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SYNERGISTIC ADDITIVES WHICH ENHANCE COPPER EXTRACTION WITH LIQUID ION EXCHANGERS

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Paper to be Presented by R. H. Moore
at the Northwest Mining Association
Meeting, December 1-2, 1972, Spokane,
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ABSTRACT

Extraction of copper from dilute heap leach liquors with liquid ion exchange reagents is becoming of increased importance. This process effects purification and concentration of the aqueous copper bearing stream which allows recovery of pure copper in subsequent electrowinning. Addition of certain additives (synergists), which by themselves do not extract copper, to the liquid ion exchange-solvent mixture results in marked improvement in the rate of copper extraction and capacity for extraction at low pH. This effect is accompanied by improved separation of copper from iron which is the most deleterious impurity commonly encountered.

INTRODUCTION

General Mills has introduced and is promoting the use of a line of liquid ion exchangers for extraction of copper. These are proposed for use in extraction of copper from leach solutions to effect separation from impurities which interfere with subsequent copper electrowinning. The extracted copper may be stripped with an acidic solution to achieve a concentration effect.

To date the liquid ion exchange solvent extraction process has reached commercial scale operations at two locations in the United States: at the Bluebird Mine of the Rancher's Exploration Company and at Bagdad Copper, both

in Arizona. Both of these operations entail extraction of copper from heap leach liquors to effect separation from impurities, of which iron is principally of concern. Extraction is followed by stripping with return flow electrolyte from an electrowinning plant which is in closed cycle with the solvent extraction plant.

I would like now to briefly review the chemistry of the copper selective liquid ion exchange reagents in historical development before proceeding to the effect of synergistic reagents.

The extraction of copper with the liquid ion exchange reagents LIX-64 and LIX-64N has been shown by Atwood and Miller⁽¹⁾ to obey the stoichiometry illustrated in Figure 1. Here two moles of the organic ligand are required for each gram-ion of copper. It should also be noted that two equivalents of hydrogen ion are produced. Clearly, the extraction reaction can be reversed upon the addition of acid and this affords a ready means by which Cu may be stripped from the extractant so as to regenerate its extractive capacity and return the Cu to an aqueous phase.

The appearance of hydrogen ion on the right hand side of this equation is a qualified benefit, however, for while it tells us how the extractant may be regenerated, it also tells us this reaction will be pH dependent. The reaction will proceed to the right at high pH and will tend to the left at low pH.

This is a problem which has plagued the developers of LIX reagents since their first introduction in 1963. The first of these reagents was LIX-63 whose structure is illustrated in Figure 2. Habashi⁽²⁾ lists this as 5-8 diethyl-7-hydroxy-6-dodecanone-oxime which is in reasonable agreement with information disclosed in a patent assigned to General Mills.⁽³⁾ This reagent is relatively non-selective in its reactions with metal ions and has not been utilized in commercial processes for Cu recovery because the pH for efficient extraction of Cu lies above 4.0 ($pH_{50} = 4.8$).⁽¹⁾

In 1965 General Mills introduced LIX-64 whose structural features are illustrated in Figure 3. It is important to note that the $-C=N$ -bond restricts free rotation. This gives rise to the possibility of two isomers in cis-trans configuration as shown. Only one of these has the capability to react with copper ions because of the steric hindrance of the oxime hydroxyl

WHERE R STANDS FOR THE REACTIVE ORGANIC LIGAND

(1) R.L. ATWOOD AND J.D. MILLER, "STRUCTURE AND COMPOSITION OF COMMERCIAL COPPER CHELATE EXTRACTANTS", PAPER PRESENTED AT THE ANNUAL MEETING, AIME, SAN FRANCISCO, FEBRUARY 20-24, 1972.

FIGURE 1. Stoichiometry of the Reaction of Copper With LIX Reagents⁽¹⁾

5-8-DIETHYL-7-HYDROXY-6-DODECANONE OXIME⁽²⁾

⁽²⁾ HABASHI, FATHI, "PRINCIPLES OF EXTRACTIVE METALLURGY, VOL. II", GORDON AND BREACH SCIENCE PUBLISHERS, NEW YORK, N. Y. (1970).

⁽³⁾ U.S. PATENT NO. 3,294,842 ISSUED TO R. R. SWANSON, ASSIGNOR TO GENERAL MILLS, INC. DECEMBER 27, 1966

FIGURE 2. Structure of LIX-63

THE PARENT STRUCTURE IS GIVEN BY CERRAI⁽⁴⁾ AND IN A PATENT TO SWANSON⁽⁵⁾. THE IMPORTANT THING TO NOTE IS THAT LIX-64 IS A MIXTURE OF PHENOXIMES ONLY ONE OF WHICH IS Cu REACTIVE.

⁽⁴⁾ CERRAI, E. AND GHERSINI, ANALYST, 94, 599 (1969)

⁽⁵⁾ U. S. PATENT NO. 3,428,449 ISSUED TO R. R. SWANSON FEBRUARY 18, 1969.

FIGURE 3. Structure and Composition of LIX-64

group. LIX-64 is thus a mixture of isomers, one of which is reactive and one which is not, and it contains some LIX-63 which, as was shown in a patent assigned to General Mills,⁽⁵⁾ markedly enhanced the rate of extraction of Cu by the substituted 2-hydroxy-benzophenoximes. Figure 4 illustrates the effect on the rate of extraction by additions of from 0.5 - 5.0 percent LIX-63 to 2-hydroxy-5-dodecyl benzo phenoxyoxime. The effect of LIX-63 additions appears to peak near 1%, and Cerrai⁽⁴⁾ reports this is its approximate concentration in LIX-64 available commercially.

LIX-64N became available in 1970 and its structure is illustrated in Figure 5. It differs from LIX-64 in that only the active isomer is present. The gain in performance is not as great as might have been hoped for, however, for Atwood and Miller⁽¹⁾ report that the commercial reagent contains about 53 percent of aliphatic compounds which do not extract copper. This dilution was evidently required to lend desirable physical properties (phase disengaging) to the extractant. Thus there is only a slight gain in copper extraction capacity.

LIX-70 introduced in 1971, differs from LIX-64N in that it contains a halogen substituent in the phenyl ring, probably in the position ortho to the phenol hydroxy group. The purpose of this substituent is to increase the acidity of the phenolic hydrogen atom to permit extraction at lower pH. This reagent was not available at the time the work reported here was undertaken and has not been evaluated by BNW. That the chloride substituent increases the extraction efficiency is amply attested by General Mills personnel⁽⁶⁾ who have shown the reagent extracts Cu efficiently from solutions as concentrated as 60 g/l with an equilibrium H₂SO₄ concentration as high as 100 g/l. As would be expected, sulfuric acid of 300 g/l is required for efficient stripping. This acidity may prohibit subsequent recovery of Cu by electrowinning though "blue stone" could be produced without difficulty.

More recently LIX-65N, LIX-71, and LIX-73 have appeared. In general, these reagents exhibit increased extraction efficiency for Cu at acidities intermediate between those suitable for LIX-64N at one extreme and LIX-70 at the other. Their stripping characteristics are likewise intermediate. Their extraction kinetics are slower than kinetics exhibited by LIX-64N and LIX-65N and LIX-71 require above ambient temperatures for optimum performance and this entails an added increment of cost which must be justified.

FIGURE 4. Effect on Extraction Rate of Additions to 2-Hydroxy-5-Dodecylbenzophenoxime⁽⁵⁾

GENERAL MILLS GIVES
A MOLECULAR WEIGHT
FOR THE BENZOPHENOXIME
AS 339⁽¹⁾. THIS WOULD
REQUIRE THAT THE
R BE $-(CH_2)_8CH_3$. THE
REAGENT IS STATED TO
CONTAIN 1% LIX-63

⁽¹⁾R.L. ATWOOD AND J. D. MILLER, *op. cit.*

FIGURE 5. Structure of LIX-64N

BNW STUDIES OF SYNERGISTIC EFFECTS

Early in 1969 Battelle commenced study of the then available L1X-64 reagent in an effort to discover synergistic reagents which might, when added in small amounts to L1X-64, enhance the extraction of Cu. This work was subsequently extended following availability of L1X-64N.

In the literature of solvent extraction of metal ions (until very recently) work referencing synergistic effects dealt primarily with the technology of the Atomic Energy industry. Familiar examples are those involving addition of neutral phosphate esters (TBP) and alkyl phosphine oxides (TOPO) to TTA (theonyltrifluoroacetone) or to di-2-ethylhexyl phosphoric acid.⁽⁷⁾ Thus additions of 0.003 F TBP to TTA enhances the extraction coefficient for extraction of U^{+6} from 0.01 M HNO_3 solution 5000 fold. The effect of trioctylphosphine oxide (TOPO) is even greater. In both instances the synergist (TBP) or (TOPO) was chemically combined with the uranyl-TTA complex, for in this instance, TTA alone does not fully saturate the coordinating ability of the uranyl ion.

The dictionary defines synergism as an overall effect of a combination which exceeds the effects of the constituents when considered separately. Thus, in the example of extractions with TTA the effect of TBP and TOPO is markedly synergistic. There are numerous examples that could be cited, but to get on with our story it is necessary to speculate on the nature of materials which might prove synergistic when added to L1X-64. It seemed that synergism might result either from mixed complex formation or from action of reagents which complex the acid produced when L1X-64 reacts with copper.

We first established the base line extraction behavior of L1X-64 in a kerosene solvent, at e.g. 20 w/o L1X-64. This behavior was then compared with that of solvents containing the same amount of L1X-64, but with a portion of the kerosene replaced by up to 10 w/o of the additive under test. In all cases C.P. $CuSO_4$ solution containing 4.0 g/l Cu^{+2} was used in the aqueous phase with various additions of H_2SO_4 to adjust the initial aqueous pH to the range 1.5 - 3.0.

Extractions were conducted in a small stirred contactor where the stirrer acts as a pump to disperse the aqueous phase into the overlying organic phase. This device simulates the extraction section of a mixer-settler. When the agitator is stopped, the time for disengagement of the phases can be approximated.

In these first tests, additions of 10 w/o TBP, TOPO, and Aliquat-336 (a quaternary amine) were found to completely inhibit extraction of Cu by LIX-64. These reagents have good extraction capacity for inorganic acids and it appears the hypothesis that synergism might be accompanied by co-extraction of acid generated by reaction of Cu with LIX-64 is untenable.

Figure 6 shows the marked synergistic effect of additions of di-2-ethylhexyl phosphoric acid (DEHPA) to LIX-64. The effect on the rate is quite similar to the effect of additions of ~ 1% LIX-63 to the benzophenoximes of which LIX-64 is mainly composed. However, LIX-64 has already benefited from the addition of LIX-63 and it is clear a very marked further increase in rate occurs here. With 10% DEHPA the approach to equilibrium is 85% complete in 30 seconds versus 9% complete in the absence of DEHPA. The effect of DEHPA is somewhat concentration dependent, but the differences are small between the effect at 2% versus 15%. The curve of Figure 6 is drawn through points at 10% DEHPA. In the absence of LIX-64, DEHPA does not extract copper at this pH.

It should be pointed out that this method of data display does not adequately disclose the effect of pH. The starting pH is shown, but the final pH depends upon the amount of copper extracted and is lowest at high extraction efficiency. The improvement due to DEHPA addition is, therefore, greater than is immediately apparent here. This subject will be treated more adequately below.

Figure 7 shows that while the behavior of DEHPA encourages the belief that a satisfactory synergist may be found, DEHPA will be of little practical importance. The reason lies in the marked propensity for DEHPA to extract iron in this pH range, an extraction that can be reversed only by caustic additions.

The lower dashed curve illustrates the extraction behavior of iron with a mixture containing 20% LIX-64 and 10% HEDTA. Just above is a curve showing the behavior of DEHPA (10%) with no LIX-64 present. It is clear that addition of DEHPA to LIX-64 solvents would destroy the ability of LIX-64 to separate Cu from iron which almost invariably accompanies copper and must be separated.

FIGURE 6. Synergistic Effect of DEHPA Additions
(Initial pH, 4.0 g/l Cu^{+2} Solution = 1.45)

FIGURE 7. Behavior of Iron with DEHPA
(2) Behavior of DBP

The upper curve of Figure 7 illustrates the synergistic effect of dibutyl phosphate (DBP) additions. DBP chemically resembles DEHPA and its synergistic effect is of the same intensity. Like DEHPA it should cause coextraction of iron. Moreover, it is of lower molecular weight than DEHPA and tends to partition with a higher concentration in the aqueous phase. This results in a tendency to produce stable emulsions.

Dinonylnaphthyl sulfonic acid (DNNSA) extracts copper at high pH, is a strong acid, and when added to LIX-64 strongly enhances the rate and magnitude of Cu extraction. As shown in Figure 8 its effect substantially exceeds the effect due to DEHPA. Most importantly, DNNSA has no tendency to enhance extraction of iron. In fact, the higher Cu loading achieved in the presence of DNNSA appears to result in displacement of iron which would normally be co-extracted by LIX-64 with the result that separation factors (Cu/Fe) are substantially increased. This is illustrated by data in Figure 9 where data at various DNNSA concentrations are compared versus data for LIX-64 with no DNNSA additions. The improvement in iron separation is approximately a factor of 6 with 10% DNNSA additions.

At about this point in time LIX-64N became available and it was decided to undertake a systematic investigation of the effect of DNNSA additions to the available extractants LIX-64 and LIX-64N using heap leach and vat leach liquors supplied by a mining company in lieu of synthetic Cu solutions.

For this work Cu-64 tracer was procured to simplify analysis of the more complex heap and vat leach liquors. After addition of the tracer and prior to contacts with the organic extractants, the leach solutions were heated to approximately 50°C for 10-15 minutes to ensure isotopic equilibration of the copper. The solution was cooled to room temperature prior to extraction.

Copper extractions were made by intimately mixing the two liquid phases with Teflon covered magnetic stirring bars in capped bottles. The phases were separated by centrifugation and equal volumes (3 ml) of each phase were analyzed for Cu-64 in a well counter and RIDL-400 channel analyzer. Preliminary distribution determinations as a function of mixing time showed that extraction equilibrium was obtained with this type of mixing within 10 minutes with both LIX-64 and LIX-64N. In the presence of DNNSA equilibrium was attained within two minutes.

FIGURE 8. Synergistic Behavior of Dinonylnaphthyl Sulfonic Acid
Aqueous: 4.0 g/l Cu^{+2} , pH = 1.45

<u>ORGANIC PHASE</u>	<u>$E_{Cu}^{o/a}$</u>	<u>$E_{Fe}^{o/a}$</u>	<u>S. F.</u>
20% LIX-64 (NO DNNSA)	0.72	0.0074	97
20% LIX-64 5% DNNSA)	1.63	0.0065	251
20% LIX-64 10% DNNSA	1.76	0.0030	586
5% DNNSA (NO LIX-64)	0.14	0.0069	20

*AQUEOUS: 4.0 G/L Cu^{+2}
 4.0 G/L Fe^{+3} (+ Fe-59 TRACER)
 pH = 1.386

FIGURE 9. Separation Factor, Cu/Fe as a Function of DNNSA Concentration

To extend the pH range of the measurements, sulfuric acid was used to adjust the initial pH of the solution.

Results are shown in Figure 10 where the copper distribution ratio is plotted versus the final (equilibrium) pH. The lower line is plotted through the points (open circles) for extractions with 20% LIX-64. Points for LIX-64N (open squares) lie but slightly above those for LIX-64. Thus, there is very little difference between the equilibrium extraction coefficients of these two reagents at any pH. It must be emphasized these are equilibrium, not maximum loadings.

The effect of 1.8% DNNSA on LIX-64 extractions is shown by the upper curve. The effect is dramatic and becomes increasingly important at low pH. This is of considerable practical importance because extraction with these reagents is invariably accompanied by a decrease in pH.

The effect of 1.8% DNNSA on LIX-64N is shown by the middle curve. The effect is significant but not as great as with LIX-64. These data show, that with DNNSA addition, LIX-64 is a more efficient extractant than LIX-64N. At a pH of 0.4, e.g., the extraction coefficient with DNNSA-LIX-64 exceeds that for DNNSA-LIX-64N by more than a factor of two. There is no immediately obvious explanation for this difference in behavior but it seems probable it is related to differences in concentration of Cu active species in the reagents.

The effect of the synergist can be illustrated in quite another way. Figure 11 shows equilibrium extraction isotherms for 20% LIX-64 and 20% LIX-64 plus 1.8% DNNSA. These were developed by equilibrating the organic and aqueous phases in varying phase volume ratios. As would be anticipated from earlier data, the isotherm taken with DNNSA present lies well above that with LIX-64 present alone. If one sketches in an operating line, these data indicate that four stages of extraction with LIX-64 will be required to reduce the copper concentration in the aqueous phase below 1 g/l. In the presence of 1.8% DNNSA, the same result can be achieved in two stages.

The potential for economies in plant design is readily apparent. It also follows that the effect on extraction capacity of an existing plant can be substantial.

The point in time wherein improved extraction technology needs to be applied is in advance of construction of a combined solvent extraction - electro-winning facility. This combination is designed so the solvent extraction plant

FIGURE 10. Copper Extraction* as a Function of Equilibrium pH.

FIGURE 11. Equilibrium Extraction Isotherms

handles exactly the amount of copper removed from the electrolyte in a single pass. (It might be more correct to state that the solvent extraction plant replaces that amount of copper when the solvent is stripped with return electrolyte.) Operators of such plants are reluctant to make changes of any kind, once the plant is on-stream and operating properly.

CONCLUSIONS

To sum up, it appears that the performance of these LIX reagents can be significantly improved by incorporation of a synergistic additive in small concentrations. Of such additives examined to date, DNNSA appears to be the best. This material is widely available at costs of 20-30¢ per pound. This is a fruitful area for further research. The LIX-64N series of reagents are fairly expensive. It would be most interesting if by the addition of synergists, low cost materials like the naphthenic acids could be induced to extract copper at low pH. If you think this is merely blue sky dreaming, it's not! D. S. Flett in England has shown that the pH for extraction of Cu with naphthenic acid is shifted from $\text{pH}_{50} = 4.5$ to $\text{pH}_{50} = 1.75$ by addition of 10% LIX-63.⁽⁸⁾ It could be that by allowing General Mills to conduct all its research on Cu extraction, that the Mining Industry is overlooking some good bets.

References Cited

1. Atwood, R. L. and J. D. Miller, "Structure and Composition of Commercial Copper Chelate Extractants," Paper presented at the Annual Meeting AIME, San Francisco, Feb. 20-24, 1972.
2. Habashi, Fathi, "Principles of Extractive Metallurgy, Vol. II," Gordon and Breach Science Publishers, New York, N.Y. (1970).
3. Swanson, R. R., U. S. Patent No. 3,294,842, December 27, 1966.
4. Cerrai, E. and Ghersini, Analyst, 94, 559 (1969).
5. Swanson, R. R., U. S. Patent No. 3,428,449, February 18, 1969.

6. Agers, D. W. and E. R. DeMent, "Evaluation of New LIX Reagents for Extraction of Copper and Suggestions for the Design of Commercial Mixer-Settler Plants," Presented at the Annual Meeting of AIME, Birmingham, Alabama, October 1972.
7. Emeleus, H. J. and A. G. Sharpe, "Advances in Inorganic Chemistry and Radiochemistry, Vol. 9," Academic Press, New York and London (1966).
8. Flett, D. S. and S. Titmuss, J. Inorg. and Nucl. Chem., 31, 2612 (1969).