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FIELD TEST OF LIQUID EMULSION MEMBRANE TECHNIQUE FOR COPPER RECOVERY FROM MINE SOLUTIONS

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ABSTRACT

The U.S. Bureau of Mines investigated the use of unsupported liquid emulsion membranes (LEM's) for the extraction of copper from heap-leach and mine solutions with the specific objective of developing innovative water purification technology. A mobile, continuous circuit used simple equipment designs for all units of the system. The formulation of the emulsion membrane was optimized so that the emulsion had good stability during extraction, but was broken with relatively mild conditions in an electrical coalescer. The recovered organic phase was recycled without apparent problems and the oxime extractant was regenerated with a hydroxylamine salt solution. Copper was recovered from solution in an electrowinning cell using fairly standard parameters. A 9-day, around-the-clock test was completed at a copper mine in Arizona during which 5,600 gal of solution was processed. Three different solutions were used during the test. They were (1) normal plant pregnant leach liquor (PLS) containing 1.43 g/L Cu, (2) PLS diluted with mine water to 500 ppm Cu, and (3) PLS diluted with mine water to 320 ppm Cu. The latter two solutions simulated waste streams that were of interest to the mine operator. All three solutions contained suspended solids that did not adversely affect the LEM system. Copper extractions averaged 98.0% for the first solution, 95.7% for the second solution, and 91.6% for the third solution. Membrane swelling averaged less than 8% and membrane leakage less than 0.1% for the test.

Keywords
Liquid Membrane and Copper Recovery.

INTRODUCTION

Background

The U.S. Bureau of Mines (USBM) has investigated the use of nonsupported liquid emulsion membranes (LEM) for the extraction of metals from dilute, aqueous solutions since 1988. Originally, the USBM was interested in using the LEM technique both to selectively recover metals from dilute solutions and to help clean up minerals processing solutions. Two types of solutions were investigated: waste streams containing various levels of copper, and dilute heap-leach solutions. As part of this research study, the USBM, in cooperation with an industrial partner, investigated Cu extraction from three types of mine solutions using an LEM precommercial demonstration unit (PDU) at an Arizona copper mine from September 13–25, 1993. This paper reports the results of this experimental test program.

Conventional solvent extraction (SX) techniques frequently are inadequate for removing metals from dilute acidic solutions. Resin ion exchange frequently is not selective enough to be cost efficient for the recovery of metals from dilute acidic solutions. LEM technology often is superior to the above metal extraction methods since it can selectively remove metals from solutions that contain metals in the parts per million level, and LEM technology can remove metals from acidic solutions with pH values below 2.0. Ion exchange resins often show very little selectivity towards specific individual metals and remove them as a combined solid product, frequently of little commercial value. When used in combination with metals recovery by electrowinning (EW), LEM provides a means for recovering Cu from dilute acidic solutions. The useful product is cathodic Cu.

The LEM technique was first proposed by Li [1] in the 1960's. Initially, Li's work concentrated on the separation of hydrocarbons with liquid emulsion membranes and, later, on the removal of dissolved constituents (phenols, phosphoric acid, sodium nitrate, and ammonia) from aqueous solutions. During the 1970's, research on this technique was extended to the removal of Cu from acidic leach solutions and the extraction of U from wet-process phosphoric acid [2–3]. Research in Japan involved the extraction of NH_3, Cr^{+6}, Hg^{2+}, Cd^{2+}, and Cu^{2+} from industrial waste water [4]. Draxler, Furst, Protsch, and Marr investigated the extraction of Zn from a waste water stream at a rayon plant in Austria [5–6]. The Zn level reportedly was reduced to <3 ppm. The plant was closed by fire in 1987 after about a year of operation.

Description of the LEM System

Unsupported LEM's were made by forming an emulsion from two immiscible phases and then dispersing that solution into a third phase (a feed solution). The emulsions used in the field tests and in previous USBM research were a water-in-oil type. In a typical arrangement (Figure 1), the internal solution (also called the stripping solution) and the organic phase are emulsified to form extremely fine droplets of the internal solution dispersed in the organic phase. The organic phase contains a conventional SX extractant to facilitate the selective transport of the metal through the organic membrane. 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 surfactant that is used to stabilize the emulsion. The emulsion then is dispersed into the feed solution, forming the globules similar to the idealized individual sketch shown in Figure 1. The surface-active agent (surfactant) is shown arranged on the surfaces of the emulsion membrane droplet (globule) with the lipophilic tail in the organic phase and the hydrophilic polar head in the water phases. Metal is extracted at the outside surface of the globule by the SX extractant, transported across the organic membrane as a metal-organic complex, and then stripped and stored in the internal solution. Typically, a strong acid solution is used as the internal solution. Thus, extraction and stripping operations are combined in a single process in the LEM technique.

Three critical parameters by which LEM performance is judged are (1) metal extraction, (2) membrane swelling, and (3) membrane leakage. Membrane swelling refers to the increase in volume of the emulsion membrane during the extraction process, and membrane leakage refers to the mass transfer of the internal aqueous phase through the emulsion membrane into the aqueous feed solution. Metal extraction, membrane swelling, and membrane leakage are greatly influenced by the organic globule and internal droplet diameters. Generally, the smaller the emulsion membrane globule and internal droplet sizes, the greater the metal extraction becomes owing to the increase in surface area for mass transfer. Conversely, greater membrane swelling and leakage occur as the globule and internal droplet sizes decrease. USBM research has focused on maximizing metal extraction while minimizing membrane swelling and leakage. Performance goals for the LEM PDU were a Cu extraction ≥90%, membrane swelling to a maximum 3%, and membrane leakage to <0.1%.

Copper recovery from the feed solution can be simplified into a three-step process. First, Cu combines with the extractant that is in the organic globule. This is represented by the following equation:

$$Cu^{2+}(\text{feed}) + 2RH(\text{extractant}) \rightleftharpoons CuR_2(\text{organic phase}) + 2H^+(\text{feed}) \quad (1)$$

where R = organic group.

Next, the Cu is transferred from the extractant in the organic globule to the acidic internal trapping solution:

CuR_2(organic phase) + $2H^+$(internal) $\rightleftharpoons$ Cu^{2+}(internal) + 2RH(organic)(2)

Cu is removed and recovered from the internal solution as a cathodic plate by EW. This also regenerates the acid that was lost to the feed in the first reaction. The EW process can be represented by the following reaction:

Cu^{2+}(internal) + H_2O + $2e^-$ $\rightleftharpoons$ Cu^0(cathode) + 1/2 $O_2\uparrow$(anode) + $2H^+$(internal)).(3)

As the organic phase is recycled through a continuous LEM circuit for an extended period of time, some data indicated that the maximum Cu loading capacity decreases slightly. Previous testing at the USBM with a laboratory-scale, continuous LEM unit established the rate of extractant decomposition to be 0.1 mol%/h using an organic phase that contained 7.5% P5100 extractant, 1.0% Paranox 100 surfactant, and 91.5% Isopar L diluent. The maximum Cu loading capacity of the organic phase had decreased to 70% of its original capacity after 100+ h use in the continuous circuit. However, the organic was successfully regenerated by contacting it for 30 min with a hydroxylamine salt, restoring the organic loading capacity to ≥85% of its original value. The regeneration step was incorporated in the larger scale pilot plant and was used during the testing in Arizona.

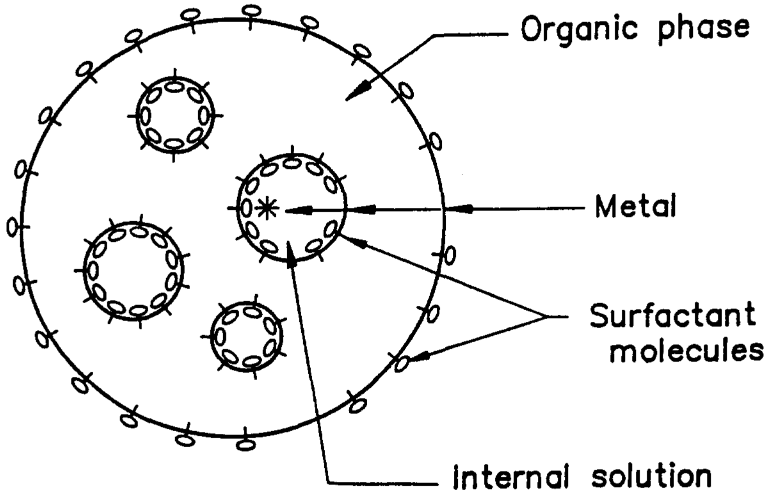

Fig.1 Idealized sketch of liquid emulsion membrane droplet (globule).

EQUIPMENT AND EXPERIMENTAL RUN CONDITIONS

Equipment

A simplified flow sheet of the LEM continuous circuit that was used in this research program is shown in Figure 2. The USBM process is composed of three main unit operations. The first operation consists of combining the organic phase with the internal solution phases in the dispersion unit to form a stable emulsion. Next, the emulsion is contacted with the feed solution containing the metal ion of interest—in this case, Cu—in the extraction unit. Moderate agitation is used in this step to form small globules of emulsion in the feed solution that average between 0.3 and 0.6 mm in diameter. The Cu ions are extracted into the organic phase and then stripped into the internal solution, where they are concentrated. The large surface area provided by the small internal-droplet size, usually about 5 µm, facilitates the rapid transfer of the metal ions across the organic phase and into the internal solution. Next, the "loaded" emulsion is separated from the feed solution (now depleted of Cu ions) and transferred to a device to break the emulsion for recovery of both the organic phase and the Cu-loaded internal solution phase. The third step uses an electrical coalescer to break the emulsion. Following breaking and separation, the extracted metal is recovered by EW. The organic phase and regenerated internal solution then are recycled to the beginning of the process to form more emulsion.

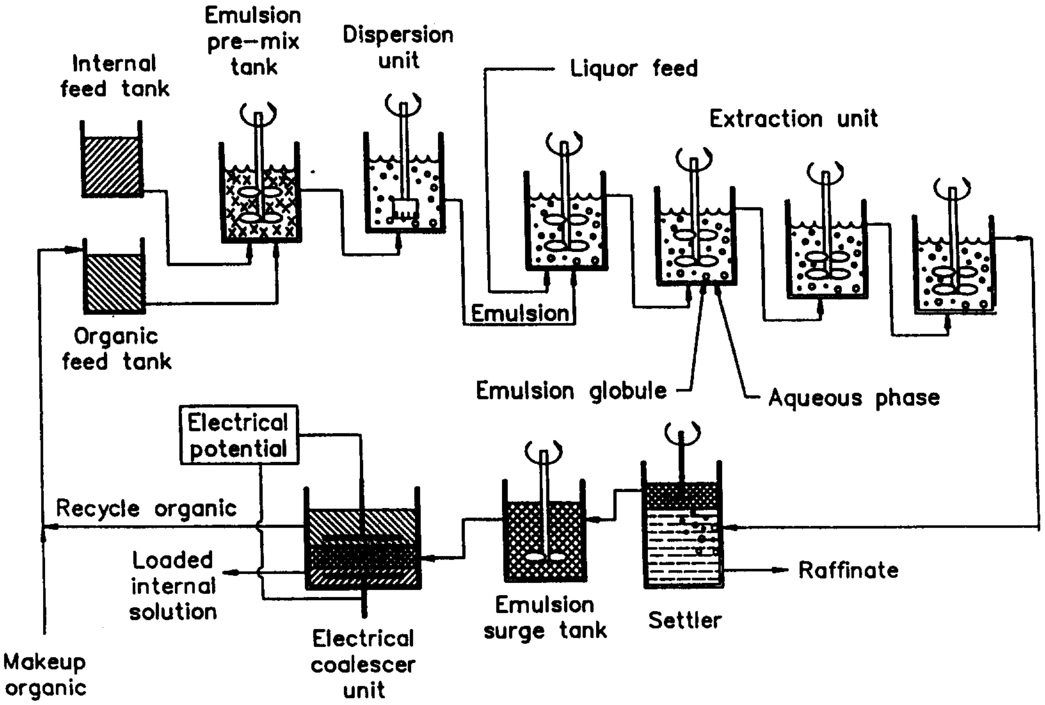

Fig.2 Simplified flow sheet for laboratory-scale continuous LEM circuit.

The emulsion-membrane generation circuit contains feed tanks from which internal and organic solutions are measured and mixed together in the premix tank, then pumped into the emulsion generation unit. The emulsion generator is a commercial dispersion unit that consists of a slotted stator and an internal rotor that normally operates at speeds of 7,000 rpm. The four-stage, concurrent extraction process is accomplished in individual tanks in which the emulsion is mixed with the aqueous feed liquor. The tanks are constructed of acrylic and fitted with a double-set of three-bladed marine-type propellers. After passing through the extraction stages, the emulsion and aqueous raffinate flow by gravity into a settler. After separation, the emulsion phase flows out near the top of the settler, and the raffinate, out the bottom. The raffinate then flows through a coalescer to remove any retained organic phase before exiting the process. The emulsion flows out of the settler into an electrical coalescer which uses a 60-cycle ac potential applied between two electrodes to break the emulsion into two separate phases, an aqueous internal solution and an organic solution. Copper is removed from the internal solution in an EW cell before mixing with the organic again in the front end of the circuit to recreate the emulsion. The organic is regenerated in a bleed stream with a hydroxylamine-salt solution before being recycled to be mixed with the internal solution to form the emulsion.

Test Conditions

Three different Cu solutions were used in the LEM continuous circuit during the field test in September. The first solution contained 1.43 g/L Cu and was the Cu producer's heap leach liquor, which normally was processed by conventional SX and EW to produce a Cu cathode product. Data obtained from processing this feedstock would be used to make a direct cost comparison between LEM and traditional SX techniques for Cu extraction and removal. The second and third solutions approximated waste streams that the Cu manufacturer wanted the USBM to investigate for applicability of the LEM technology in waste clean-up. A total of 5,579 gal of feed was processed by the LEM pilot plant while in Arizona, and the equipment was operated for a total time of 196 h. Both the EW and solvent regeneration systems were used on all three feeds. A summary of operating conditions and results are shown in Table 1.

TABLE 1 Summary of LEM Field Test

Operating conditions:	
Organic composition	7.5 wt% Acorga M5640 1.0 wt% P100 surfactant 95.5 wt% 50–50 Isopar M & V
Organic viscosity	7.1 cp
Lean internal composition	20 g/L Cu, 165 g/L H_2SO_4
Overall retention time in extraction stages	22 min
Organic regeneration	10% of total organic flow
Retention time	30 min
Overall results:	
Total elapsed run time	196 h
Total aqueous feed processed	5,579 gal
Overall organic/internal ratio	4.44
Overall membrane swell*	8.3%
Results—test condition 1:	
Aqueous feed	PLS at 1.43 g/L Cu
Elapsed time	115 h
Total feed solution	2,796 gal
Aqueous/emulsion ratio	1.29
Copper extraction	98.0%
Membrane swell**	5.3%
Results—test condition 2:	
Aqueous feed	PLS diluted with mine water to 520 ppm Cu
Elapsed time	48 h
Total feed solution	1,583 gal
Aqueous/emulsion ratio	3.9
Copper extraction	95.7%
Membrane swell**	11.1%
Results—test condition 3:	
Aqueous feed	PLS diluted with mine water to 320 ppm Cu
Elapsed time	33 h
Total feed solution	1,200 gal
Aqueous/emulsion ratio	5.16
Copper extraction	91.6%
Membrane swell**	11.4%

*Based on samples collected.
**Based on solution analytical analysis.

RESULTS AND CONCLUSIONS

Copper extractions from all three solutions tested were very good, especially from the first two solutions. The average Cu extractions for the three solutions were 98.0%, 95.7%, and 91.6%, respectively. Membrane swelling was only 5.3% for the first solution, and 11.1% and 11.4% for the final two solutions. The higher swell with the last two solutions was due to the fact that the mixers in the extraction stages were operated at a higher speed than desired owing to some difficulties in transferring the raffinate and emulsion mixture to the settler from the extraction stages. (In field tests of the LEM system subsequent to the September 1993 Arizona field test, this problem was eliminated by repositioning the settler and last extractor.) Average globule diameters in the extractors while processing the second and third solutions were 0.2 to 0.3 mm, as opposed to 0.4 to 0.5 mm for the first solution.

Extractant regeneration was accomplished by taking a bleed stream of organic that amounted to 10% of the total organic flow and contacting it with an aqueous hydroxyl amine solution. A 30-min retention time was used in this regeneration step. The regeneration operation maintained the active extractant concentration at a constant level during the entire test. The active extractant level stabilized at about 85% of the initial level in the "fresh" organic phase.

One of the advantages of the LEM technique over SX is that generally, significantly less organic is lost in the raffinate with the LEM technique. This feature can be especially important from the cost standpoint in the processing of dilute solutions. Based on a limited number of raffinate samples taken during the field test to get an order-of-magnitude indication of organic losses, the total contained organics were 4.6 ppm for the first solution (PLS), 11.9 ppm for the second (520 ppm Cu), and 5.7 ppm for the third (320 ppm Cu). These data indicate that the loss of organic in the raffinate would be expected to be quite low with the LEM technique. For reference purposes, literature indicates that typical raffinates from commercial SX units can contain 50 to 100 ppm total contained organics.

The EW unit was operated on all three feeds at a current density of 10 to 30 A/ft^2 and at a temperature of 40°C. The concentration of the strong electrolyte was approximately 26 g/L Cu and 160 g/L H_2SO_4, and the concentration of the lean electrolyte was approximately 20 g/L Cu and 165 g/L H_2SO_4. Since copper EW is well known technology, no attempt was made to optimize the EW parameters in the PDU. Actual run times for the second and third portions of the test were of relatively short duration; therefore, these test data were combined to obtain an overall current efficiency for that portion of the test that dealt with dilute solution treatment. The copper electrolyte used in the pilot plant did not contain any additives to control the "leveling" of the deposit. The major parameters and results are shown in Table 2.

TABLE 2 EW Operating Conditions

PLS:	
Current density	20 A/ft^2
Rectifier voltage	2.1 V
Copper recovered	31.5 lb
Current efficiency	93.1%
520-ppm Cu solution:	
Current density	14 A/ft^2
Rectifier voltage	1.8 V
Copper recovered	Combined with third portion of test
Current efficiency	Combined with third portion of test
Current efficiency	93.1%
320-ppm Cu solution:	
Current density	10 A/ft^2
Rectifier voltage	1.7 V
Copper recovered	3.2 lb (total of second and third portions of test)
Current efficiency	92.6% (combined second and third portions of test)

The first part of the field test used pregnant leach solution (PLS) that was fed to the system through an in-line filter. The final 24 h of this portion of the test used unfiltered PLS. No noticeable change in system performance occurred after switching to the unfiltered PLS. The next two portions of the test used PLS that was diluted with mine water to 520 ppm and 320 ppm, respectively. These solutions were filtered prior to processing because they contained a heavy solids concentration. Even after filtering, the solutions were still quite murky, indicating that suspended solids were still present, and again, no noticeable change in system performance occurred.

All three solution that were fed to the PRU contained more iron than copper. For example, the Cu/Fe ratios were: 0.81 for the PLS, 0.29 of the 520 ppm solution, and 0.19 for the 320 ppm solution. Based on a relatively limited amount of data, the relative transfer ratios of Cu/Fe into the internal solution ranged from about 350 in the processing of the PLS to about 100 in the processing of the dilute solutions. It should be noted that since iron was precipitating in the LEM system while the dilute solutions were being processed, some entrained iron precipitates were likely to be carried to the copper electrolyte. This would have "artificially" lowered the relative Cu/Fe transfer rates in the dilute solution treatment. The same copper internal solution (electrolyte) was recycled many times and used throughout the test. The iron level in the internal solution built up to just under 2 g/L Fe and stabilized at this point.

A preliminary economic evaluation based on laboratory data obtained prior to the September 1993 field test was developed by the USBM's Process Evaluation Group for a process to extract Cu from a heap-leach solution using LEM technology [7]. Also in this preliminary economic evaluation, a comparison was made of the LEM technology with an equivalent SX circuit based on published information. The LEM circuit also included an extractant regeneration system. The predicted accuracy of the economic evaluation is within 30% of the actual plant costs. The LEM circuit was designed to treat 4,000 gal/min of leach solution containing 1.36 g/L Cu. The estimated unit operating cost for the LEM circuit was $0.129 per pound of Cu recovered as opposed to $0.123 per pound for an equivalent SX unit. Economic evaluations of the September 1993 and subsequent field tests are in process.

SUMMARY

A continuous LEM circuit was designed and operated by the USBM to extract Cu from relatively dilute heap-leach solutions in an around-the-clock, 196-h test in Arizona in September 1993. No major equipment or mechanical failures were experienced, and industrial grade Cu plate was produced with Cu extractions averaging over 90%. The emulsion formation was optimized so relatively mild conditions could be used in the electrical coalescer to break the emulsion. The resultant recycled organic phases contained <1% aqueous phase (residual internal solution), and an extractant regeneration system was used to maintain good performance throughout the entire length of the run. A preliminary economic evaluation indicated that operating costs for the LEM unit were equivalent to those of an SX circuit in processing a low-to-medium strength heap-leach solution (about 1.4 g/L Cu). It is believed that LEM technology has significant advantages over SX when processing extremely dilute and highly acidic solutions similar to those found in many industrial waste streams.

FUTURE RESEARCH

Future USBM LEM research will focus on recovering Cu from more dilute solutions (less than 100 ppm) and at a lower pH (below 2.0), where the LEM technology may have significant advantages over SX. LEM research also will be expanded to recover other metals, such as Zn and Co, from industrial processes and waste waters, and another field test is being planned at the Midnite Mine site in Spokane, Washington, to remove waste contaminates from U processing. The LEM technique will be included in the USBM's Water Treatment Systems modular approach to treat acid mine drainage; the LEM technology will be used as a primary method of treatment and will then be linked to USBM polishing treatments, such as beads containing immobilized extractants, zeolites, and/or ion elutriation, to produce an effluent that will meet or exceed current drinking water standards. Another different application of LEM technology that will be explored in future years involves the recovery of anions such as sulfate from waste waters.

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