This article summarizes the evolution of modified strong copper extractants, focusing on the fairly recent requirement to effectively extract copper from high-concentration aqueous feeds derived from the hydrometallurgical processing of sulfidic copper ores.

**INTRODUCTION**

Improvements in solvent extraction reagents over the years have been key to the evolution of lower-cost primary copper production. As leaching regimes to treat sulfidic ores evolve, existing modified strong copper extractants are successfully processing high concentrations of copper through commercial solvent-extraction operations. In particular, Acorga™ Limited’s discovery of nonylsalicylaldoxime in the early 1980s enabled significantly lower capital and operational costs. While this discovery continues to be the basis of virtually every copper solvent extraction reagent in use, the refinement of reagent formulations has continued. Aecia’s Metal Extraction Products (MEP) research in the early 1990s led to the current state-of-the-art in ester-modified reagents. Those reagents, introduced in 1992, offer a number of technical advantages and are robust enough to use in treating high concentrations of copper. Today, products based on the unique and patented ester modifiers have increasingly become the choice to solve a number of operational issues.

**OXIME DEVELOPMENT**

Solvent extraction for copper was first used commercially in 1968. The copper-specific ligands introduced to the industry at that time were based on formulations of 2-hydroxybenzophenone oxime (ketoxime). These were followed by other ketoxime-based formulations or first-generation extractants using 2-hydroxy-5 nonyl acetophenone. Because ketoxime reagents suffered from low loading capacity and were very sensitive to low pH values, large multi-stage operations were required to effectively recover the copper. In 1979, Acorga Limited discovered and patented the much stronger aldoxime extractant 5-nonylsalicylaldoxime. The new aldoxime, second-generation copper extractant used with a modifier, improved the stripping capacity. As a result, the overall transfer capacity was increased.

The introduction of modified strong copper extractants based on 5-nonylsalicylaldoxime continue to play a key role in the growth of solvent extraction for copper in the early 1980s–2000s. Optimizing copper transfer and as a consequence of the significant improvements in phase separation and strength of these newer reagents, the industry could now design smaller plants, reducing both capital and operational costs. Today, essentially all commercially available extractants are based on Acorga’s 5-nonylsalicylaldoxime.

**MODIFIER DEVELOPMENT**

The established principle has been that while the extraction of copper by o-hydroxyaryloxime extractants is an interfacial reaction, in the bulk phase the modifier alters the strength of the hydrogen bonding of the metal-loaded ligand complex in the non-polar diluent.

With an extractant formulation containing an oxime and a modifier, equilibria exist involving dimerization of the oxime by H-bonding, interaction of the oxime with the modifier, and absorption of oxime at the interface. Since compounds used for equilibrium modifiers can typically hydrogen bond, when the extractant is uncomplexed some of the modifier may interact with the oxime molecule. In the metal-complexed state, the modifier is free in solution. From a
physical standpoint it is best to use bulky molecules as modifiers because they have difficulty packing at the interface and minimize interaction with solids. In practical terms, equilibrium modifiers can affect shape and position of the isotherm, copper-transfer efficiency, copper recovery, kinetics, selectivity, phase disengagement, and hydrolytic stability.

Formulations evolved and products were developed containing both aldoxime and non-chelating modifiers.

In 1979, MEP introduced the first modified reagents to the market, Acorga P5100 and P5300, using nonylphenol and they became the extractants of choice during the first boom of copper solvent extraction (SX) in the early 1980s.

Aliphatic alcohols such as tridecanol proved to be much stronger equilibrium modifiers than nonylphenol. For example, a similar modifying effect could be achieved with 40% (by weight) less tridecanol than nonylphenol. At the same time, it was shown by MEP that other reagent properties changed with modifier selection when compared to nonylphenol- or aldoxime/ketoxime-based products. Because the equilibrium modifier significantly improved many of the extractant properties, the MEP group studied other classes of compounds that potentially could be used as modifiers. This study, undertaken ten years ago, provided a better understanding of the principles involved and how choice of the modifier affects the physical and chemical properties of the extractant. The test results again confirmed that the selection of the appropriate modifier offered a powerful approach to reagent development.

A major advance was made with the discovery that modification of 5-nonyl-salicylaldoxime with a specific ester would significantly improve Cu:Fe selectivity, entrainment losses, crud generation, and hydrolytic stability. Optimizing the formulation further would also improve transfer capacity while maintaining higher recoveries at low pH when compared to the aldoxime/ketoxime mixtures.

MEP introduced Acorga M-5640 in 1992 as the first commercial ester-modified reagent. The company gained patents on this class of reagents and developed unique ester components. After 1992, many operations around the world switched from older-generation products to an Acorga ester-modified product for reasons of selectivity recovery at low pH and treating high concentrations of pregnant leach solution (PLS). For example, in South America more than 500,000 tonnes of copper cathode are produced annually using these ester-modified reagents.

### SELECTIVITY

The primary metal contaminant of copper leach liquors is iron, which occurs so widely that it is almost always a major consideration. The transfer of excessive iron into the electrolyte from the PLS either by entrainment or complexation results in lower current efficiency and, consequently, an increased bleed requirement with its associated costs.

In conventional heap leach applications, the modified aldoxime reagent formulations are significantly more selective than the aldoxime/ketoxime mixtures. The data presented in Table I are from a pilot-plant circuit with two extract stages and one strip stage, treating a conventional heap leach PLS.

In solvent extraction systems containing higher copper concentrations, selectivity of copper over iron is significantly better than in heap leach operations and rejection ratios of greater than 10,000 are regularly achieved by Avicea’s ester-modified range of extractants.

In the hydrometallurgical processing of copper concentrations and ores, a wide range of minor metals are solubilized into the leach solution. A very high degree of selectivity over these metals is required from the solvent extractant in order to produce LME Grade A copper cathode by electrowinning.

Using the ester-modified product, a selectivity ratio of Cu:metal minor of > 40,000:1 was achieved during the pilot plant evaluation for Zn, Sb, Sn, Pb, Se, Te, Bi, and Ni.

### STABILITY

Reagent stability refers to the resistance of a reagent formulation to degradation of the oxime component and is an important criterion when selecting a suitable reagent when treating higher-temperature solutions. The primary route is hydrolytic degradation,

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**Table II. Hydrolytic Degradation Comparison (Model Conditions)**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxime concentration (g/L)</td>
<td>100</td>
</tr>
<tr>
<td>Fraction of time organics in strip stage</td>
<td>0.2</td>
</tr>
<tr>
<td>Volume of organic (m³)</td>
<td>2,200</td>
</tr>
<tr>
<td>PLS flow rate (m³/h)</td>
<td>1,400</td>
</tr>
<tr>
<td>Lean electrolyte flow rate (m³/h)</td>
<td>400</td>
</tr>
<tr>
<td>O/A entrainment (ppm)</td>
<td>25</td>
</tr>
<tr>
<td>Time (days)</td>
<td>365</td>
</tr>
<tr>
<td>Oxime in product (wt.%)</td>
<td>50</td>
</tr>
</tbody>
</table>