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1. Introduction

The 20th century saw a marked expansion in the requirements for various metals and global need grew rapidly. Development of nations such as China and India as well as advances in metal application technologies has fueled increased demand for metals.

To meet the needs of modern society for metals in general and higher purity metals in particular, the mining industry has had to find more effective and efficient methods for processing ores and recovering the metal values to overcome the challenges associated with decreasing ore grades and increasingly stringent environmental regulations. The development of hydrometallurgical processing has played a significant role in helping to overcome these challenges and will provide many of the new processes required to meet the challenges of the future. Solvent extraction (SX) technology will play an integral role in many of these new processes.

The first example of the use of liquid-liquid solvent extraction to recover and purify a metal can be traced back to the extraction of uranyl nitrate into ethyl ether by Peligot in 1842\(^1\). The analytical chemistry literature contains thousands of references to the use of solvent extraction to isolate, purify and concentrate materials to facilitate analysis. This work in analytical chemistry has resulted in the development of a large pool of fundamental knowledge with regards to solution chemistry and organic based extractants\(^2\).

Starting in the 1950’s, solvent extraction was applied on a commercial scale to the recovery of uranium, vanadium and molybdenum\(^3\). The Mining Solutions business of BASF, which traces at least a part of its roots to the former General Mills Chemicals, developed Alamine\(\text{®} \) 336 and introduced it in 1957 for the recovery of uranium\(^4\). Alamine\(\text{®} \) 336 remains the reagent of choice to this day for the solvent extraction of uranium. The introduction of Alamine\(\text{®} \) 336 to the mining industry was followed by the development and introduction of LIX\(\text{®} \) 64 for the recovery of copper by solvent extraction. The first successful application of the leach-solvent extraction-electrowinning process for the recovery of copper was marked by the startup of the Ranchers Bluebird Mine copper solvent extraction plant (Design = 5,000 tonnes Cu/yr) in 1968\(^5\). This was quickly followed by the commissioning of the Cyprus Bagdad copper solvent extraction plant (Design= 6,600 tonnes Cu/yr) in 1969.

The Bagdad copper solvent extraction plant is now part of Freeport McMoRan and is the oldest operating solvent extraction plant in the world\(^6\). This was followed by the commissioning of the Nchanga Tailings Leach Plant (Design = 54,000 tonnes Cu/yr) in 1974\(^7\). Since it’s earliest beginnings, the Mining Solutions group has been committed to and remains committed to the development of solvent extraction technology and solvent extraction reagents.

The use of copper solvent extraction has grown dramatically since the late 1960’s. There are a total of more than 119 copper solvent extraction plants currently operating around the world producing an estimated 3.7 MM tons of copper in 2012. Given that total copper production in 2012 was estimated to be approximately 16.97 MM tons\(^8\), copper SX represented 22 % of the global copper production.
The Mining Solutions group’s dedication to improving solvent extraction technology has led to a number of industry “firsts”:

- Developed tertiary amines (Alamine® reagents) and quaternary amines (Aliquat® reagents) for metal extraction.
- Conceptualized leaching-solvent extraction-electrowinning for copper.
- Developed first commercially successful phenolic oxime reagents (LIX® reagents) for extraction of copper and nickel.
- Developed first alcohol modified aldoxime blend for copper extraction.
- Conceptualized and developed the “Picket Fence”.
- Introduced “Clay Treatment” and scrubbing processes for cleaning of contaminated circuit organics.
- Developed non-modified aldoxime/ketoxime blends.
- Conceptualized and developed use of wash stage technology in copper solvent extraction.
- Conceptualized and developed precipitation/releach flow sheet for recovery of nickel and cobalt from laterite ores.
- Developed non-modified aldoxime / ketoxime blends.
- Conceptualized and developed improved flowsheets
  - Modified Series Parallel
  - Optimum Series Parallel
  - Split Circuit
  - Sequential Circuit

The goal of this book is to familiarize the reader with the fundamental concepts of solvent extraction technology as well as with the LIX®, Alamine® and Aliquat® solvent extraction reagents and their applications. This booklet will also introduce other reagents, systems and services provided by the Mining Solutions business of BASF. More detailed information about specific reagents, metals, or process systems is available on request.

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* Isocalc® is a registered trademark in Brazil, Canada, Mexico, Peru and the US
2. Solvent Extraction

Solvent extraction (SX) as used in this booklet refers to a liquid-liquid extraction process for separating species in solution by their distribution between two immiscible solvents. In the metal recovery operations of interest, the SX process involves a chemical reaction of the metal species of interest with an organic extractant in an organic diluent such as a petroleum distillate cut similar to kerosene. The reaction of the metal species with the organic extractant results in a hydrocarbon soluble metal complex. The chemistry involves equilibria as a result transfer of the metal species into (extraction) and out of (stripping) the hydrocarbon phase can be controlled by altering conditions such as the pH of the aqueous.

As part of a metal recovery process, solvent extraction using BASF extractants has three primary objectives:

- Purification of the metals from unwanted impurities.
- Extract desired metal(s) away from impurities.
- Extract impurities away from desired metal(s).
- Concentration of the metal values to reduce downstream processing costs.
- Conversion of the metal values to a form which simplifies final recovery.

In any given solvent extraction process, one, two, or all three objectives may be necessary.

A key point for the reader to understand is illustrated in Figure 1. Solvent extraction is only one unit process in a series of unit processes in going from the metal bearing ore to the final metal product. The leaching process delivers a metal bearing solution whose nature will vary depending on the actual ore and the conditions required to achieve effective solubilization of the metal values. The solvent extraction process must be able to efficiently transfer the metal values from this incoming leach solution into the organic phase.

The final metal recovery step will determine the conditions under which the metal values will be transferred from the metal loaded organic to generate a concentrated and purified aqueous metal solution.

Leaching/SX/metal recovery are interlocking processes whose overall success is dependant on the effectiveness of each step. To develop an effective metal recovery process, it is critical to know the nature of the leach solution that is to be treated and the recovery process that will be used to produce the desired metal product. Each sets criteria within which the solvent extraction process must operate.

The solvent extraction process is conceptually simple:

- The metal bearing leach solution (Pregnant Leach Solution, PLS) is fed into a mixer along with an immiscible hydrocarbon solution of a metal extractant (Barren Organic) where the two solutions are intimately mixed.
- The resultant emulsion overflows from the extraction mixer into the settler. As it progresses down the settler, the solutions separate to give a metal loaded organic (LO) solution on top and a metal depleted aqueous solution (raffinate) on the bottom.
- The raffinate is discharged via an underflow weir and recycled to leaching. The LO passes over a weir and flows to a second mixer where it is intimately mixed with a strip solution.
- The resultant emulsion overflows from the strip mixer into the corresponding settler where it separates into a metal barren organic (BO) which is returned to extraction and a concentrated aqueous solution (Pregnant Strip Solution) of the desired metal in a form from which it can be readily recovered.

Figure 2 illustrates a copper solvent extraction plant consisting of 2 stages of countercurrent extraction and 2 stages of countercurrent stripping.

Formula 1

\[
2RH_{(Organic)} + Cu^{2+}_{(Aqueous)} \rightleftharpoons R_2Cu_{(Organic)} + 2H^+_{(Aqueous)}
\]
Each mixer-settler represents one stage of extraction or stripping. In conventional circuit flowsheets, E1 designates the stage into which the PLS is introduced and S1 designates the stage into which the loaded organic is introduced. In some cases, “wash” or “scrub” stages may be required to prevent or reduce the transfer of unwanted species on the organic phase from extraction to strip or vice versa. The combination of proper reagent choice, ability to use a variable number of mixer-settler stages, adjust flow rates, and use of wash stages allows a great deal of flexibility in designing a plant to meet the requirements for a given metal recovery problem.

To develop a successful flow sheet for the recovery of a metal, it is important to know the composition of the aqueous feed solution in terms of the metal species and other species including anions that are present. With respect to metals, the extractable species can be classified into 4 types:

1. Metal cations, for example Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺
2. Complex metal anions such as UO₂(SO₄)³⁻, Mo₈O₂₆⁴⁻, H₂V₆O₁₇²⁻, CoCl₄²⁻
3. Complex metal cations such as MoO₂²⁺
4. Neutral metal species such as UO₂(NO₃)₂
The metal species listed above have all been recovered commercially in solvent extraction plants at one time or another. It represents only a small sample of the many extractable chemical species that may be present.

Metal extractants are divided up into five separate classes dependent upon the structure of the extractant, the mechanism of extraction and nature of the metal species extracted:

- Chelating extractants.
- Ion pairing extractants.
- Organic acids.
- Extractants that function by ligand substitution.
- Extractants that function by solvation.

BASF markets chelating reagents and ion pairing reagents. Chelating reagents function by forming chemical bonds with a cationic metal ion at two sites similar to grasping an object between the ends of one's thumb and index finger. The LIX® reagents based on the phenolic oximes are examples of chelating reagents. Ion pairing extractants function by forming an organic soluble ion pair between an organic soluble cationic species and a complex anionic metal species. The Alamine® and Aliquat® reagents are examples of ion pairing extractants. The Alamine® reagents are based on tertiary amines having long alkyl chains. They accept a proton from acid solutions to form a cationic ammonium ion which can then pair with an anion in the organic phase. Aliquat® reagents are based on quaternary amine salts. The Aliquat reagents function similarly to the Alamine® reagents; the difference being that the quaternary amine is always positively charged. Since there is no need to form a cation by protonation, the Aliquat® reagents can also extract anionic species from alkaline aqueous solutions.

Successful reagent selection requires matching the chemical characteristics of the extractant with those of the metal species present in the incoming aqueous feed solution. While chemists have identified metal extractants for carrying out chemical separations of just about all metals in one form or another, the number of extractants available to carry out commercially viable large scale metal recovery processes is relatively small.

In order to be commercially successful, a metal extractant must meet the following criteria at least in part:

1. Have a cost conducive to good process economics.
2. Extract the desired metal(s) with some degree of selectivity from the aqueous feed solution.
3. Strip the metal values from the loaded organic into an aqueous solution which facilitates final metal recovery.
4. Be stable to the operating conditions through many cycles of extraction and stripping.
5. Load and strip metal at a rate fast enough to permit use of economical mixing times.
6. Exhibit good phase separation properties.
7. Be nonflammable with low toxicity, non-carcinogenic, etc.
8. Soluble both as the extractant and as the metal complex in an inexpensive organic diluent.
9. Avoid transfer of species from stripping to extraction that might interfere with extraction.

While no extractant meets 100 % of each of these criteria, successful reagents possess a good balance of all the properties in the list. BASF reagents possess this balance of properties.

Reagent selectivity is often an issue. Very few, if any, extractants demonstrate selectivity for only one metal over a broad range of conditions. Many extractants, however, are reasonably selective for one metal over another under a certain set of conditions. The selectivity is dependent on the conditions and the challenge is to match the conditions associated with the given leach solution with the selectivity characteristics of the available reagents. A perfect match is seldom achieved. One either settles for a reagent that performs reasonably well or one tries to alter the leaching process to produce a leach solution which will allow an extractant to be more selective. To do this successfully, one needs a very good understanding of the chemistry of the leaching process as well as the chemistry of the extraction process. A BASF technical representative can help to provide the necessary understanding of the chemistry.
All modern commercial copper solvent extraction reagents are based on phenolic oxime type molecules. They can be classified into two general types, aldoximes and ketoxime.

They form a complex (I) with copper by loss of the phenolic hydrogen as a proton and formation of chemical bonds from the phenolic oxygen (dark red) to the copper ion and from the nitrogen (dark blue) of the oxime to the copper ion. The complex is very non-polar and hydrocarbon soluble. They belong to a group of molecules described as bidentate chelating agents since they grasp the copper ion between the two sites in a pincer like fashion. The R group is typically a highly branched hydrocarbon chain consisting of either 9 or 12 carbon atoms.

In the process of forming a complex, two hydrogen ions are released into the aqueous solution for every copper ion that is extracted. The chemistry is summarized in the following equation where RH represents the extractant (Formula 1).

A key parameter in controlling the equilibrium position of this reaction is the acid content of the aqueous phase. Low concentrations of acid in the aqueous favor extraction and high acid concentrations favor stripping. This behavior can be represented graphically as a pH isotherm. Typical pH isotherms for ketoxime and C9 aldoxime are represented in Figures 1 and 2.

Figure 1: pH Isotherms for Several Metals with KetoXime
Table 1: Relative Extraction Power of Ketoxime and Aldoxime for Metals at pH 2.0

<table>
<thead>
<tr>
<th>Metal</th>
<th>Relative Extractive Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>Very strongly extracted</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>Slightly extracted</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>Moderately extracted</td>
</tr>
<tr>
<td>V(V)</td>
<td>Slightly extracted</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>Nil</td>
</tr>
<tr>
<td>Sn(II)</td>
<td>Nil</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>Nil</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>Nil</td>
</tr>
<tr>
<td>As(III)</td>
<td>Nil</td>
</tr>
<tr>
<td>Al(III)</td>
<td>Nil</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>Nil</td>
</tr>
<tr>
<td>Si(IV)</td>
<td>Nil</td>
</tr>
<tr>
<td>Co(II)</td>
<td>Nil</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Nil</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

1) The chemistry of Mo(VI) and V(V) on the acid side is quite complex. They do not normally present a problem in copper solvent extraction circuits.
Consideration of extraction isotherms and selectivity data allow the metallurgist to develop metal separation schemes. Where such data is not available for a particular system, one can develop the required information by screening the reagent against the metals most likely to be found in the aqueous feed solutions of interest under conditions similar to those expected in the solvent extraction process. The resultant selectivity data holds only at the conditions under which it is determined. Small changes in the test conditions can result in significant shifts in the extraction isotherms and selectivity.

These conditions include:
- The nature of the reagent.
- The nature of the anions present in the aqueous solution.
- The metal and reagent concentrations.
- The oxidation state of the metal.
- The pH of the aqueous feed solution.
- The temperature at which extraction occurs.
- The organic-aqueous contact time.

Modern metallurgists have a broad spectrum of copper extractant formulations based on the aldoximes and ketoxime available to aid them in developing effective recovery schemes for copper from a broad range of leach solutions. As can be seen from a comparison of the Cu pH-isotherms in Figures 1 and 2, the aldoximes by themselves are much stronger copper extractants than is the ketoxime. While their extractive strength is a potential advantage, it is also a problem. The aldoximes do not readily give up the extracted copper when contacted with typical lean electrolyte solutions that are generated by standard copper tank house operations. As a result, only a relatively small percentage of the overall loading capacity is utilized in the transfer of copper from extraction to stripping (Net Transfer).

Two approaches have been utilized to increase the net transfer of reagents formulated with aldoximes. One approach is to combine the aldoxime, either C9 or C12, with ketoxime. The aldoxime and ketoxime form a synergistic mixture, i.e. the combination strips more readily than one would expect based on a simple combination of the properties of the two components. Blending the two components results in no significant impact on copper loading capacity in extraction while greatly improving stripping. This translates into an increase in copper net transfer capability relative to an aldoxime by itself. As illustrated in Figure 3 and Table 2, increasing the proportion of ketoxime relative to aldoxime results in increased ease of stripping (lower residual copper on the stripped organic) consistent with a decrease in extractive strength. The decrease in extractive strength is also reflected in the fact that the net transfer capability falls off faster as the acid concentration increases (lower pH).

Table 2: Proportions of LIX® 84-I and LIX® 860N-I in Standard Non-modified Reagents

<table>
<thead>
<tr>
<th>Reagent</th>
<th>% v/v LIX® 84-I</th>
<th>% v/v LIX® 860N-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIX® 84-I</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>LIX® 937N</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>LIX® 984N</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>LIX® 973N</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>LIX® 860N-I</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

1) Ketoxime dissolved in a hydrocarbon diluent.
2) C9 aldoxime dissolved in a hydrocarbon diluent.
By blending the aldoxime and ketoxime in varying proportions, BASF Mining Solutions can tailor a reagent to fit the specific extraction and stripping requirements of a particular application. Formulations consisting of mixtures of an aldoxime with ketoxime are classified as non-modified reagents or blends.

The second approach takes advantage of the fact that the aldoxime will form complexes by hydrogen bonding with a wide variety of chemical compounds. The most commonly used classes of compounds in commercial formulations are alkyl phenols as well as higher molecular weight alcohols and esters. These materials are commonly referred to as thermodynamic modifiers in this application. Increasing the relative amount of the thermodynamic modifier results in a shift in performance similar to that observed with the ketoxime as illustrated in Figure 4 where LIX® 860N-I represents no modifier and the level of modifier, an ester, increases as one progresses from LIX® 654N-LV to LIX® 684N-LV, the most heavily modified formulation in the series. Formulations consisting of a mixture of a thermodynamic modifier with an aldoxime are classified as modified reagents or modified aldoximes.

Table 3: Comparison of Properties for Reagents based on Ketoximes, Aldoximes, Non-modified Blends and Modified Aldoximes

<table>
<thead>
<tr>
<th>Property</th>
<th>Ketoxime</th>
<th>Aldoxime</th>
<th>Non-Modified Blend</th>
<th>Modified Aldoxime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractive Strength</td>
<td>Moderate</td>
<td>Very Strong</td>
<td>Customized</td>
<td>Customized</td>
</tr>
<tr>
<td>Stripping</td>
<td>Very Good</td>
<td>Poor</td>
<td>Customized</td>
<td>Customized</td>
</tr>
<tr>
<td>Cu/Fe Selectivity</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Very Fast</td>
</tr>
<tr>
<td>Extraction Kinetics</td>
<td>Very Good</td>
<td>Very Fast</td>
<td>Fast</td>
<td>Fast</td>
</tr>
<tr>
<td>Phase Separation</td>
<td>Fast</td>
<td>Fast</td>
<td>Very Good</td>
<td>Very Good</td>
</tr>
<tr>
<td>Stability</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Crud Generation3)</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Variable4)</td>
</tr>
</tbody>
</table>

1) Formulations based on C9 aldoximes tend to be slightly faster than those based on C-12 aldoxime.
2) Dependent on the particular thermodynamic modifier used in the formulation.
3) Dependent on the composition of the leach liquor and the modifier.
4) In many cases, the presence of thermodynamic modifiers increases crud formation.

Figure 4: Effect of Increasing Ester Modifier Content on Stripping of Cu and Cu Net Transfer with Modified Aldoxime Reagents*

Table 3: Comparison of Properties for Reagents based on Ketoximes, Aldoximes, Non-modified Blends and Modified Aldoximes

- * Procedure was identical to that described for Figure 3.
One can also blend thermodynamic modifiers with mixtures of aldoxime with ketoxime to form a third class of extractant formulations, modified aldoxime/ketoxime blends. BASF Mining Solutions has the capability of offering all three classes of extractant formulations.

A general comparison of the copper extraction characteristics of ketoxime, aldoximes, non-modified blends and modified aldoximes is summarized in Table 3.

Presents the operators of copper solvent extraction plants with a wide choice of reagents from which to choose.

The availability of:

- Pure aldoxime based extraction reagents
  - LIX® 860-I, a C12 aldoxime based formulation and LIX® 860N-I, a C9 aldoxime based formulation
- Modified aldoxime reagents
  - LIX® 622N, and the ester based series: LIX® 654N-LV, LIX® 664N-LV, LIX® 674N-LV and LIX® 684N-LV
- Pure ketoxime based extraction reagents
  - LIX® 84-I and LIX® 8180
- Non-modified aldoxime/ketoxime blends
  - LIX® 973N, LIX® 984N, and LIX® 937N
- Modified aldoxime/ketoxime blends
  - LIX® 1552N-LV

Since ketoxime based reagents are moderately strong copper extractants, they operate best when the pH of the leach solution is relatively high (above pH 1.8) and the solution is relatively warm (20 °C or higher). Since they strip very well, they can effectively be used with only one strip stage and they can be used efficiently when the amount of acid in the lean electrolyte exiting the copper tank house is relatively low (less than 160 g/L H2SO4). They have also been effectively used in cases where the leach solution contains nitrate which will degrade modified aldoximes7.

Modified aldoxime reagents have excellent metallurgical properties even at low temperatures, low pH’s or when the copper content of the leach liquor is very high and high copper recoveries are needed. However, in many cases, the use of a modified aldoxime formulation carries with it higher entrainment rates and/or greater crud generation resulting in increased carryover of impurities to the electrolyte and higher reagent consumption per ton of copper produced4,6,9.

The non-modified aldoxime/ketoxime mixtures also operate well at lower pH’s, lower temperatures, and with leach liquors having a higher copper content. They tend to be slightly slower kinetically at lower temperatures depending on the ketoxime content of the formulation as compared to modified aldoxime formulations. They also tend to be slightly less selective for copper over iron as compared to an ester modified aldoxime formulation. In terms of physical performance under a wide variety of conditions, they tend to give more stable mixer continuities, lower entrainment of aqueous in the loaded organic and generate less crud than modified aldoxime formulations. Some of these physical advantages can be attributed to the fact that these reagents are the lowest density and lowest viscosity copper solvent extraction reagents available.

Clearly there is not “a single reagent of choice” for the extraction of copper from sulfuric acid leach liquors. Your BASF Mining Solutions technical representative can help you decide on the best reagent for your needs.