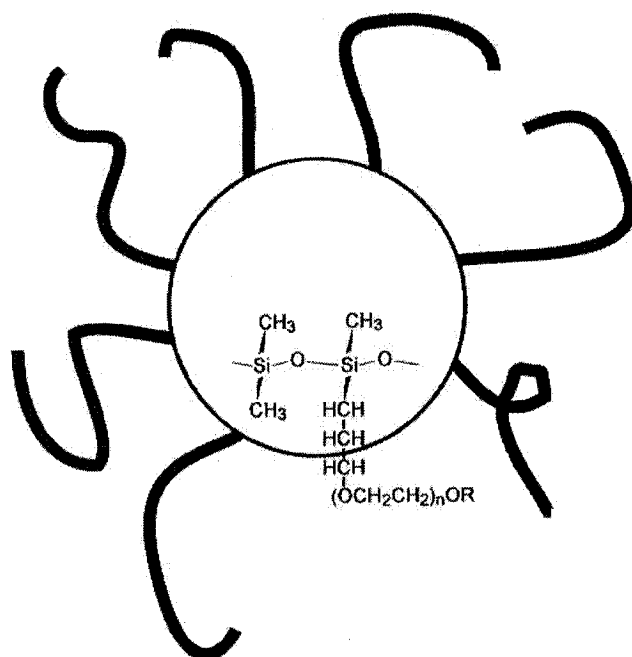**Figure B.8.** Structure of silicone polymer

Figure B.9. Polysiloxane surfactant molecule in water

B.1. References

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