

RI 9375

**RI 9375**

**REPORT OF INVESTIGATIONS/1991**

PLEASE DO NOT REMOVE FROM LIBRARY

LIBRARY  
SPOKANE RESEARCH CENTER  
RECEIVED

JUL 24 1991

U.S. BUREAU OF MINES  
E 315 MONTGOMERY AVE  
SPOKANE, WA 99207

# Copper Extraction From Aqueous Solutions With Liquid Emulsion Membranes: A Preliminary Laboratory Study

By D. N. Nilsen, B. W. Jong, and A. M. Stubbs

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES



**Mission:** As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for the public lands and promoting citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.

**Report of Investigations 9375**

**Copper Extraction From Aqueous  
Solutions With Liquid Emulsion  
Membranes: A Preliminary  
Laboratory Study**

**By D. N. Nilsen, B. W. Jong, and A. M. Stubbs**

**UNITED STATES DEPARTMENT OF THE INTERIOR  
Manuel Lujan, Jr., Secretary**

**BUREAU OF MINES  
T S Ary, Director**

**Library of Congress Cataloging in Publication Data:**

**Nilsen, D. N.**

Copper extraction from aqueous solutions with liquid emulsion membranes : a preliminary laboratory study / by D.N. Nilsen, B.W. Jong, and A.M. Stubbs.

p. cm. — (Report of investigations; 9375).

Includes bibliographical references (p. 16).

Supt. of Docs. no.: I 28.23:9375.

1. Copper—Metallurgy. 2. Membrane separation. I. Jong, B. W. II. Stubbs, A. M. III. Title. IV. Series: Report of investigations (United States. Bureau of Mines); 9375.

TN23.U43 [TN780] 622 s—dc20 [622'.343] 91-10799 CIP

## CONTENTS

	<i>Page</i>
Abstract .....	1
Introduction .....	2
Description of LEM system .....	3
Equipment and experimental conditions .....	5
Equipment .....	5
Experimental conditions .....	6
Results .....	7
Preliminary tests .....	7
Membrane optimization studies .....	8
Multimetal extraction .....	10
Extraction rate experiments .....	12
Single-stage extraction tests .....	13
Two-stage extraction tests .....	13
Emulsion membrane breakage .....	13
Organic phase recycling .....	14
Organic decomposition .....	14
Conclusions .....	15
References .....	16

## ILLUSTRATIONS

1. Idealized sketch of LEM droplet .....	3
2. Conceptual flowsheet of LEM circuit for recovery of metal from aqueous solutions .....	4
3. Emulsifier .....	5
4. Dispersion unit .....	5
5. Batch extraction vessel .....	6
6. Batch electrostatic coalescer .....	7
7. Effect of extractant type on copper extraction with Paranox 100 .....	11
8. Effect of extractant type on copper extraction with PA-18 .....	11
9. Effect of initial pH on metal extraction .....	12
10. Effect of organic and internal phase compositions on copper extraction .....	12
11. Effect of voltage on breakage of copper-loaded emulsions .....	14

## TABLES

1. Effect of emulsion makeup O-I ratio on LEM performance .....	8
2. Effect of Paranox 106 concentration on LEM performance .....	8
3. Effect of P5100 concentration on LEM performance .....	9
4. Effect of surfactant type on LEM performance .....	9
5. Effect of different concentrations of P5100 and Paranox 100 on LEM performance .....	10
6. Effect of surfactant type on Fe <sup>3+</sup> extraction .....	11
7. Effect of time on copper extraction and membrane stability .....	12
8. Effect of internal drop size on breakage of copper-loaded emulsions .....	13
9. Effect of Paranox 106 and P5100 concentrations on breakage of copper-loaded emulsions .....	14

## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
cm	centimeter	mL	milliliter
ft/min	foot per minute	mm	millimeter
gal/min	gallon per minute	μm	micrometer
g/L	gram per liter	mol/L	mole per liter
h	hour	pct	percent
Hz	hertz	ppm	part per million
kV	kilovolt	r/min	revolution per minute
lb	pound	V ac	voltage alternating current
lb/yr	pound per year	vol pct	volume percent
L/min	liter per minute	wt pct	weight percent

# COPPER EXTRACTION FROM AQUEOUS SOLUTIONS WITH LIQUID EMULSION MEMBRANES: A PRELIMINARY LABORATORY STUDY

By D. N. Nilsen,<sup>1</sup> B. W. Jong,<sup>2</sup> and A. M. Stubbs<sup>3</sup>

---

## ABSTRACT

The U.S. Bureau of Mines investigated the use of unsupported liquid emulsion membranes (LEM's) for the extraction of copper from relatively dilute aqueous solutions ( $\leq 0.3$  and  $2.5$  g/L Cu). The performance characteristics of the three main unit operations of an LEM circuit (emulsion generation, metal extraction, and emulsion breaking) were assessed in laboratory-scale batch tests. In single-stage extraction tests using  $2.5$ -g/L Cu feed solution, emulsion membranes extracted up to 94 pct of the copper from solutions without pH adjustment and 99.7 pct when the pH was maintained at about 2.5. Simulated two-stage crosscurrent and countercurrent circuits extracted all but 3 and 4 ppm of the original copper content, respectively. Extraction data from solutions containing mixtures of metals indicated a strong preference for  $\text{Cu}^{2+}$  extraction when oxime-type extractants were used in the LEM; however, some coextraction of  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  was experienced. An electrostatic coalescer was used to break the copper-loaded emulsions for separation of the component phases. Up to 96 pct of the contained stripping solution (internal solution) containing the extracted copper was separated from the organic phase of the emulsion membrane. The recovered organic phase was recycled without apparent problems.

---

<sup>1</sup>Supervisory chemical engineer.

<sup>2</sup>Chemical engineer.

<sup>3</sup>Chemical engineer (now with Westinghouse, Richland, WA).  
Albany Research Center, U.S. Bureau of Mines, Albany, OR.

## INTRODUCTION

Dilute metal concentrations are often found in mine drainage waters, process waste waters, and leach solutions. Metals found in solutions such as these may constitute an environmental hazard and, in some instances, may represent a potential source for critical and valuable metals. For example, the runoff water in Bucktail Creek and portions of Deer Creek, which drain a part of the Blackbird mining area in north-central Idaho, contains as much as 500 ppm Cu and 100 ppm Co. It has been estimated that as much as 34,000 lb/yr Cu and 8,000 lb/yr Co could be recovered just from Bucktail Creek alone. Other similar examples of areas with mine leachate problems in the western mining States are the Bohemia mining district in Oregon and the Shasta mining district in northern California. In addition, many dilute leach solutions contain valuable metals and/or impurities at low concentrations that are difficult to remove economically or to recover with present-day technology.

Conventional technologies such as resin ion exchange and precipitation often have difficulty removing metals selectively and removing them to low levels. In addition, suspended solids and/or dissolved organics that are frequently encountered in runoff waters and leach solutions often cause problems with some of the other available techniques, such as the solid-membrane technologies.

The need for new and improved technologies has been recognized by the U.S. Bureau of Mines. One of the techniques investigated was the application of surfactant-stabilized liquid emulsion membranes (LEM) to the selective extraction of metals from dilute solutions.

The study of multiple emulsions (emulsions within emulsions) can be traced back at least to the late 1800's. Kessler and York (1)<sup>4</sup> described some of the early work and further described multiple emulsions and their formation. Sandblom (2-3) studied the transport of ions through liquid membranes. However, Li was the first to recognize the industrial applicability of LEM and is frequently credited with their invention in 1968 (4). Since then, several research groups have studied the LEM technique: Li at Exxon Research and Engineering Co. (4-14); Hatton and Wardius at Massachusetts Institute of Technology (15-16); Marr and Kopp at Institute for the Fundamentals of Process Engineering, Austria (17-20); and Halwachs and Schugerl at Technical University of Hannover, Germany (21-22).

Li's initial work (4-5) concentrated on the separation of hydrocarbons with liquid membranes and, later, on the removal of dissolved constituents (phosphoric acid, sodium nitrate, and ammonia) from aqueous solutions. Research

on this technique was extended to the removal of copper from acidic leach solutions (6-7). This work was scaled up to a bench-scale pilot plant, where data were obtained for an economic evaluation. The evaluation showed that the LEM technique for treating an acid leach solution containing 2.5 g/L Cu had a 40-pct investment savings compared with conventional solvent extraction (6). This study indicated that the operating costs of LEM would be comparable to those of conventional solvent extraction (about 1.7¢/lb in 1981). The work of the Exxon group was extended to the extraction of uranium from wet-process phosphoric acid in a small (1-L/min) continuous pilot plant (8). Although the economic evaluation based upon this research showed no definite capital cost advantage for LEM over conventional solvent extraction, the estimated operating cost for uranium recovery was \$15/lb of U<sub>3</sub>O<sub>8</sub> for the LEM technique, compared with about \$21/lb for conventional solvent extraction.

The application of the LEM technique to the extraction of substances (e.g., phenol, ammonia, and metals) from waste waters has also been proposed (9). In the mid-1970's a license agreement was arranged between the Exxon Research and Engineering Co. and the Takuma Co., Ltd., of Japan (10) for further development and eventual commercialization of the LEM technique. Takuma was primarily interested in the application of LEM to industrial waste water problems (11). In particular, Takuma investigated the extraction of NH<sub>3</sub>, Cr<sup>6+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup>. Because of increased emphasis by the Japanese Government on higher standards for solid waste disposal, a decision was made (10) to put high priority on the treatment of effluents from "night-soil" (sewage) treatment plants (ammonia extractions). Results of batch laboratory experiments showed >99 pct NH<sub>3</sub> removal in 20 min from waste water containing 50 ppm NH<sub>3</sub> (11). However, recent governmental regulations issued in Japan for sewage treatment plants did not contain the anticipated restrictions on ammonia effluents (9).

According to the literature surveyed, only one industrial application of the LEM technique has been made for metal extraction, to this point. A rayon plant in Austria used an LEM circuit to extract zinc from a waste water stream (18). The stream contained about 0.5 g/L Zn and some calcium at a flow rate of about 300 gal/min. The zinc level reportedly was reduced to <3 ppm. The paper (18) indicated that, compared with other processes (precipitation, ion-exchange resins, and solvent extraction), the LEM technique proved to be the most economical process for this situation. Unfortunately, a fire in the plant caused its shutdown in 1987.

Despite the encouraging economic studies comparing the LEM technique with conventional solvent extraction,

<sup>4</sup>Italic numbers in parentheses refer to items in the list of references at the end of this report.

no commercial-scale LEM plants have been built in the hydrometallurgical industry (18), and only one was built for the treatment of waste water. This may be caused partly by the general lack of knowledge in the industry of this technique and/or possibly by the lack of confidence in the technical viability of this technique. In particular, there is a lack of detailed data in the literature surveyed describing LEM performance in situations where mixtures of metals, suspended solids, and dissolved organics are present in the feed solution. For example, Protsch and Marr (20) described zinc extraction from waste water in pilot-plant tests and commented that suspended solids and humic materials had no effect on mass transfer, but when emulsion droplets coalesced, there was some occlusion of these materials. In comparison to solvent extraction, three to five times higher levels of crud were observed. Protsch and Marr stated that the crud tended to disintegrate emulsions, but addition of more surfactant stopped the effect. No further details were given. Research needs to be conducted to quantify the effect of suspended solids on LEM performance.

Few of the papers reviewed discussed the question of metal selectivity in LEM circuits. One exception (9) gave results for the ratio of copper-to-iron extraction from

pilot-plant runs (the ratio varied between 70 and 325, with an average of 130). However, selectivity ratios for other impurities were not addressed. It has been reported (23) that a ratio for copper to iron of about 300 was observed in commercial solvent extraction operations using a similar extractant. It appears that the selectivity of copper to iron with emulsion membranes will not be as high as that obtained with an equivalent solvent extraction system.

The Bureau investigated the use of the LEM technique for the extraction of metals from aqueous solutions in batch laboratory-scale tests. The objectives of this research were to (1) identify the significant parameters that affect the operation of the LEM technique and then (2) apply the technique to industrial situations to determine actual circuit performance. As a step toward identifying the significant parameters to be studied, precursor batch tests were conducted. Results are presented in this report from preliminary research that investigated the effects of some parameters (e.g., surfactant and extractant type and concentration, internal phase ratio, and diluent type) on LEM performance in the extraction of copper. This research was in support of the Bureau's program to make better use of domestic mineral resources through innovative technologies.

## DESCRIPTION OF LEM SYSTEM

Unsupported LEM's are made by forming an emulsion from two immiscible phases and then dispersing that emulsion into a third phase (a feed solution). The emulsion can be either an oil-in-water or a water-in-oil type; the latter type is discussed in this report. In LEM extraction, the extraction and stripping operations are combined in a single process. In a typical arrangement (fig. 1), the strip solution (also called trapping solution or internal solution) and the organic phase are emulsified to form extremely fine droplets of the internal solution dispersed (encapsulated) in the organic phase. The organic phase may contain a conventional solvent extraction reagent to facilitate the transport of metal through the organic membrane. However, for example, if the desired extracted species is ammonia, only an oil in which ammonia has an appreciable solubility needs to be used (11). The organic phase must not be miscible with either the feed solution or the internal solution if the resultant emulsion is to remain stable. The organic phase also contains a surface-active agent (surfactant) that is used to stabilize the emulsion. In figure 1, the surfactant is shown arranged on the surface of the emulsion membrane droplet (globule) with the lipophilic tail in the organic phase and the hydrophilic polar head in the aqueous phases (internal solution and feed).

A conceptual flow sheet of an LEM circuit is shown in figure 2. In the first step, the organic phase and the internal solution phase are combined to form a stable emulsion. The stable emulsion is then contacted with the feed solution containing the substance to be extracted (e.g., metal ions). Moderate agitation is used in this step to form small globules of the emulsion in the feed solution. Next, the "loaded" emulsion is separated from

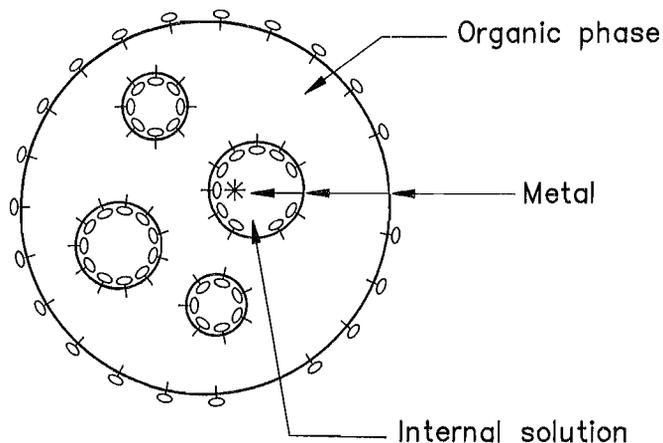


Figure 1.—Idealized sketch of LEM droplet (globule).

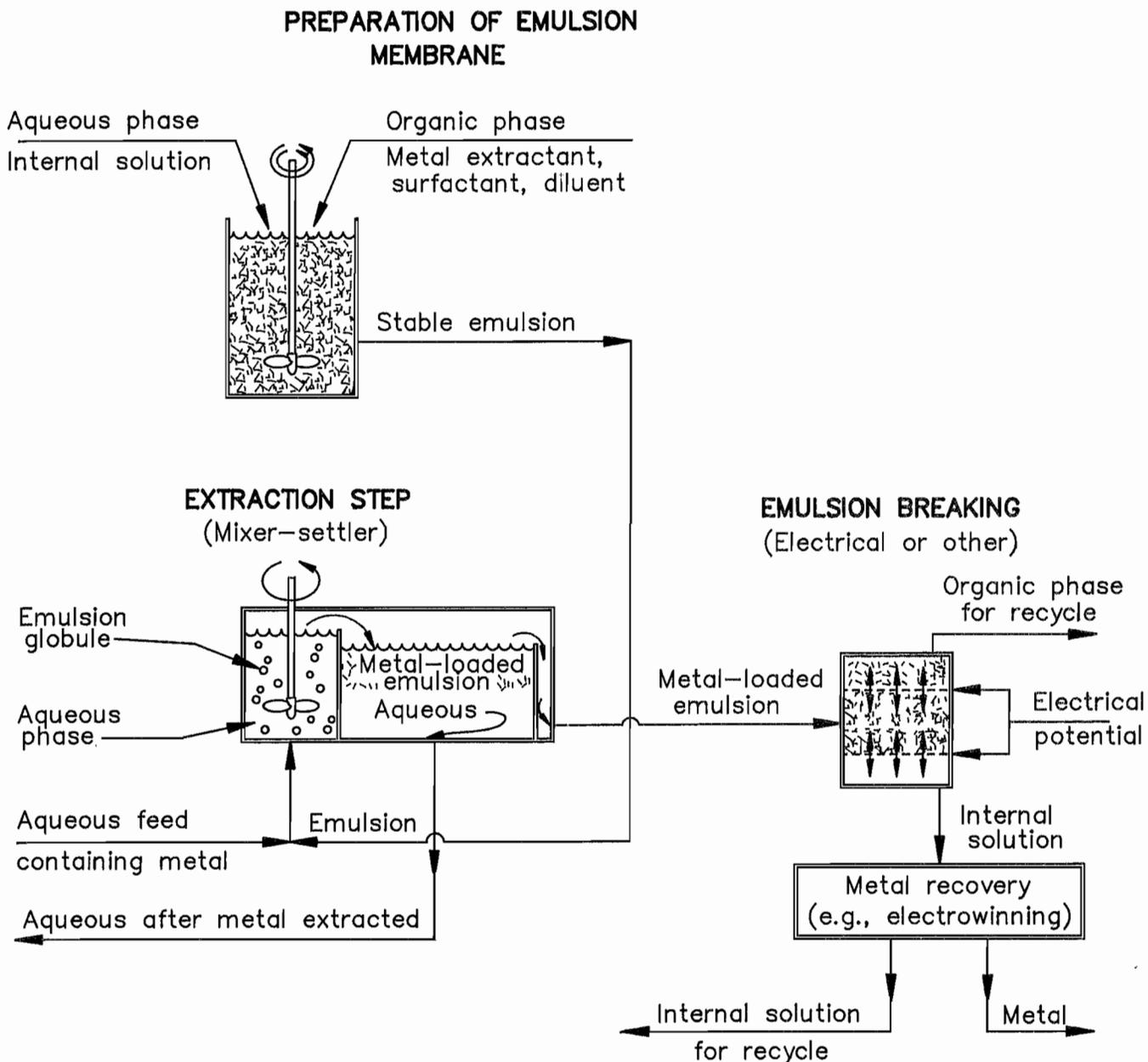


Figure 2.—Conceptual flowsheet of LEM circuit for recovery of metal from aqueous solutions.

the feed solution (now depleted in metal ions) and transferred to a device to break the emulsion for recovery of both the organic and loaded internal solution phases. Electrostatic methods have been found to be the simplest and lowest cost technique for breaking LEM's (7). Following breaking and separation, the extracted material

may be recovered from the internal solution by any appropriate method. The recovery of an extracted metal by electrowinning is shown in figure 2. The organic and internal solution phases then are recycled for generation of more emulsion for further extraction.

## EQUIPMENT AND EXPERIMENTAL CONDITIONS

The Bureau conducted preliminary tests to aid in the identification of the significant parameters that control the performance of an LEM circuit. The goals of the initial research were to develop appropriate laboratory-scale equipment for the main unit operations of an LEM circuit and to formulate membrane mixtures that possessed the proper stability and extraction characteristics for use in a circuit. The membranes must be stable enough so that during the extraction step they do not rupture (internal solution leaks into the surrounding feed solution) or form an emulsion with the feed solution. However, the membrane must not be too stable or difficulty will be experienced in a later step when the membrane is broken for recovery and recycling of the loaded internal solution and the organic phase.

### EQUIPMENT

In this research, batch equipment was developed and used for the three main unit operations (membrane generation, extraction, and membrane breaking). Three types of mixers were used for the generation of the emulsion membranes. The standard mixer consisted of a baffled vessel and a turbine agitator. A variation of this apparatus, designated the "emulsifier," used similar equipment except that a bottom plate that had a stationary turbine attached to it was fitted into the vessel (fig. 3). The agitators in these two mixing devices were operated at either 3,000 or 4,600 r/min, depending on the surfactant used

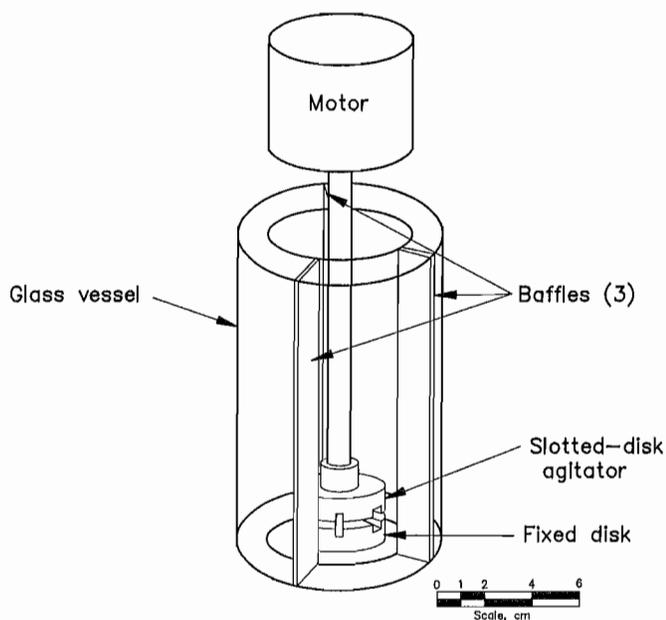


Figure 3.—Emulsifier.

(tip speed of 1,150 or 1,770 ft/min). The third apparatus was a commercial-type dispersion unit (fig. 4). The unit consisted of a water-cooled mixing vessel and a variable-speed electric motor for driving the generator. The generator consisted of a slotted stator and an internal rotor. The internal rotor was usually operated at either 3,000 or 7,500 r/min (tip speed of 785 or 1,960 ft/min), depending on the surfactant used. These apparatuses were capable of producing emulsions with quite a range of internal droplet sizes.

A test series investigated the effect on membrane performance of different-sized droplets. Emulsions were prepared in which average diameters for the droplets ranged from  $<1$  to  $12\ \mu\text{m}$ . Results from these tests indicated that emulsion membranes with internal phases with average diameters between 1 and  $5\ \mu\text{m}$  yielded the best performance. The performance was evaluated in terms of the rate of copper extraction, membrane swelling, internal phase leakage, and emulsion membrane breakage. Therefore, an attempt was made in all subsequent tests to produce emulsions that contained internal droplets with an average diameter that ranged from 1 to  $5\ \mu\text{m}$ . The diameters of the internal droplets were estimated by taking a sample of the emulsion and viewing it under a microscope ( $\times 640$ ). Unless otherwise indicated, the dispersion unit was used to generate emulsions used in the tests discussed in this report.

In the extraction step, a balance was needed so that adequate agitation was provided for efficient mass transfer,

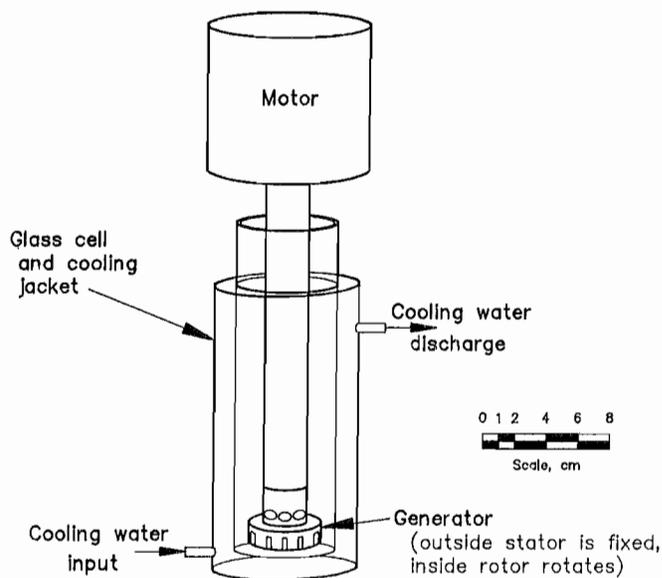


Figure 4.—Dispersion unit.

but excessive shear forces had to be avoided so that membrane integrity was maintained. The most successful equipment developed to this point consisted of a vessel with three baffles that used an agitator shaft with a double set of three-bladed marine propellers (fig. 5). Unless otherwise indicated, the agitator was operated at a relatively low speed (tip speed of 118 ft/min).

An electrostatic coalescer was used to break the emulsions. It consisted of a variable-ac-voltage transformer (maximum output of 12 kV) and a cylindrical glass cell that contained two electrodes and space for the emulsion samples (fig. 6). The transformer operated at 60 Hz. The glass cell had a diameter of 4.8 cm and a height of 17.0 cm and held about 100 mL of emulsion. In addition, a rectangular cell (7.6 cm wide by 7.6 cm long by 15.0 cm high) was constructed from acrylic sheet and was used to test 200-mL samples of emulsion. The rectangular cell was used to evaluate the effect of voltage and electrical field strength on the breakage of copper-loaded emulsion membranes. It was relatively easy in the rectangular cell to position the vertical distance (D) and the horizontal distance (C) to equal lengths for evaluation of the effect of electrical field strength (voltage divided by distance between electrodes) on the breakage of the emulsions. The electrodes were fabricated from stainless steel (AISI Type 308), and the high-voltage electrode was insulated with a polyvinyl chloride (PVC) sheath. The space between the stainless steel electrode and the inside of the PVC sheath was filled with an electrolyte (1 mol/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution). The electrode design was adapted

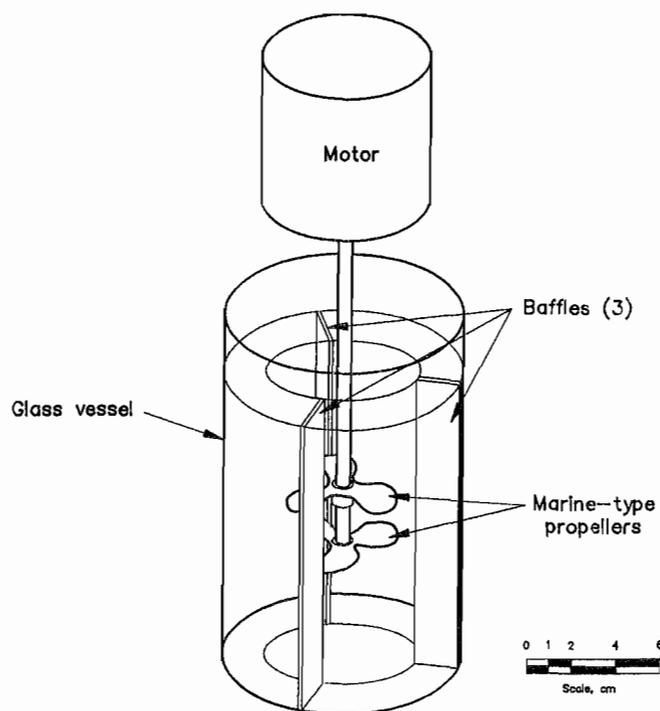


Figure 5.—Batch extraction vessel.

from that described by Wagner (13). Electrode spacing for the cells is shown in figure 6. Because of the good insulating qualities of PVC, very little current passed through the emulsion samples. Although power consumption was not calculated for these preliminary tests, it was thought to be quite low.

## EXPERIMENTAL CONDITIONS

Depending upon the test series, feed solutions for the extraction tests contained about 2.5 g/L Cu or between 100 and 300 ppm Cu. The selectivity of copper extraction was investigated in several test series. In those tests, various combinations of impurity metals (e.g.,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Co}^{2+}$ ) were added to the feed solutions. The concentrations of these impurities ranged from 100 to 200 ppm. The more concentrated copper solutions imitated leach solution from the heap leaching of copper oxide ore, and the solutions with low copper concentrations imitated mine drainage water. Unless otherwise stated, the initial pH of the feed solutions was adjusted to about 2.5 with  $\text{H}_2\text{SO}_4$  and/or NaOH. In all tests, the initial internal solution contained about 150 g/L  $\text{H}_2\text{SO}_4$  and 8 g/L K (used as a tracer). In one test series, the equivalent of 25 g/L Cu was added to the initial internal solution. All other tests were conducted with no copper initially in the internal solution. All solutions were prepared from reagent-grade chemicals, and all extraction tests were conducted at room temperature (18° to 23° C). The variation of temperature within this range had minimal effects on LEM performance.

Unless otherwise indicated, the extraction tests were conducted for a 2-h period and at a ratio of 4:1 (feed solution to emulsion phase). In most cases, two or more tests were performed for each set of variables. Therefore, most of the data presented are based on the averages from several tests. The differences in copper extraction on repeat tests averaged about 6 pct. Generally, the largest differences were experienced for the first few samples taken in a test (2.5- and 5-min samples), with later samples yielding very repeatable results. Unless otherwise indicated, the calculations for metal extractions were based upon analyses of metals present in the initial feed solutions and in the raffinate samples.

Standardized conditions were developed for the emulsion breakage tests. The cylindrical cell was used at an applied voltage of 6 kV at 60 Hz. The exception was the test series that investigated the effect of voltage on emulsion breakage. All tests used a 5-min time period for application of the electric field.

The organic phase decomposition tests were conducted by gently mixing together equal volumes of organic and aqueous phases for 1-month periods. An orbital-action laboratory shaker was used to contact the phases at a controlled temperature of 25° C. Samples of both phases

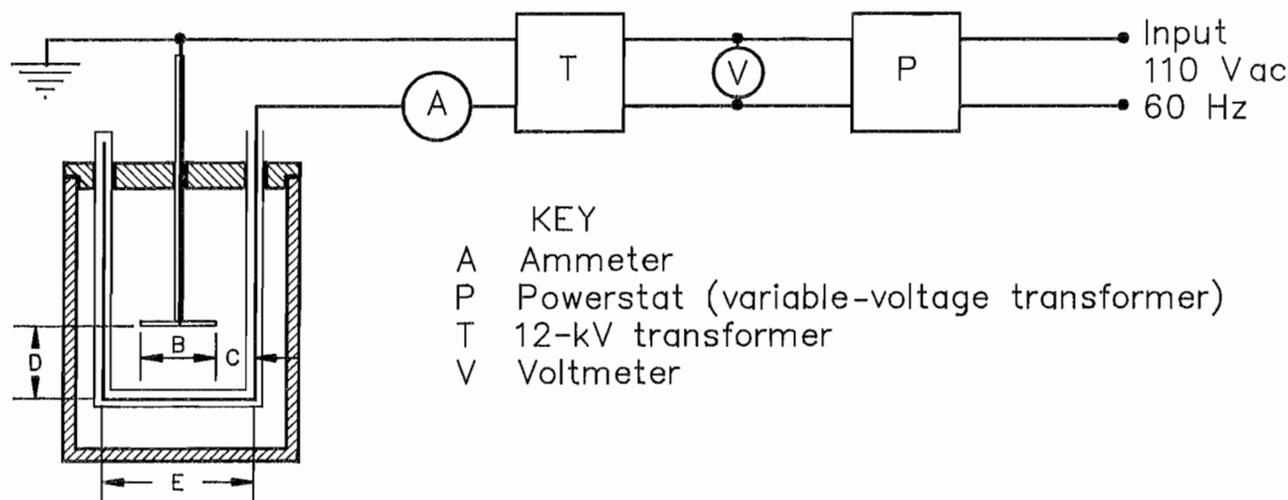


Figure 6.—Batch electrostatic coalescer. Dimensions, in centimeters, are as follows:

	<i>Cylindrical cell</i>	<i>Rectangular cell</i>
Electrode:		
B .....	1.30	1.3 or 2.5
C .....	.85	1.9 or 2.5
D .....	2.50	1.9 or 2.5
E .....	3.00	6.3
Cell:		
Height .....	17.0	15.0
Diameter .....	4.8	NAp
Width .....	NAp	7.6
Length .....	NAp	7.6
NAp	Not applicable	

were periodically withdrawn for evaluation. Changes in the organic phase were monitored by infrared (IR) analyses and/or by measuring copper-loading capacities. The maximum copper-loading capacity of the organic phases was determined to assess changes in the effectiveness of the extractant. The maximum capacity was

measured by repeatedly contacting an aliquot of organic phase with aliquots of a 2.5-g/L Cu solution (pH of 4.5). The contacts were continued until the raffinate analyses showed no further copper extraction. The organic phase was then analyzed for copper.

## RESULTS

### PRELIMINARY TESTS

Preliminary screening tests were run for the purpose of comparing the stability and copper extraction characteristics of emulsion membranes using many different surfactants. A partial list of the surfactants tested includes Paranox 100,<sup>5</sup> Paranox 106, PA-18, Span 80, Tween 80, BRIJ52, Triton X-35, Arlacel A, ECA 4999, MNPA-510, and Pluronic L61. Based upon the results from these initial tests, Paranox 100, Paranox 106, and PA-18 were

selected for further tests.<sup>6</sup> The emulsifier was used in these early tests to generate the emulsion membranes.

An important variable that can greatly affect membrane performance is the ratio of organic phase to internal phase (O-I) in the emulsion membrane. A variety of O-I ratios were tested with an organic that contained 5 wt pct P5100 extractant, 1.5 wt pct PA-18, and 93.5 wt pct Isopar L

<sup>5</sup>Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

<sup>6</sup>Paranox 100 and 106 are nonionic surfactants (polyamines) manufactured by Exxon Oil Co. PA-18 is composed of copolymers of maleic anhydride and 1-octadecene and was obtained from SERVA Fine Biochemicals, Inc.

diluent.<sup>7</sup> The results, shown in table 1, indicated that based upon overall performance (copper extraction, internal phase leakage, membrane swell, and subsequent breakage of the copper-loaded membrane in the electrostatic coalescer), an O-I ratio of 2:1 appeared to be the best choice. Two other extractant and surfactant mixtures also were tested using several O-I ratios. They were (1) 2.5 wt pct LIX 64N<sup>8</sup> extractant, 2 wt pct Paranox 100, and 95.5 wt pct Isopar L and (2) 5 wt pct P5100, 2 wt pct Paranox 100, and 93 wt pct Isopar L. Results from these tests were very similar to those shown in table 1. All further tests were conducted with emulsion membranes that contained an O-I ratio of 2:1.

**Table 1.—Effect of emulsion makeup O-I ratio<sup>1</sup> on LEM performance, percent**

Emulsion makeup ratio (O-I)	Cu extracted <sup>2</sup>	Internal phase leakage	Membrane swell <sup>3</sup>	Emulsion breakage <sup>4</sup>
1:2	96.8	3.0	NA	0
1:1.5	97.6	.5	23.8	57
1:1	95.2	4.2	3.8	74
1.5:1	96.4	1.1	6.2	71
2:1	95.6	.5	.0	89
3:1	89.6	1.7	.0	88

NA Not available.

<sup>1</sup>Organic phase contained 5 wt pct P5100, 1.5 wt pct PA-18, and 93.5 wt pct Isopar L. Emulsion membranes were generated in emulsifier.

<sup>2</sup>Feed solution contained 2.5 g/L Cu.

<sup>3</sup>30-min test.

<sup>4</sup>Amount of breakage in electrostatic coalescer in 5 min at 6 kV, 60 Hz.

The membrane swell was estimated by measuring the volume of the emulsion before and after the extraction. The measurement took into account both water transfer

<sup>7</sup>P5100 contains 5-nonyl salicylaldehyde as the active metal extractor and is manufactured by Acorga. Isopar L is a commercial-grade solvent, manufactured by Exxon Oil Co., which contains about 92.7 pct paraffin and 7.0 pct naphthenes.

<sup>8</sup>LIX 64N contains  $\alpha$ -hydroxy oxime and  $\beta$ -hydroxy benzophenone oxime and was manufactured by Henkel Corp. It is no longer made.

through the organic phase into the internal phase by osmotic pressure and the physical entrapment of the feed solution (or raffinate) in the emulsion membrane. Previous workers (12) had determined that a membrane swell (internal phase) of up to 10 pct was acceptable. If membrane swelling becomes excessive, it can disrupt the water balance of the overall process. The breakdown of the emulsion membrane was measured indirectly by measurement of potassium in the raffinate. Potassium was added to the internal phase to act as a tracer. Any leakage of internal phase into the raffinate resulted in some transfer of potassium to the raffinate. As a point of reference, with the volume ratios used in this research, a value of 12 ppm K in the raffinate corresponded to a leakage of about 2 vol pct of the internal phase.

## MEMBRANE OPTIMIZATION STUDIES

To determine the range of surfactant concentrations that should be studied in subsequent tests, a series of tests using Paranox 106 was conducted, in which the surfactant concentration was varied from 0.5 to 10.0 wt pct (table 2). The amount of membrane swell steadily increased as the surfactant concentration increased; however, the efficiency of the copper extraction peaked when about 1.0 wt pct surfactant was used, and then declined as the surfactant level was increased. Since both the extractant (P5100) and the surfactant (Paranox 106) are surface-active compounds and tend to concentrate near the interface, it is likely that at high concentrations of surfactant, some of the area usually available for the extractant to occupy was taken up by the surfactant molecules. Thus, the extraction of copper was impaired somewhat at high surfactant concentrations. (Similar results were obtained with Paranox 100.) Mikucki and Osseo-Asare (24) observed similar results in their work. Compared with conventional solvent extraction systems, metal extraction with emulsion membranes is expected to have lower extraction rates (25). As measured by the potassium leakage, the internal phase leakage decreased as the surfactant concentration was increased. Generally, subsequent tests were conducted with surfactant concentrations of 2 wt pct or lower.

**Table 2.—Effect of Paranox 106 concentration<sup>1</sup> on LEM performance**

Paranox 106 conc, wt pct	Cu extracted, <sup>2</sup> pct, at 5 sampling periods					Membrane swell, <sup>3</sup> pct	K leakage, <sup>3</sup> ppm
	15 min	30 min	45 min	60 min	90 min		
0.5	41	38	79	86	95	1.5	5.8
1.0	32	64	84	94	97	4.6	2.5
2.0	22	56	80	91	96	6.2	1.0
5.0	16	49	71	85	94	6.9	.7
10.0	16	40	76	76	93	7.7	.7

<sup>1</sup>Organic phase of emulsion membrane contained Paranox 106 at weight percents noted, 2.5 wt pct P5100, and balance was Isopar L.

<sup>2</sup>Feed aqueous solution initially contained  $\approx$ 2.5 g/L Cu at pH 2.5.

<sup>3</sup>At end of 90-min test.

To determine the range of extractant concentration that should be studied in subsequent tests, a series of tests using P5100 was conducted, in which the extractant concentration was varied from 1 to 20 wt pct (table 3). Generally, the initial rate of copper extraction increased as the extractant concentration increased. The internal phase leakage reached a minimum when 5 wt pct extractant was used, whereas the membrane swell increased as the extractant concentration was increased. Considering overall performance, an extractant concentration of 5 wt pct was chosen for most subsequent tests.

As mentioned before, screening tests had identified three potentially useful surfactants for emulsion membranes (Paranox 100, Paranox 106, and PA-18). Tests were run to compare the performance of emulsion membranes made with these surfactants at one concentration level (1.5 wt pct). The results (table 4) indicated that each of these surfactants possessed both strong and weak features. Generally, emulsions with PA-18 exhibited rapid extraction of copper and low membrane swelling, but relatively high internal phase leakage. Paranox 100 and 106 showed similar copper extraction rates, except that Paranox 106 had lower membrane swelling and Paranox 100 had lower internal phase leakage. The IR

spectra for Paranox 100 and 106 were very similar, indicating that they are similar compounds. The results from these tests did not indicate that one surfactant was superior to the others tested; therefore, subsequent research investigated the use of all three surfactants in emulsion membranes.

The effect of several different concentrations of P5100 extractant and Paranox 100 surfactant and their interactions were investigated (table 5). Generally, increasing the concentration of surfactant decreased the internal phase leakage, increased membrane swell in some cases, and slightly reduced the rate of copper extraction. Generally, increasing the concentration of extractant increased slightly the internal phase leakage, increased the rate of copper extraction, and increased the membrane swell. For the concentrations of reagents used in these tests, membrane swell was influenced somewhat more by the extractant concentration rather than by the surfactant concentration. This was also the case in comparing the data contained in tables 2 and 3. Many of the combinations identified in table 5 appeared to offer potentially good overall performance characteristics (e.g., 2.5 wt pct P5100 and 1.0 wt pct Paranox 100, or 5 wt pct P5100 and 1.0 to 2.0 wt pct Paranox 100).

Table 3.—Effect of P5100 concentration<sup>1</sup> on LEM performance

P5100 conc, wt pct	Cu extracted, <sup>2</sup> pct, at 5 sampling periods					Membrane swell, <sup>3</sup> pct	K leakage, <sup>3</sup> ppm
	15 min	30 min	45 min	60 min	90 min		
1.0 . . . . .	8	28	61	79	95	0.0	14.1
2.5 . . . . .	41	38	79	86	95	1.5	5.8
5.0 . . . . .	31	64	99	99	97	7.7	.9
7.5 . . . . .	48	81	93	96	96	16.9	1.3
10.0 . . . . .	32	78	93	96	96	23.1	2.6
20.0 . . . . .	59	91	97	94	96	37.7	3.9

<sup>1</sup>Organic phase of emulsion membrane contained P5100 at weight percents noted, 0.5 wt pct Paranox 106, and balance was Isopar L.

<sup>2</sup>Feed aqueous solution initially contained  $\approx 2.5$  g/L Cu at pH 2.5.

<sup>3</sup>At end of 90-min test.

Table 4.—Effect of surfactant type on LEM performance<sup>1</sup>

Surfactant and Initial Cu conc, ppm	Cu extracted, pct, at 6 sampling periods						Membrane swell, <sup>2</sup> pct	K leakage, <sup>2</sup> ppm
	2.5 min	5 min	10 min	15 min	30 min	45 min		
PA-18: <sup>3</sup> 100 . . .	69.1	86.9	98.0	99.7	99.7	NA	6.1	9.6
Paranox 100:								
<sup>4</sup> 200 . . . . .	NA	66.0	NA	96.3	96.3	97.8	20.0	.7
<sup>5</sup> 100 . . . . .	58.6	81.1	96.1	99.2	99.2	99.4	19.3	2.2
<sup>4</sup> 180 . . . . .	NA	56.6	96.0	98.8	99.7	99.8	18.5	1.8
Paranox 106:								
<sup>5</sup> 100 . . . . .	NA	59.6	90.5	97.2	99.2	99.5	11.1	4.0
<sup>5</sup> 200 . . . . .	NA	63.8	91.0	97.5	99.5	99.8	10.0	2.9

NA Not available.

<sup>1</sup>Organic phase of emulsion membrane contained 1.5 wt pct surfactant, 5 wt pct P5100, and 93.5 wt pct Isopar L.

<sup>2</sup>PA-18 data at end of 30-min test; all other data at end of 45-min test.

<sup>3</sup>Feed solution also contained  $\approx 200$  ppm  $\text{Fe}^{3+}$  and  $\approx 100$  ppm  $\text{Co}^{2+}$  at pH 2.5. Essentially no  $\text{Fe}^{3+}$  or  $\text{Co}^{2+}$  was extracted.

<sup>4</sup>Feed solution contained only Cu at pH 3.5.

<sup>5</sup>Feed solution contained only Cu at pH 2.5.

Table 5.—Effect of different concentrations of P5100 and Paranox 100 on LEM performance<sup>1</sup>

P5100 conc, wt pct	Paranox 100 conc, wt pct	Cu extracted, <sup>2</sup> pct, at 4 sampling periods				Membrane swell, <sup>3</sup> pct	K leakage, <sup>3</sup> ppm
		5 min	15 min	30 min	45 min		
2.5 . . . . .	0.5	76.0	98.6	99.6	99.8	12.3	3.9
	1.0	58.6	98.1	99.7	99.8	16.9	2.5
	2.0	55.7	93.0	97.7	97.9	18.0	.1
5.0 . . . . .	1.0	71.9	97.0	97.9	97.9	20.0	1.2
	1.5	66.0	96.8	96.3	97.8	20.0	.7
	2.0	61.6	96.1	96.9	97.9	20.0	1.4
10.0 . . . .	2.0	81.0	99.2	99.7	99.7	26.2	2.4

<sup>1</sup>Organic phase of emulsion membrane contained P5100 and Paranox 100 at weight percents indicated, and Isopar L diluent.

<sup>2</sup>Feed aqueous solution initially contained ≈200 ppm Cu at pH 3.5.

<sup>3</sup>At end of 45-min test.

The effect on copper extraction of three different extractants (P5100, LIX 84, and LIX 34)<sup>9</sup> was determined with emulsion membranes containing Paranox 100 or PA-18 (figs. 7-8). When Paranox 100 was used to stabilize the emulsion membrane, the extraction characteristics were fairly similar for the three extractants. P5100 and LIX 84 behaved essentially the same, and copper extraction with LIX 34 was only slightly depressed. However, when PA-18 was used, great differences existed among the extraction characteristics of the three extractants. P5100 was clearly superior in this case. It was found to be necessary to add a small amount of nonylphenol (2 wt pct) to the organic containing LIX 34 so that PA-18 could be solubilized in that phase. The reason that PA-18 seems to emphasize the difference among the extractants is not known. It is interesting to note that in comparing the results for P5100 between figures 7 and 8, the P5100 and PA-18 combination appeared to result in faster copper extraction than the P5100 and Paranox 100 combination (e.g., 90 pct extraction in 6 min versus 12 min). This result is not completely conclusive since the tests with Paranox 100 used 2 wt pct surfactant and those with PA-18 just 1.5 wt pct. However, the data in table 5 show little impeding of copper extraction with P5100 and Paranox 100 within the surfactant range of 1 to 2 wt pct. Therefore, although different surfactant amounts were used, it is likely that PA-18 does not slow copper extraction by P5100 to the same extent as does Paranox 100. Most of the subsequent tests used P5100 in combination with either Paranox 100 or PA-18.

#### MULTIMETAL EXTRACTION

Very little information was found in the literature regarding the selectivity of emulsion membranes in multi-metal systems. In the LEM technique, the extraction and

stripping operations are combined into one operation so that kinetic factors primarily control the separation of extracted metals. Therefore, in LEM systems it is not possible to use crowding or scrubbing stages, as are often used in solvent extraction, to improve the selectivity of metal extraction. In solvent extraction, the separation of metals is controlled primarily by equilibrium factors. It has been suggested (18) that the LEM technique will be limited to solutions that contain a limited number of metals.

To provide some information on this area, batch extraction tests were conducted with various combinations of metals (Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, and Zn<sup>2+</sup>) and emulsion membranes containing different extractants and surfactants. Several series of tests were run with feed solutions containing about 0.1 g/L Cu<sup>2+</sup>, 0.1 g/L Co<sup>2+</sup>, and 0.2 g/L Fe<sup>3+</sup> at an initial pH of 2.5. The emulsion membranes contained P5100, LIX 84, or LIX 34 extractants in combination with Paranox 100 or PA-18 surfactants. Isopar L was used in all cases as the diluent. In these tests, copper extraction was very good with the P5100- and LIX 84-containing membranes, but membranes with LIX 34 showed considerably slower rates of copper extraction. There was considerable scatter in the data of these tests, but the general trends were clear. Emulsions containing P5100 or LIX 84 appeared to extract some Fe<sup>3+</sup> (up to 19 pct by 30 min). Emulsions containing P5100 exhibited slightly higher Fe<sup>3+</sup> extraction than emulsions with LIX 84. Under the conditions of these tests, LIX 34 in combination with either surfactant extracted very little Fe<sup>3+</sup>; however, the LIX 34 rate for Cu<sup>2+</sup> extraction was also rather low (figs. 7-8).

The extraction data tended to indicate that the surfactant used had some influence upon the Fe<sup>3+</sup> extraction. Further extraction tests were conducted in which the resultant metal-loaded membrane was broken and the internal solution was analyzed for copper, cobalt, and iron (table 6). These tests measured the resultant transfer of the metals to the internal solution. These results showed that P5100 emulsions containing PA-18 surfactant tended

<sup>9</sup>LIX 84 contains 2-hydroxy-5-nonylaceto-phenone oxime as the active metal extractor. LIX 34 contains 8-(alkaryl-sulfonamido) quinoline as the active metal extractor. Both are manufactured by Henkel Corp.

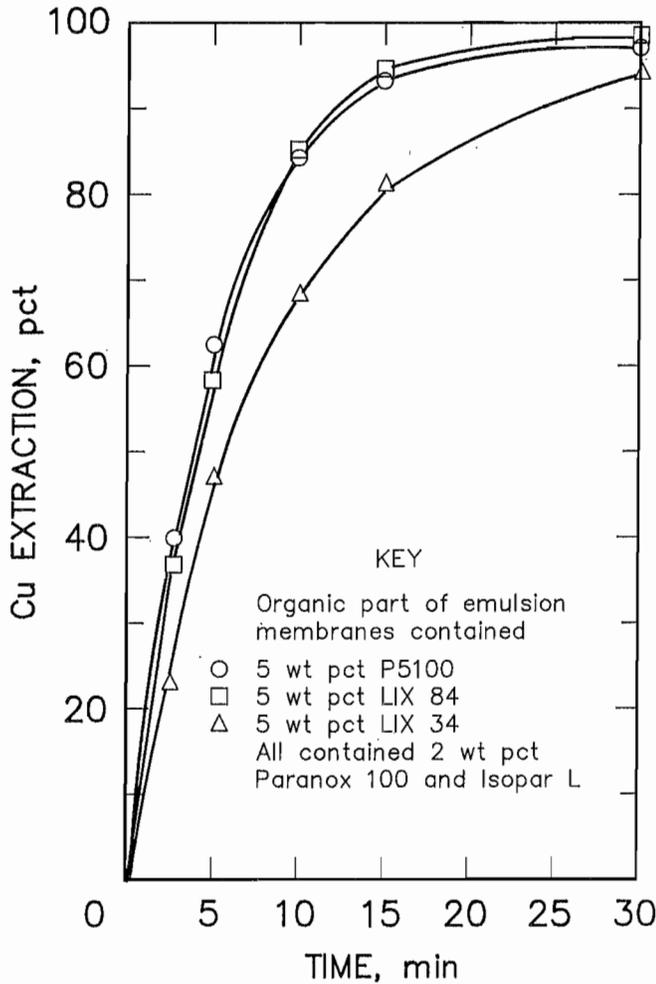


Figure 7.—Effect of extractant type on copper extraction with Paranox 100. Feed solution contained  $\approx 100$  ppm  $\text{Cu}^{2+}$ ,  $\approx 200$  ppm  $\text{Fe}^{3+}$ , and  $\approx 100$  ppm  $\text{Co}^{2+}$  at pH 2.5.

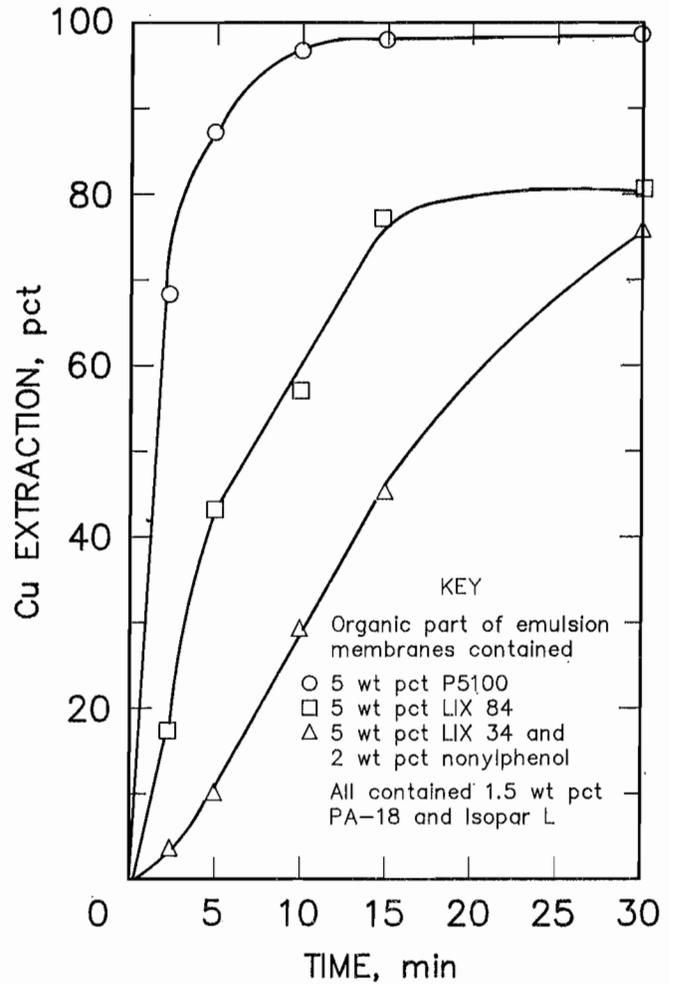


Figure 8.—Effect of extractant type on copper extraction with PA-18. Feed solution contained  $\approx 100$  ppm  $\text{Cu}^{2+}$ ,  $\approx 200$  ppm  $\text{Fe}^{3+}$ , and  $\approx 100$  ppm  $\text{Co}^{2+}$  at pH 2.5.

to transfer greater amounts of  $\text{Fe}^{3+}$  than emulsions containing Paranox 100 (an average of 2.5 times as much). The average transfer ratio of copper to iron into the internal solution during these tests was about 25 for emulsions using Paranox 100 and only 7.6 for emulsions using PA-18. Essentially no cobalt was extracted and transferred to the internal phase in any of these tests. In addition, other tests showed insignificant extraction of  $\text{Fe}^{2+}$  in the pH range of 1.5 to 3.5.

Tests were made with emulsion membranes containing Paranox 100 to determine if effective separation of  $\text{Cu}^{2+}$  from  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  could result through pH adjustment of the feed solution before extraction. The effect on metal extraction of the initial pH is shown in figure 9. The results indicated that copper extraction was good at starting pH levels of 1.5 and above. The best copper extraction occurred at the higher pH levels. The  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  data tended to scatter; however, the general trend was for increased extraction at the higher pH levels. Zinc extraction was essentially zero for the test where the initial pH level was 0.5; however, some  $\text{Fe}^{3+}$  was extracted even

in that test. At starting pH levels of 2.5 and above,  $\text{Fe}^{3+}$  extraction seemed to increase as the contact time was extended. At an initial pH level of 2.5, the copper extraction reached  $>99$  pct and the  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  extraction was  $<7$  pct at the end of the test.

Table 6.—Effect of surfactant<sup>1</sup> type on  $\text{Fe}^{3+}$  extraction, grams per liter

Surfactant	Feed solution			Resultant internal solution	
	Cu	Co	Fe	Cu	Fe
PA-18 . . . . .	0.20	0.00	0.22	1.70	0.12
	.09	.08	.35	.94	.30
	.13	.09	.21	.76	.14
Paranox 100 . .	.20	.00	.22	1.78	.03
	.09	.08	.35	.92	.15
	.13	.09	.21	.76	.08

<sup>1</sup>Organic phase of emulsion membrane contained 1.5 wt pct surfactant, 5 wt pct P5100, and 93.5 wt pct Isopar L.

## EXTRACTION RATE EXPERIMENTS

Batch extraction tests were conducted with emulsion membranes containing organic phases with 2 wt pct Paranox 100 surfactant and either 2.5 or 5 wt pct P5100 extractant (fig. 10). The initial internal solution contained either no copper or 25 g/L. The results indicated that under the conditions of the tests, the concentration of copper in the internal solution had a relatively small effect on the extraction of copper from the feed solution. Draxler (19) found the same effect and commented that the driving force for copper extraction depended on the concentration difference of the countercurrent ion (protons in this case). The data shown in figure 10 indicate that for the extractant range tested, the concentration of extractant had a relatively significant effect on copper extraction. The emulsion membranes containing an organic phase with 5 wt pct extractant reached the 90-pct extraction level in about 55 min, whereas the emulsion with half the extractant took about 80 min. It should be noted that no attempt was made in these tests to optimize the conditions so that high extraction rates (or fast kinetics) were attained. The emulsion membranes used in these tests were generated in the emulsifier.

Several tests were run in which the speed of the agitator in the batch extraction vessel was increased in increments from the standard speed (tip speed of 118 ft/min) to a tip speed of 170 ft/min. At tip speeds of  $\geq 144$  ft/min,

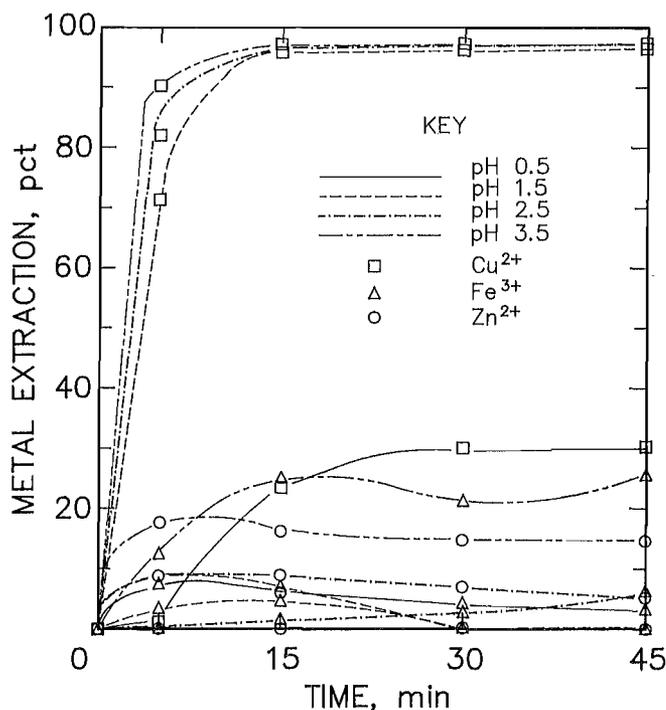


Figure 9.—Effect of initial pH on metal extraction. Feed solution contained  $\approx 240$  ppm  $\text{Cu}^{2+}$ ,  $\approx 130$  ppm  $\text{Fe}^{3+}$ , and  $\approx 180$  ppm  $\text{Zn}^{2+}$  at indicated pH. Organic part of emulsion contained 5 wt pct P5100, 2 wt pct Paranox 100, and 93 wt pct Isopar L.

the emulsion membranes containing an organic phase with 5 wt pct P5100 and 2 wt pct Paranox 100 reached the 90-pct extraction level for copper in  $\leq 20$  min. This increased agitation speed resulted in the generation of smaller globules than were produced at the standard speed (estimated at  $< 0.5$  mm versus 1 to 2 mm in diameter). Thus, the surface area for mass transfer was increased. The internal phase leakage remained fairly constant at  $< 1$  pct except at the highest tip speed, where it increased to  $> 2$  pct. The membrane swell increased with each increment of tip speed increase. The swell became excessive (75 pct) at the highest speed tested. Thus, the choice of agitator speed in the extraction vessel had to weigh fast copper extraction against emulsion membrane swell and leakage problems.

Swelling of the membrane was affected to a degree by the length of contact time during the extraction of copper (table 7). A similar conclusion was reached by other investigators (9, 16). Therefore, an added incentive for accomplishing the extraction rapidly was to minimize the membrane swelling. With most of the emulsion membranes used in these tests, contact times up to 45 min had a negligible effect upon the internal phase leakage.

Table 7.—Effect of time on copper extraction and membrane stability<sup>1</sup>

Test duration, min	Cu extracted, pct	Membrane swell, pct	K leakage, ppm
5	56.6	0.0	1.3
10	96.0	1.5	1.1
15	98.8	1.5	1.2
30	99.7	10.8	1.7
45	99.8	18.5	1.8

<sup>1</sup>Organic phase of emulsion membrane contained 1.5 wt pct Paranox 100, 5 wt pct P5100, and 93.5 wt pct Isopar L.

<sup>2</sup>Initial aqueous solution contained 182 ppm Cu at pH 2.5; agitator tip speed was 157 ft/min.

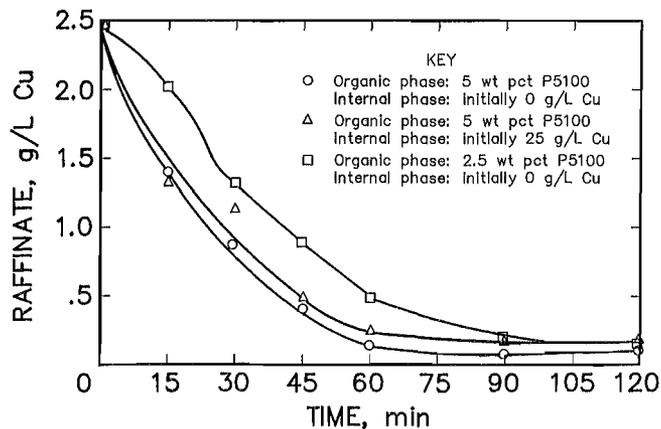


Figure 10.—Effect of organic and internal phase compositions on copper extraction.

## SINGLE-STAGE EXTRACTION TESTS

Several different circuit configurations and procedural changes were tried in order to determine the limit of copper extraction with the current level of optimization of membrane mixtures and laboratory-scale equipment. A batch extraction test was conducted in the standard manner except that the pH of the raffinate was adjusted back to the initial level of the feed solution (pH of 2.5) at the 30- and 60-min time periods. This test used a feed solution with an initial concentration of about 2.5 g/L Cu. The rate of extraction was similar to that depicted by the two lower curves in figure 10, except that the extraction of copper continued throughout the entire 2-h period. The final raffinate contained only 7 ppm Cu (99.7-pct extraction). The internal phase leakage was low (<2 pct) and the membrane swell was about 6 pct. A similar test without pH adjustment resulted in a final raffinate containing about 150 ppm Cu (94-pct extraction). A relatively low tip speed (118 ft/min) was used in these single-stage tests and in the two-stage extraction tests.

Using the standard procedures and equipment of previous tests, a feed solution that contained 0.3 g/L Cu at pH 2.5 was contacted with an emulsion membrane in a single-stage test. The copper concentration of the feed solution was reduced to <1 ppm after about 45 min of contact (99.8-pct extraction). No pH adjustment was made in this test (raffinate pH was 1.9). The internal phase leakage was again very low; however, the membrane swell at the end of the 2-h test was about 24 pct. Since the extraction was essentially completed at the 45-min point, the swell would likely have been considerably lower had the test ended at that point.

## TWO-STAGE EXTRACTION TESTS

A two-stage extraction test was conducted using fresh emulsion in both batch stages. This test simulated a crosscurrent extraction circuit. A contact time of 60 min was used in each stage. The first contact reduced the copper concentration of a 2.5-g/L Cu feed solution to about 83 ppm (96.7-pct extraction). The copper-loaded emulsion was replaced with fresh emulsion, and the second contact of the feed solution resulted in a final level of about 3 ppm Cu. No pH adjustment was made in this test, and the final raffinate pH was 1.3. The internal phase leakage was again very low. There was no measured membrane swelling during the first contact; however, the second contact resulted in a swell of about 9 pct.

A batch (pseudo) countercurrent multistage extraction test was conducted. This test simulated a two-stage continuous countercurrent circuit and used the same feed solution and residence time per stage as in the previous test. The copper concentration of the raffinate from the

simulated second stage averaged about 4 ppm (99.8-pct extraction). No pH adjustment was used in this test. The internal phase leakage was very low (<1 pct), and the average membrane swell was about 9 pct.

## EMULSION MEMBRANE BREAKAGE

Screening tests were conducted using several different techniques for the breaking of copper-loaded emulsion membranes. The techniques tested for emulsion breakage included solid media (employing selective surface wetting), centrifugation, ultrasonic energy, electrical fields (ac), thermal cycling (including rapid freezing), microwave heating, and magnetic fields. Of these techniques, only the tests with high electrical fields resulted in effective breakage of typical copper-loaded emulsion membranes. The breakage of emulsions with electrical fields has also been done by other researchers (13-14). The electrostatic coalescer was used to investigate the effect on emulsion breakage of the following parameters: internal droplet size, membrane components, and applied voltage.

Emulsions containing Paranox 106 surfactant and P5100 extractant were generated in the dispersion unit at rotor speeds between 4,600 and 10,000 r/min. This produced emulsion membranes containing internal droplets with average diameters ranging from <1  $\mu\text{m}$  to about 10  $\mu\text{m}$  (table 8). These emulsions were then used to extract copper (2.5 g/L) in batch tests before being placed in the cylindrical cell for breakage. The results indicated that under the conditions of these tests (6 kV and 5-min periods), breakage of emulsions was difficult with internal droplet sizes of <1  $\mu\text{m}$ . The emulsions with larger internal droplets (5 and 10  $\mu\text{m}$ ) were almost completely broken (about 95 pct). The percentage of breakage was calculated based upon a material balance for copper that related the amount of copper in the recovered internal phase to the total amount of copper in the emulsion membrane. Copper loading on the organic phase was taken into account in the calculation.

Table 8.—Effect of internal drop size on breakage of copper-loaded emulsions<sup>1</sup>

Av internal drop diam, $\mu\text{m}$	Emulsion generation speed, <sup>2</sup> r/min	Emulsion breakage, pct
<1 . . . . .	10,000	48
5 . . . . .	7,500	95
10 . . . . .	4,600	96

<sup>1</sup>Organic phase of emulsion membrane contained 0.5 wt pct Paranox 106, 2.5 wt pct P5100, and 97 wt pct Isopar L.

<sup>2</sup>Emulsion membrane was generated in dispersion unit with 3-min mixing time at indicated speed.

The effect of surfactant (Paranox 106) and extractant (P5100) concentrations on the breakage of emulsions was also investigated (table 9). The emulsion membranes for these tests were generated in the dispersion unit at a rotor speed of 7,500 r/min for a period of 3 min (corresponding to conditions producing internal droplets of about 5  $\mu$ m in diameter). The data indicated that breakage of the emulsion membranes was sensitive to both the surfactant and extractant concentrations of the organic phase. The breakage of the emulsions at standard conditions decreased as those concentrations were increased. Based upon these data, the preferred surfactant concentration was  $\leq 2$  wt pct, and the preferred extractant concentration was  $\leq 5$  wt pct.

**Table 9.—Effect of Paranox 106 and P5100 concentrations on breakage of copper-loaded emulsions<sup>1</sup>**

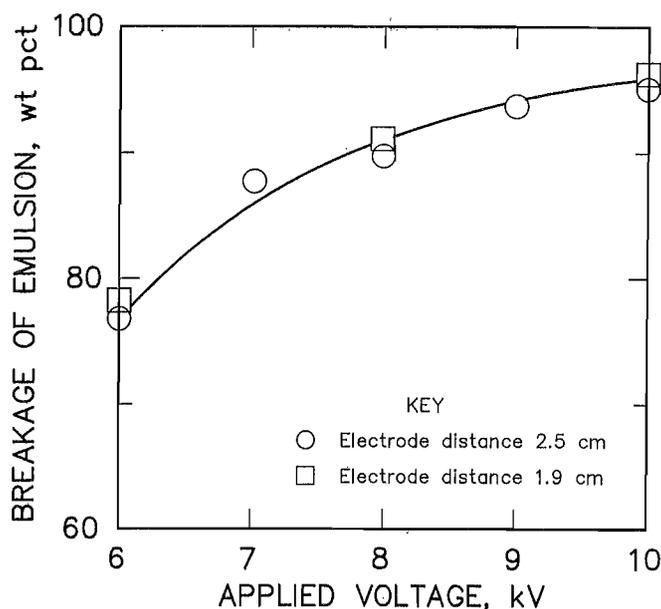
Concentration, wt pct	Breakage, pct
Paranox 106 surfactant: <sup>2</sup>	
0.5 .....	96
1.0 .....	90
2.0 .....	88
5.0 .....	86
10.0 .....	79
P5100 extractant: <sup>3</sup>	
1.0 .....	93
2.5 .....	96
5.0 .....	94
7.5 .....	87
10.0 .....	83
20.0 .....	67

<sup>1</sup>Emulsions were generated in dispersion unit at speed of 7,500 r/min with 3-min mixing time.

<sup>2</sup>Organic phase of membrane contained indicated amount of Paranox 106, 2.5 wt pct P5100, and balance was Isopar L.

<sup>3</sup>Organic phase of membrane contained indicated amount of P5100, 0.5 wt pct Paranox 106, and balance was Isopar L.

The effect of applied voltage and field strength on the breakage of copper-loaded emulsions was investigated (fig. 11). Emulsion membranes were prepared from an organic phase containing 2 wt pct Paranox 106, 2.5 wt pct P5100, and Isopar L. The standard internal phase was emulsified into the organic phase in the dispersion unit at a speed of 7,500 r/min. The emulsion was then used to extract copper (2.5 g/L) in standard batch tests before testing in the rectangular cell. The electrode configuration shown in figure 6 was used in these tests (rectangular cell). Two electrode distances (2.5 and 1.9 cm) were tested at each voltage level. At an electrode spacing of 2.5 cm, the breakage of emulsions increased from 76 at 6 kV to 94 pct at 10 kV, respectively. At the same voltage levels, the breakage was 2 to 3 pct higher for the 1.9-cm spacing. Under the conditions of these tests, the applied voltage had a larger influence on emulsion breakage than did the electrode spacing.



**Figure 11.—Effect of voltage on breakage of copper-loaded emulsions. Organic part of emulsion contained 2.5 wt pct P5100, 2 wt pct Paranox 106, and 95.5 wt pct Isopar L.**

## ORGANIC PHASE RECYCLING

Of paramount importance to an LEM circuit is the recycling of the separated phases after they have been broken. A very brief series of tests was run in which emulsion membranes were generated, were used to extract copper, and were broken, and the organic phase was recycled for another complete cycle. Although only two emulsion making-breaking cycles were completed, it is important to note that no degradation of performance was observed. The organic phase that went into the emulsion membrane contained 2.5 wt pct P5100 extractant and 2.0 wt pct Paranox 100 surfactant. The copper extraction for both cycles was about 95 pct. By visual inspection, essentially complete breaking of the copper-loaded emulsion was experienced for both cycles. Further tests of this type will be conducted in a laboratory-scale continuous circuit.

## ORGANIC DECOMPOSITION

Upon completion of some of the extraction and breaking tests, a white material formed at the interface between the separated phases. Draxler (18) commented that decomposition of the extractant (PT5050) had been observed and the process apparently was accelerated by the presence of surfactants (ECA 4360 and Span 80). No further details were given. The extractant and one of the surfactants (ECA 4360) mentioned by Draxler were similar to some of the compounds used in this investigation. To determine if changes were occurring in the organic phase, IR measurements were made before and after contact with

an internal solution. In this test, an organic phase containing Paranox 100 surfactant and P5100 extractant was contacted with a standard copper-containing internal solution for a 1-month period in a temperature-controlled laboratory shaker. Gentle agitation was used throughout the test. Comparison of the IR spectra indicated that a new organic species had been formed during the contact.

Cursory tests were then conducted to determine if prolonged contact between organic phases containing P5100 extractant and either internal solution or feed solution would reduce the effectiveness of the extractant. Paranox 100 was used as the surfactant in these tests. The tests were conducted for 1-month periods as described previously. The maximum copper-loading capacity was determined for the initial organic phases and on samples of organic phase that were drawn during the tests. The loading capacities were then related to various parameters that were investigated. There was considerable scatter in the resulting data, but several trends were apparent.

Generally, there was a reduction in copper-loading capacity for organic phases that contained P5100 and Paranox 100 after the organic phases were contacted with internal solutions containing appreciable  $H_2SO_4$  concentrations (levels of 90 to 200 g/L were tested). The decrease in maximum copper-loading capacity ranged up to 14 pct, depending on the solutions used in the tests. These results cannot be used to predict the rate of decomposition in a continuous operating system, but they do indicate that under some conditions changes occurred to the extractant.

Generally, the copper-loading capacity decreased as the acid concentration of the internal phase was increased. Results relating the surfactant concentration (1 to 4 wt pct) and copper concentration in the internal phase (0 to 25 g/L) to the reduction in copper-loading capacity were inconclusive. Further research needs to be done in this area. The mechanism involved with extractant decomposition should be identified, and the rate of decomposition in a continuous circuit needs to be quantified.

## CONCLUSIONS

Based upon the data and conclusions in the previously cited published reports and the preliminary research by the Bureau, reported here, the LEM technique appears to offer intriguing potential for the extraction of substances from aqueous solutions. However, based upon the literature search conducted, there seems to be a lack of detailed information concerning several aspects of the LEM technique. For example, there is little information concerning the performance of LEM circuits in industrial situations where mixtures of metals, suspended solids, and/or dissolved organics are present in the feed solutions. In addition, few data were found concerning the mechanisms or controlling parameters for the decomposition of oxime-type extractants in emulsion membranes. Detailed information in these areas is necessary before it is possible to fully appraise the potential of the LEM technique.

Preliminary research by the Bureau showed that three surfactants offered good performance characteristics: Paranox 100, Paranox 106, and PA-18. Several extractants were identified that functioned well when used with Paranox 100 (P5100, LIX 64N, LIX 84, and LIX 34). Emulsion membranes that contained LIX 34 did not extract copper as well as the other extractants; however,  $Fe^{3+}$  rejection was better. Data showed that P5100 was the superior extractant of copper when PA-18 was used to stabilize the emulsion membranes. However, emulsions containing P5100 appeared to yield better  $Fe^{3+}$  rejection when Paranox 100, rather than PA-18, was used as the stabilizer. Generally, extraction data with the above-mentioned extractants and surfactants indicated good  $Cu^{2+}$  extraction, some coextraction of  $Fe^{3+}$ , slight coextraction

of  $Zn^{2+}$ , but essentially complete rejection of  $Co^{2+}$  and  $Fe^{2+}$ . The preferred extractant and surfactant concentrations in the organic phases of the emulsion membranes were  $\leq 5$  wt pct and  $\leq 2$  wt pct, respectively.

Nearly complete extraction of copper resulted in tests with LEM. The copper concentration of a 2.5-g/L Cu feed solution was reduced to 7 ppm (99.7-pct extraction) in a single-stage batch test when the pH was maintained at a relatively constant level (pH of 2.5). Copper concentrations were reduced to 3 and 4 ppm, respectively, in tests that simulated two-stage crosscurrent and countercurrent circuits. These batch tests were conducted without pH adjustments and effectively extracted copper from the 2.5-g/L Cu feed solution. The internal phase leakage was low in all cases ( $< 2$  pct), and membrane swells ranged from 6 to 9 pct. A single-stage batch test treated a feed solution containing 0.3 g/L Cu. After about 45 min of a 2-h test, the copper level of the raffinate was reduced to  $< 1$  ppm (99.8-pct extraction) without a pH adjustment. However, this test resulted in a large membrane swell (24 pct).

As shown in preliminary tests, the ability of LEM to extract copper to low levels shows the potential applicability of this technique for waste water treatment. It is expected that through further optimizing studies of the membrane mixtures and the equipment designs, the rates of extraction can be increased and the membrane swells can be reduced. The data indicate that a balance must be found in the extraction unit between agitation intensity and residence time so that copper extraction is maximized, while membrane swelling and leakage are minimized.

Emulsion breaking tests resulted in separation and recovery of up to 96 pct of the internal phase from copper-loaded emulsion membranes. The recovered organic phase was recycled through two complete cycles without apparent problems. Some apparent decomposition of the

extractant (P5100) was experienced in 1-month continuous contact tests when Paranox 100 was used as the emulsion stabilizer. The rate of decomposition needs to be quantified in long-duration continuous circuit tests.

## REFERENCES

1. Kessler, D. P., and J. L. York. Characteristics of Inclusions in the Dispersed Phase of Liquid-Liquid Suspensions. *AIChE J.*, v. 16, No. 3, 1970, pp. 369-374.
2. Sandblom, J. Liquid Ion-Exchange Membranes With Weakly Ionized Groups. I. A Theoretical Study of Their Steady State Properties. *J. Phys. Chem.*, v. 73, No. 1, 1969, pp. 249-256.
3. \_\_\_\_\_. Liquid Ion-Exchange Membranes With Weakly Ionized Groups. II. The Resistance and Electromotive Force of a Thin Membrane. *J. Phys. Chem.*, v. 73, No. 1, 1969, pp. 257-264.
4. Li, N. N. Separating Hydrocarbons With Liquid Membranes. U.S. Pat. 3,410,794, Nov. 12, 1968.
5. Li, N. N., R. P. Cahn, and A. L. Shrier. Liquid Membrane Process for the Separation of Aqueous Mixtures. U.S. Pat. 3,779,907, Dec. 18, 1973.
6. Frankenfeld, J. W., R. P. Cahn, and N. N. Li. Extraction of Copper by Liquid Membranes. *Sep. Sci. and Technol.*, v. 16, No. 4, 1981, pp. 385-402.
7. Li, N. N., R. P. Cahn, D. Naden, and R. W. M. Lai. Liquid Membrane Processes for Copper Extraction. *Hydrometallurgy*, v. 9, 1983, pp. 277-305.
8. Hayworth, H. C., W. S. Ho, and W. A. Burns, Jr. Extraction of Uranium From Wet Process Phosphoric Acid by Liquid Membranes. *Sep. Sci. and Technol.*, v. 18, No. 6, 1983, pp. 493-521.
9. Griffiths, R. F. (ed.). Liquid Membrane Applications in Waste Water Treatment and Metals Recovery (Proc. seminar held at UMIST, Manchester, U.K., Apr. 22, 1980). Univ. Manchester, Manchester, England, 1980, 88 pp.
10. Hayworth, H. C. A Case in Technology Transfer. *Chem. Technol.*, v. 11, June 1981, pp. 342-346.
11. Kitagawa, T., Y. Nishikawa, J. W. Frankenfeld, and N. N. Li. Wastewater Treatment by Liquid Membrane Process. *Environ. Sci. and Technol.*, v. 11, No. 6, 1977, pp. 602-605.
12. Cahn, R. P., J. W. Frankenfeld, N. N. Li, D. Naden, and K. N. Subramanian. Extraction of Copper by Liquid Membranes. Ch. 4 in *Recent Developments in Separation Science*. CRC Press, v. 4, 1981, pp. 51-64.
13. Wagner, J. P. Coalescer Apparatus for Electrostatically Resolving Emulsions. U.S. Pat. 4,391,698, July 5, 1983.
14. Hsu, E. C., and N. N. Li. Electrodes for Electrical Coalescence of Liquid Emulsions. U.S. Pat. 4,415,426, Nov. 15, 1983.
15. Hatton, T. A., and D. S. Wardius. Analysis of Staged Liquid Surfactant Membrane Operations. *AIChE J.*, v. 30, No. 6, 1984, pp. 934-944.
16. Thien, M. P., T. A. Hatton, and D. I. C. Wang. Separation of Amino Acids From Fermentation Broth Using Liquid Emulsion Membranes. Paper in Proceeding of International Solvent Extraction Conference, Munich, Fed. Repub. Germany, Sept. 11-16, 1986. Deutsche Gesellschaft für Chemisches Apparatewesen, Frankfurt, Fed. Repub. Germany, v. 3, 1986, pp. 685-693.
17. Marr, R., and A. Kopp. Liquid Membrane Technology—A Survey of Phenomena, Mechanisms, and Models. *Int. Chem. Eng.*, v. 22, No. 1, 1982, pp. 44-60.
18. Draxler, J., W. Furst, and R. Marr. Separation of Metal Species by Emulsion Liquid Membranes. Paper in Proceedings of International Solvent Extraction Conference, Munich, Fed. Repub. Germany, Sept. 11-16, 1986. Deutsche Gesellschaft für Chemisches Apparatewesen, Frankfurt, Fed. Repub. Germany, v. 1, 1986, pp. 553-560.
19. Draxler, J., R. Marr, A. Bouvier, A. Kriechbaumer, and M. Protsch. Scale-Up of Liquid Membrane Permeation Plants. Paper in Proceedings of International Solvent Extraction Conference, Denver, CO, Aug. 26-Sept. 2, 1983. *Int. Solvent Extr. Conf.*, Denver, CO, 1983, pp. 282-283.
20. Protsch, M., and R. Marr. Development of a Continuous Process for Metal Ion Recovery by Liquid Membrane Permeation. Paper in Proceedings of International Solvent Extraction Conference, Denver, CO, Aug. 26-Sept. 2, 1983. *Int. Solvent Extr. Conf.*, Denver, CO, 1983, pp. 66-67.
21. Halwachs, W., and K. Schugerl. The Liquid Membrane Technique—A Promising Extraction Process. *Int. Chem. Eng.*, v. 20, No. 4, 1980, pp. 519-528.
22. Melzner, D., A. Mohrmann, W. Halwachs, and K. Schugerl. Selective Extraction of Zinc in a Countercurrent Kuhni Extractor Using Liquid Surfactant Membrane Emulsions. Paper in Proceedings of International Solvent Extraction Conference, Denver, CO, Aug. 26-Sept. 2, 1983. *Int. Solvent Extr. Conf.*, Denver, CO, 1983, pp. 64-65.
23. General Mills Chemical, Inc., Minerals Industries and Research Groups (now part of Henkel Corp., Tucson, AZ). LIX 70—A Major Advance in Liquid Ion Exchange Technology. *Tech. Inf. Booklet*, 1971, 33 pp.
24. Mikucki, B. A., and K. Osseo-Asare. The Liquid Surfactant Membrane Process: Effect of the Emulsifier Type on Copper Extraction by LIX 65N-LIX 63 Mixtures. *Hydrometallurgy*, v. 16, 1986, pp. 209-229.
25. Kondo, K., F. Nakashio, and K. Funatsu. Extraction Kinetics of Copper With Liquid Surfactant Membranes Containing Hydroxyoxime in a Stirred Transfer Cell. Paper in Proceedings of International Solvent Extraction Conference, Denver, CO, Aug. 26-Sept. 2, 1983. *Int. Solvent Extr. Conf.*, Denver, CO, 1983, pp. 286-287.