The effect of modifier properties on the performance of copper solvent extraction reagents

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Modified vs Non-Modified Reagent

- Non-modified reagents are typically a ketoxime or ketoxime/aldoxime blends

- Modified reagents are aldoximes or aldoxime/ketoxime blends that contain an equilibrium modifier

- Typical modifiers used in copper solvent extraction include alcohols (TDA), multifunctional esters (TXIB and DBA), and ketones (various C-11/C12 ketones)
Modified Reagent

• Intra and intermolecular hydrogen bonding in hydroxy oximes shifts the equilibrium towards the copper free hydroxy oximes.

• This shift in equilibrium is relatively small, therefore, “equilibrium modifiers” can be added to shift the equilibrium further in the direction of hydroxy oximes.

• This shift in equilibrium makes it easier to strip copper from strongly held copper chelates, such as those formed with aldoximes.

• Ketoximes and ketoxime/aldoxime blends are more easily stripped and do not require modification.
History of Modified Reagents

1968  Ashland Chemical - Kelex® reagent (based on 8-hydroxyquinoline) - modified with nonylphenol (NP) or isodecanol

1977  Acorga Company – P 5000 series – C9 aldoxime modified with nonylphenol (NP)

1979-81  Henkel - LIX® 622 – C12 aldoxime modified with tridecanol (TDA)

1981  Acorga Company – PT-5050 – C9 aldoxime modified with TDA

1986  ICI – Acorga® M5640 – C9 aldoxime modified with TXIB

Present  Acorga reagents – C9 aldoxime formulations modified with TXIB or alcohol

BASF reagents – C9 or C12 aldoxime formulations with ketones, esters or alcohol.
Modified Reagent Effects

• Modified reagents can influence many aspects of the reagent and its properties.
  – Copper/iron selectivity
  – Oxime stability
  – Entrainment
  – Crud Formation
  – Viscosity of the organic
Crud Generation

- The Anamax plant noted a large increase in crud generation shortly after adding modified reagents (Acorga PT5050 and LIX 6022).

- A side-by-side pilot plant study was conducted using a modified and an unmodified reagent. The crud was isolated and centrifuged. The quantities of crud for each set of pilot plant runs are given below.

- Modified reagents produced twice as much crud as unmodified reagents.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Circuit hours</th>
<th>Compacted Crud (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5 vol % HS-LIX 64N</td>
<td>9.5</td>
<td>5</td>
</tr>
<tr>
<td>10.5 vol% HS-LIX 64N + 2.5 vol % TDA</td>
<td>9.5</td>
<td>10</td>
</tr>
<tr>
<td>8.5 vol% LIX 864</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>8.5 vol% LIX 864 + 2.5 vol% TDA</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td>8.5 vol% LIX 864</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>8.5 vol% LIX 864 + 2.5 vol% NP</td>
<td>10</td>
<td>14</td>
</tr>
</tbody>
</table>
Adsorption Studies

- Crud is a solid stabilized emulsion. The solid particles in the aqueous phase interact with surface active species in the organic phase.

- These studies determined the adsorption of modifiers and oximes onto solid particles.

- Once oximes are loaded with copper, they are no longer surface active. The residual modifiers are no longer hydrogen bonded to oximes and are more likely to migrate to the organic surface.
Reagent Usage

• Anamax also noted an increase in reagent usage when using modified reagents.

• Reagent usage
  – Modified reagents used in 81-82 and 90-91
  – Non-modified reagents used in 78-80, 83-84, 89-90, and 91-92
Viscosity Effects

• While viscosity effects are not straightforward, an organic with a higher viscosity is expected to have increased entrainment and other operational issues.

• Port Pirie (Nystar) is a plant that has had viscosity related problems.

• Port Pirie plant conditions:
  – PLS – 40 gpl Cu, 20 gpl acid, 20 gpl chloride, and significant soluble silica at 40°C
  – Configuration – 2E x 1W x 2S
  – 30-35 volume % reagent
Port Pirie

• In 1990, Acorga® M5640 was added to the Port Pirie plant.

• In early 2004, the plant organic had a very high viscosity, very slow separation rate in organic continuity, slow stripping kinetics, and a lower than expected copper net transfer.

• In April 2004, Port Pirie switched to a lower viscosity non-modified LIX® reagent.

• Over time the viscosity lowered, separation rates increased, strip kinetics improved, and metallurgical performance improved.
Port Pirie – Chloride in Electrolyte
Port Pirie – Organic Phase Viscosity

Start of LIx conversion

Clay treatment stopped

Clay treatment resumed
El Salado – Chloride

- El Salado PLS has consistently had high chloride concentrations (50-70 gpl).

- Plant has expanded several times since start-up.

- Chloride concentration in electrolyte has decreased with the conversion to an non-modified reagent.

<table>
<thead>
<tr>
<th>Year</th>
<th>Pregnant Leach Solution</th>
<th>Copper Cathodes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu g/L</td>
<td>Chloride g/L</td>
</tr>
<tr>
<td>2001</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>2003</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>2005</td>
<td>5</td>
<td>60</td>
</tr>
<tr>
<td>2008</td>
<td>5</td>
<td>70</td>
</tr>
</tbody>
</table>
El Salado Plant

• Reduction in chloride concentration in the electrolyte at El Salado was not exclusively due to the non-modified reagent
  – It was calculated that the reagent accounted for ~40% of the decrease in chloride concentration while changes in plant design and operational practices accounted for ~60% of the change.

• Viscosity at El Salado was similar before and after the 2,400 tpy expansion. This suggests that viscosity is not the only factor in chloride transfer to electrolyte.
Reagent Stability

- Aldoximes and ketoximes hydrolyze to the corresponding hydroxy-aldehydes and hydroxy-ketones.

- Hydroxy aldehydes and ketones, nonylphenol, TXIB, DBA, TDA, and mixed ketone modifiers do not degrade appreciably under normal conditions.

- Thus the concentration of oxime relative to modifier and hydrolysis products decreases over time. Since modifiers and hydrolysis products increase viscosity, modified reagents are expected to increase in viscosity over time.

- An example of this is that at Port Pirie in 2004, the expected M5640 in the plant contained 36% more TXIB than in a M5640 formulation.
Conclusions

• The limited plant data for non-modified versus modified reagents suggests that modified reagents increase crud.

• Modified reagents also increased the carryover of chloride even in plants with a wash stage. This will affect the transfer of impurities from the PLS to the electrolyte.

• Once modifier has been added to a system it can take a long time to significantly reduce its concentration (~3 years at Port Pirie).
Conclusions (Cont.)

• Both El Salado and Port Pirie use high concentrations of reagent. Using lower concentrations of reagent might reduce some of the negative effects of modifiers.

• Anamax used 8-10 vol/vol% reagent and still had crud related issues when using modified reagents.

• Modified reagents will continue to fill an important role in copper solvent extraction. However, each plant should carefully test reagents to avoid potential negative effects.