OVERVIEW OF GANGUE MINERALOGY ISSUES IN OXIDE COPPER HEAP LEACHING

By

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Presented by

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1. INTRODUCTION

Copper heap leaching projects are sometimes evaluated without adequate attention to mineralogy, despite the fact that ore and gangue mineralogy is probably the single most important parameter affecting operating costs and recoveries and can change significantly from one area of the resource to another. A wide range of mineralogy issues needs to be considered in maximizing the efficiency of copper recovery and minimizing the consumption of acid by gangue.

The following review lists the major gangue and ore minerals that may be present, and highlights some of the more important mineralogy issues involved in leaching oxide copper ores. Special emphasis is given to both acid-consuming and acid-regenerating reactions involving silicate and limonite gangue minerals, which can be potential major sources of acid consumption and can readily be overlooked in comparison to more obvious sources of acid consumption such as carbonates. The review is intended to serve as a refresher on the role of ore and gangue minerals in leaching and to encourage greater attention to mineralogy assessment in future heap leaching projects.

2. GANGUE ACID CONSUMPTION AND REGENERATION REACTIONS

Silicate and limonite gangue minerals consume sulphuric acid during initial reaction with acid. However, the reaction by-products can partially regenerate sulphuric acid in subsequent reactions with each other and/or fresh ore. Acid consuming and regeneration reactions within particular gangue mineral groups and reaction product groups include the following:

**Acid consumption:**
Limonite minerals consume acid by breakdown to ferric ions in solution (e.g. goethite breakdown)
Silicate mineral consume acid by breakdown to a wide range of soluble solution products (e.g. K feldspar, Na feldspar, Ca plagioclase and biotite breakdown to ortho-silicic acid, $H_3SiO_4$, and various metal cations such as $Na^+$, $K^+$, $Al^{3+}$, $Ca^{2+}$, $Fe^{2+}$, $Fe^{3+}$ and $Mg^{2+}$)
Original silicate minerals can consume acid and other reaction by-products to form alteration silicate minerals (e.g. alteration of plagioclase to gypsum and pyrophyllite, Na Feldspar to magadilite and pyrophyllite, or biotite to vermiculite only (open leach system) or to vermiculite, jarosite and silica (closed leach system))

**Acid regeneration:**
Soluble silicate breakdown products regenerate acid by reaction with each other during formation of various precipitates (e.g. formation of jarosite, silica, alunite, gypsum and magadilite from soluble metal cations and/or silicic acid)
Soluble silicate breakdown products also regenerate acid by reaction with each other to form new solid silicate alteration products (e.g. formation of pyrophyllite, kaolinite, vermiculite and chlorite from silicic acid and $Al^{3+}$, $Mg^{2+}$ and $Fe^{3+}$ cations)

The net acid consumption is a balance of acid consumption and acid regeneration in the heap, supplemented by fresh acid make-up and acid regeneration from SX as each new heap undergoes reaction and reaches equilibrium with the recirculating raffinate and resulting composite pregnant leach solution.

Tables 1 to 3 and Figs 1 to 3 below provide different perspectives on the minerals involved and the reactions that take place between gangue and acid during copper heap leaching.
3. ROCK AND ALTERATION MINERALS

Table 1 shows copper heap leach mineralogy issues for rock and alteration minerals for oxidised copper ores, expressed in terms of the following parameters:

- Oxide/sulphide class e.g. oxide rock, oxide alteration, sulphide rock, precipitates, alteration products and original rock minerals in equilibrium with leach solution
- Mineral type, property and metal elements in precipitates e.g. copper minerals, minerals containing copper, gangue, gangue non-clay, stability to weathering, gangue-clay, gangue-cupriferous clay, degree of alteration, precipitate metal elements, alteration metal elements, original rock mineral metal elements
- Mineral name, e.g. chrysocolla, jarosite, biotite, chlorite etc
- Mineral formulae where available, ranging from chrysocolla to jarosite
- Cu oxidation state, ranging from 0 for metallic copper to +2 for chrysocolla
- Fe oxidation state, +3 for all oxide minerals considered
- The occurrence of the minerals in USA and Chile (where the bulk of the copper heap leach operations are located) is considered. The occurrence of the minerals in each of these countries is ranked, ranging from 1 (highest) to 5 (lowest), where available.
- Theoretical acid consumption, expressed as moles/mole mineral for oxide copper minerals, iron oxides, chlorite and Ca feldspar, or otherwise noted as being “high adsorption” for talc and clay minerals such as montmorillonite, kaolinite and smectite, which readily adsorb acid.
- Acid consumption, kg/t ore typical, where available for minerals in various gangue silicate alteration classes
- Salt products e.g. gypsum or ferric salts
- % Cu extraction in acid without aeration, where available
- Footnotes referring to reference sources\(^3\), copper recovery factors, acid consumption factors and methods for improved copper recoveries
<table>
<thead>
<tr>
<th>Oxide/ Sulphide Class</th>
<th>Mineral Type</th>
<th>Mineral</th>
<th>Formula</th>
<th>Cu Oxid. State</th>
<th>Fe Oxid. State</th>
<th>Country</th>
<th>Ranking in Country (1 = highest)</th>
<th>Theoretical Acid Consumption, moles/mole mineral</th>
<th>Acid Consumptn kg/t ore</th>
<th>Salt products</th>
<th>% Cu Extn. in H2SO4 without aeration (approx.)</th>
<th>Issues (see Notes)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxide Rock</strong></td>
<td>Copper</td>
<td>Chrysocolla</td>
<td>CuSiO3. 2H2O +2</td>
<td>USA</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>4.4</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>Diopside</td>
<td>CuSiO3. H2O +2</td>
<td>USA</td>
<td>1</td>
<td>100</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Malachite</td>
<td>CuCO3. Cu(OH)2 +2</td>
<td>Chile/Dry</td>
<td>2</td>
<td>2</td>
<td>100</td>
<td>4.2</td>
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<td></td>
<td>Azurite</td>
<td>2CuCO3. Cu(OH)2 +2</td>
<td>Chile/Dry</td>
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<td>3</td>
<td>100</td>
<td>4.2</td>
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<td></td>
<td>Brochantite</td>
<td>CuSO4.3Cu(OH)2 +2</td>
<td>Chile/Dry</td>
<td>3</td>
<td>3</td>
<td>100</td>
<td>4.2</td>
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<td></td>
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<td></td>
<td>Antlerite</td>
<td>CuSO4 +2</td>
<td>Chile/Dry</td>
<td>4</td>
<td>0</td>
<td>100</td>
<td>4.2</td>
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<tr>
<td></td>
<td>Chalcocite</td>
<td>CuSO4.5H2O +2</td>
<td>USA</td>
<td>0</td>
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<tr>
<td></td>
<td>Tenorite</td>
<td>CuO +2</td>
<td>USA</td>
<td>4</td>
<td>1</td>
<td>100</td>
<td>4.2</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Atacamite</td>
<td>Cu2(OH)3Cl +2</td>
<td>Chile/Dry</td>
<td>1</td>
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<td>Pseudo-malachite</td>
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<tr>
<td></td>
<td>Cuprite</td>
<td>CuO +1</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
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<tr>
<td></td>
<td>Delabaussite</td>
<td>Cu2O2Fe2O3 ppt. +1 +3</td>
<td>USA</td>
<td>3</td>
<td>5</td>
<td>10-50</td>
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<td></td>
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<tr>
<td></td>
<td>Native Cu</td>
<td>Cu0</td>
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<td>50</td>
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<tr>
<td></td>
<td>Containing copper Impervious silicate</td>
<td>CuSO4 +2</td>
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<td>100</td>
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<tr>
<td></td>
<td>Cupriferous FeOX</td>
<td>CuO</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
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<tr>
<td></td>
<td>Cu Wad</td>
<td>H2MnO4</td>
<td>USA</td>
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<td>2</td>
<td>50</td>
<td>2.4</td>
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<td></td>
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<tr>
<td></td>
<td>Cu Pitch</td>
<td>H2MnO4</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
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<td></td>
<td>Pitch limonite</td>
<td>CuO</td>
<td>USA</td>
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<tr>
<td></td>
<td>Gangue</td>
<td>Calcite</td>
<td>CaCO3</td>
<td>USA</td>
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<td>100</td>
<td>2.4</td>
<td></td>
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<tr>
<td></td>
<td>Quartz</td>
<td>SiO2</td>
<td>USA</td>
<td>1</td>
<td>100</td>
<td>2.4</td>
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<tr>
<td><strong>Oxide Alteration</strong></td>
<td>Gangue-non clay</td>
<td>Goethite</td>
<td>FeO(OH) +3</td>
<td>USA</td>
<td>1</td>
<td>100</td>
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<td></td>
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<tr>
<td></td>
<td>Limonite</td>
<td>2FeO3.3H2O +3</td>
<td>USA</td>
<td>3</td>
<td>5</td>
<td>100</td>
<td>2.4</td>
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<tr>
<td></td>
<td>Hematite</td>
<td>FeO3 +3</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Neotocite</td>
<td>MnSiO3.nH2O +3</td>
<td>USA</td>
<td>3</td>
<td>5</td>
<td>100</td>
<td>2.4</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Jarosite</td>
<td>KFe3(SO4)2(OH)6</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Turquoise</td>
<td>AlPO4.Al(OH)3 + H2O</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
<td></td>
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<tr>
<td></td>
<td>Increasing stability to weathering, Olivine to Quartz</td>
<td></td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>Olivine (least stable)</td>
<td>(Mg,Fe)2SiO4</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Hypersphere</td>
<td>(Fe, Mg)SiO3</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
<td></td>
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<tr>
<td></td>
<td>Augite or Pyroxene</td>
<td>Ca(Mg,Fe)SiO3</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
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<tr>
<td></td>
<td>Hornblende</td>
<td>xCa(Mg,Fe)2(SiO3)y + y(Al, Fe)(F,OH)SiO3</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
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<tr>
<td></td>
<td>Biotite</td>
<td>(H,K)2(Mg,Fe)Al4(SiO4)3</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
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<tr>
<td></td>
<td>K-Feildspar</td>
<td>KAISiO3</td>
<td>USA</td>
<td>6</td>
<td>2</td>
<td>50</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Orthoclase</td>
<td>H₂KAl₃(Si₂O₅)₃</td>
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<tr>
<td>Muscovite Mica</td>
<td>Na₂K₂Al₆(Si₂O₅)₃</td>
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<tr>
<td>Quartz (most stable)</td>
<td>SiO₂</td>
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Increasing stability to weathering, Plagioclase to K-Feldspar:

<table>
<thead>
<tr>
<th>Ca Plagioclase</th>
<th>CaAl₂Si₂O₈</th>
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<tbody>
<tr>
<td>Na Plagioclase</td>
<td>NaAlSiO₄</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>KAISiO₄</td>
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<tr>
<td>Orthoclase</td>
<td>KAlSi₃O₈</td>
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</table>

Other minerals:

<table>
<thead>
<tr>
<th>Chlorite</th>
<th>H₃(Mg,Fe)₂Si₃O₉</th>
<th>6</th>
</tr>
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<tbody>
<tr>
<td>Epidote</td>
<td>Ca₄Al(OH)₂Al₄Si₄O₁₀</td>
<td>3.1 LT</td>
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<tr>
<td>Talc</td>
<td>H₂Mg₃(Si₂O₅)₄</td>
<td>high adsorption</td>
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<tr>
<td>Ca-Feldspar</td>
<td>CaAl₂Si₂O₈</td>
<td>4</td>
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<tr>
<td>Montmorillonite</td>
<td>H₃Al₂Si₂O₁₂</td>
<td>high adsorption</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>H₄Al₂Si₂O₉</td>
<td>high adsorption</td>
</tr>
<tr>
<td>Smectite</td>
<td></td>
<td>4.3</td>
</tr>
</tbody>
</table>

Gangue-cupriferous clay:

Cu bearing clays:

| Cu bearing montmorillonite | H₃Al₂Si₂O₁₂ | high adsorption |
| Cu bearing kaolinite       | H₄Al₂Si₂O₉   | high adsorption |

Smectite              | high adsorption | 4.3 |

High-Alteration:

| Basalt               | 60             | 3.5 |
| Andesite             | 45             | 3.5 |
| Diabase              | 35             | 3.5 |
| Skarn                | 25             | 3.5 |
| Limestone            | 10             | 3.5 |
| Moderate -Alt. Q-Diorite | 60           | 3.5 |
| Granodiorite         | 45             | 3.5 |
| Q-Monzonite          | 35             | 3.5 |
| Latite               | 25             | 3.5 |
| Dacite               | 10             | 3.5 |
| Hornfels             | 0              | 3.5 |

Low-Alteration:

| Rhyolite             | 60             | 3.5 |
| Granite              | 45             | 3.5 |
| Trachyte             | 35             | 3.5 |
| Syenite              | 25             | 3.5 |
| Si Sediments         | 10             | 3.5 |
| Metamorphics         | 0              | 3.5 |

Precipitates:

<table>
<thead>
<tr>
<th>Ca,S</th>
<th>Gypsum</th>
<th>CaSO₄·2H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Silica</td>
<td>SiO₂</td>
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</table>
### Alteration Products

<table>
<thead>
<tr>
<th>Alteration Products</th>
<th>Equation</th>
</tr>
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<tbody>
<tr>
<td>Mg, Al, Si</td>
<td>Vermiculite Mg₂Al₂Si₃O₁₀(OH)₂</td>
</tr>
<tr>
<td>Mg, Fe, Si</td>
<td>Chlorite H₄(Mg,Fe)₂(SiO₄)₃</td>
</tr>
<tr>
<td>Al, Si</td>
<td>Kaolinite H₄Al₂Si₂O₇</td>
</tr>
<tr>
<td>Al, Si</td>
<td>Aliphane</td>
</tr>
<tr>
<td>Al, Si</td>
<td>Pyrophyllite H₄Al(SiO₄)₂</td>
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</tbody>
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### Original Rock Minerals in Equilibrium with Leach Solution

<table>
<thead>
<tr>
<th>Original Rock Minerals</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Quartz</td>
</tr>
<tr>
<td>Al, Si</td>
<td>Pyrophyllite H₄Al(SiO₄)₂</td>
</tr>
<tr>
<td>Si</td>
<td>Silica</td>
</tr>
<tr>
<td>K, Fe, S</td>
<td>Jarosite KFe₃(SO₄)₂(OH)₆</td>
</tr>
<tr>
<td>Fe</td>
<td>Magnetite Fe₃O₄</td>
</tr>
</tbody>
</table>

### Notes:

1. Reference sources include:
   1.1 W Baum, Cobre 99, "The use of a mineralogical data base for production forecasting and troubleshooting in copper leach operations"
   1.2 John Dreier, Copper Heap Leach, Feb 1992, "Geochemical Aspects of Copper Heap Leaching"

2. Copper recovery factors:
   2.1 Particle size
   2.2 Liberation/locking of copper minerals
   2.3 Copper adsorption by iron oxides
   2.4 Copper recoveries per Ref 1.1

3. Acid consumption factors:
   3.1 Short (S) or long term (LT) acid consumer
   3.2 Acid adsorption e.g. high
   3.3 Acid concentration effect on acid consumption e.g. high
   3.4 Acid consumption directly proportion to acid concentration
   3.5 Acid consumption by rock type as per Ref 1.1

4. Methods for Improved recoveries:
   4.2 Ore pretreatment, blending, stockpiling, stronger curing or deep heap ripping if solution penetration of ultra fine mineral blocked by gas evolution
   4.3 Ore pretreatment, blending, stockpiling, stronger curing, longer curing, polymeric binding, higher acid concentration
   4.4 Initial rapid leaching followed by slow leaching if coarse hydrous silica gels coat surface during curing and early leaching. Multiple rest periods required - Ref 1.
   4.5 Frequently misidentified as chrysocolla, coarser dioptase requires longer leach times - Ref 1

5. Dreier formula for chlorite from ACS Monograph Series No 160 (1964) is Al₂Mg₁₂(OH)₂₆Mg₃Si₆Al₂O₁₄(OH)₂

6. Pyrophyllite and vermiculite precipitates form in the heap (Dreier)

7. Precipitates, common or predicted, form from PLS and/or raffinate contact with heap
4. ACID CONSUMPTION FACTORS

Key acid consumption factors for oxide ores include carbonate presence, the presence of short and long-term other acid consumers, and the extent of acid adsorption by different non-carbonate minerals including clays, hydrous iron oxides, highly porous copper minerals and/or slimes forming minerals. The effects of acid concentration on acid consumption can also be significant.

Other issues to consider in estimating potential acid consumption during heap leaching include:

- Actual acid consumption is generally significantly less than theoretical acid consumption for the minerals being leached due to build up of highly soluble reaction products, especially aluminium, magnesium and sulphate, in the recirculating leach solution
- Acid consumption and rate of consumption can increase rapidly with increasing temperature
- Bottle roll tests carried out over similar leach times to those used in commercial heap leach cycles can overestimate actual acid consumption by several orders of magnitude. Reuse of a leach solution representative of equilibrium conditions could partially alleviate this effect
- Other reasons for overestimation of acid consumption by bottle roll tests include several other factors, such as generally finer grind size and the use of higher free acid concentration during the test.
- Another source of error could come from the assay titration method of determining free acid in the final solution e.g. in the oxalate titration method which can yield erroneously low free-acid values due to the removal of all aqueous constituents from solution before titrating for free acid.
- The pH of the solution leaving the heap should be sufficiently low (preferably below pH 2.5 or so) to ensure that there is minimum risk of copper reprecipitation in the heap, possibly as delafossite, Cu$_2$O.Fe$_2$O$_3$. Such copper precipitation may conceivably occur at any local spots where the pH may have increased to around pH 4.5 due to non-uniform wetting or high acid reactivity within the heap.
- The heap discharge pH also needs to be within the acceptable range for the available SX extractants of typically pH 0.8 to 2.0. Most heap leach solutions fall within the range of pH 1.5 to 2.0 with copper tenors of 1-4 gpl. In the special case of sulphide agitation leaches such as at Mt Gordon the pH can be as low as 0.8, due to free acid levels of around 25-30 gpl in a heavily buffered ferric sulphate leach system containing 20-30 gpl Total Fe (up to 50% Fe$_3^+$) and 25-30 gpl Cu $^+$.  

5. COPPER RECOVERY FACTORS

Key oxide copper recovery factors include particle size, liberation/locking of copper minerals, contact of the mineral surfaces with acid, concentration of acid in solution, copper adsorption by iron oxides and/or clays and heap solution permeability.

Methods for improving copper recovery include:

- Ore blending
- Finer crush size
- Longer leach cycle time
- Higher acid concentration in leach solution
6. LEACH REACTIONS

Table 2 shows leach reactions of typical minerals in copper ores, classified by the following mineral groupings:

- Original silicate mineral breakdown
- Limonite minerals breakdown
- Copper oxide minerals breakdown
- Most commonly reported precipitation products
- Most commonly reported alteration products
- Other mineral alteration products

Within each group of minerals, key reactions are shown. Footnotes to the table include additional points. Note that in the case of quartz, K feldspar, sericite, biotite and chlorite, and common rock forming minerals of copper deposits, closed circuit leaching generally consumes a lower amount of acid than open circuit leaching. However for other minerals including carbonates, calcic plagioclase, amphiboles, montmorillonite and pyroxenes, this is generally not the case.

Farlas and co-workers\(^6\) note that copper minerals such as malachite or chrysocolla react with concentrated acid to form solid copper sulphate during an acid cure stage as follows:

\[
\text{CuCO}_3 \cdot \text{Cu(OH)}_2(s) + 2\text{H}_2\text{SO}_4 + 7\text{H}_2\text{O} = 2\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) + \text{CO}_2(g)
\]

\[
\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}(s) + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} = \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) + \text{SiO}_2(s)
\]

However the same minerals, when reacting with raffinate during subsequent leaching, form aqueous copper as shown in Table 2. Reactions with chrysocolla can also form a range of silicic acid compounds, \(\text{SiO}_2 \cdot n\text{H}_2\text{O}\), where \(n = 1, 2\) and 3.
Table 2: Leach Reactions of Typical Minerals in Copper Ores.

<table>
<thead>
<tr>
<th>Mineral Breakdown</th>
<th>Chemical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Original silicate mineral breakdown:</strong></td>
<td></td>
</tr>
<tr>
<td><strong>K feldspar (not in closed circuit):</strong></td>
<td>KAlSi$_3$O$_8$ + 4H$^+$ = K$^+$ + Al$^{3+}$ + 3H$_4$SiO$_4$</td>
</tr>
<tr>
<td><strong>Na feldspar:</strong></td>
<td>NaAlSi$_3$O$_8$ + 4H$^+$ = K$^+$ + Al$^{3+}$ + 3H$_4$SiO$_4$</td>
</tr>
<tr>
<td><strong>Ca plagioclase:</strong></td>
<td>CaAl$_2$Si$_2$O$_8$ + 10H$^+$ = 2Ca$^{2+}$ + 2Al$^{3+}$ + 2H$_4$SiO$_4$</td>
</tr>
<tr>
<td><strong>Biotite (not in closed circuit):</strong></td>
<td>(H,K)$_2$(Mg,Fe)$_2$Al$_2$(SiO$_4$)$_3$ + 10H$^+$ = 2K$^+$ + 2Al$^{3+}$ + 3H$_4$SiO$_4$ + 2(Fe,Mg)$^{2+}$</td>
</tr>
<tr>
<td><strong>Montmorillonite:</strong></td>
<td>H$_2$Al$_2$(SiO$_4$)$_3$,nH$_2$O + 6H$^+$ = 2 Al$^{3+}$ + 3 H$_2$SO$_4$</td>
</tr>
<tr>
<td><strong>Pyroxene:</strong></td>
<td>Ca (Mg,Fe)(SiO$_3$)$_2$ + 4H$^+$ + 2H$_2$O = Ca$^{2+}$ + 2H$_2$SO$_4$ + Mg$^{2+}$</td>
</tr>
<tr>
<td><strong>Limonite minerals breakdown:</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Hematite:</strong></td>
<td>Fe$_2$O$_3$ + 6H$^+$ = 2Fe$^{3+}$ + 3H$_2$O</td>
</tr>
<tr>
<td><strong>Goethite:</strong></td>
<td>FeO(OH) + 3H$^+$ = Fe$^{3+}$ + 2H$_2$O</td>
</tr>
<tr>
<td><strong>Copper oxide minerals breakdown:</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Chrysocolla:</strong></td>
<td>CuSiO$_3$.2H$_2$O + 12H$^+$ = 6Cu$^{2+}$ + 8H$_2$SiO$_4$</td>
</tr>
<tr>
<td><strong>Tenorite:</strong></td>
<td>CuO + 2H$^+$ = Cu$^{2+}$ + H$_2$O</td>
</tr>
<tr>
<td><strong>Brochantite:</strong></td>
<td>CuSO$_4$.3Cu (OH)$_2$ + 6H$^+$ = 4Cu$^{2+}$ + 6H$_2$O</td>
</tr>
<tr>
<td><strong>Most commonly reported precipitation products:</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Iron or potassium:</strong></td>
<td>3Fe$^{3+}$ + K$^+$ + 2SO$_4$ + 6H$_2$O = KFe$_3$(SO$_4$)$_2$(OH)$_6$ + 6H$^+$ jarosite</td>
</tr>
<tr>
<td><strong>Silica:</strong></td>
<td>H$_2$SiO$_3$ = SO$_2$ + H$_2$O silica</td>
</tr>
<tr>
<td><strong>Aluminium:</strong></td>
<td>3H$_2$O + K$^+$ + 2SO$_4$ + 3Al$^{3+}$ = KAl$_3$(SO$_4$)$_2$ + 6H$^+$ alunite</td>
</tr>
<tr>
<td><strong>Calcium:</strong></td>
<td>H$_2$O + SO$_4$ + Al$^{3+}$ = AlOHSO$_4$ + H$^+$</td>
</tr>
<tr>
<td><strong>Sodium:</strong></td>
<td>2H$_2$O + 2SO$_4$ + Ca$^{2+}$ = CaSO$_4$.2H$_2$O gypsum</td>
</tr>
</tbody>
</table>
Na\(^+\) + 7H\(_4\)SiO\(_4\) = \text{NaSi}_7\text{O}_{13}(\text{OH})_3\cdot12\text{H}_2\text{O} + \text{H}^+  \quad \text{magadiite}

**Most commonly reported alteration product formation:**

**Pyrophyllite:**

\[
2\text{Al}^{+++} + 4\text{H}_4\text{SiO}_4 = 2\text{HAl}(\text{SiO}_3)_2 + 6\text{H}^+ + 4\text{H}_2\text{O} \quad \text{pyrophyllite}
\]

**Kaolinite:**

\[
\text{H}_2\text{O} + 2\text{Al}^{+++} + 2\text{H}_4\text{SiO}_4 = \text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O} + 6\text{H}^+ \quad \text{kaolinite}
\]

**Vermiculite:**

\[
2\text{Mg}^{++} + 2\text{Al}^{+++} + 3\text{H}_4\text{SiO}_4 = \text{Mg}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + 10\text{H}^+ \quad \text{vermiculite}
\]

**Chlorite:**

\[
\text{H}_2\text{O} + 3(\text{Fe},\text{Mg})^{++} + 2\text{H}_4\text{SiO}_4 = \text{H}_4(\text{Fe, Mg})_3\text{Si}_2\text{O}_9 + 6\text{H}^+ \quad \text{chlorite}
\]

**Other mineral alteration products:**

**Plagioclase (anorthite) alteration:**

\[
2\text{H}_4\text{SiO}_4 + \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{SO}_4 = \text{CaSO}_4\cdot2\text{H}_2\text{O} + 2\text{HAl}(\text{SiO}_3)_2 + 4\text{H}_2\text{O} \quad \text{gypsum and pyrophyllite*}
\]

**Na Feldspar alteration:**

\[
4\text{H}_4\text{SiO}_4 + \text{NaAlSi}_3\text{O}_8 + \text{H}^+ = \text{NaSi}_7\text{O}_{13}(\text{OH})_3\cdot12\text{H}_2\text{O} + 0.5 \text{HAl}(\text{SiO}_3)_2 \quad \text{magadiite & pyrophyllite*}
\]

**Biotite alteration - closed system:**

\[
(\text{H},\text{K})_2(\text{Mg,Fe})_2\text{Al}_2(\text{SiO}_4)_3 + 3\text{H}^+ + 0.5 \text{O}_2 + \text{Fe}^{+++} + 2\text{SO}_4 = 0.5 \text{Mg}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 0.5 \text{SiO}_2 \quad \text{vermiculite, jarosite & silica*}
\]

**Biotite alteration - open system:**

\[
(\text{H},\text{K})_2(\text{Mg,Fe})_2\text{Al}_2(\text{SiO}_4)_3 + 6\text{H}^+ = 0.5 \text{Mg}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + 0.5\text{H}_2\text{SiO}_4 + 2\text{Fe}^{+++} \quad \text{vermiculite, jarosite & silica*}
\]

**Notes:**

1) Theoretical acid consumption by biotite conversion to vermiculite in open circuit leaching is 0.6 kg/kg biotite versus 0.3 kg/kg biotite for aerated closed circuit leaching (Dreier Section V).

2) Hot acid soluble test - John Dreier - small amount of minus 100 to 200 mesh leached in 20 wt% or conc. H\(_2\)SO\(_4\), heated to 110°F for one hour.

3) Extracts oxide copper, possibly some of the delafossite, cuprite and native copper and very little of the sulphide copper.

4) Acid concentrations in bottle roll tests are often several order of magnitude higher than in heap leaching.

5) Quartz, K feldspar, sericite, biotite and chlorite, the most common rock forming minerals of porphyry Cu deposits, do not consume much acid in closed cycle leaching (Dreier Section VI).

6) Minerals that might consume acid include carbonates, calcic plagioclase, amphiboles, montmorillonites and pyroxenes.

7) Mineralogy can determine whether acid consuming minerals present, disposition and mineralogy of oxide Cu minerals and mineralogy and abundance of any sulphide Cu minerals.

8) Column leach rate depends on particles size, copper mineralogy, grain size & disposition in rocks, density of fractures, non-fracture rock permeability, host rock reactivity etc.

9) A log-log plot of incremental column leach recovery versus time can be used for extrapolation of leach recoveries with time.

10) Sufficient acid to be available in leach solution to avoid risk of high pH lower in heap and potential for delafossite formation - establish by testwork.

11) * Reaction not balanced.
7. GANGUE SILICATE REACTION PRODUCTS

Table 2A summarizes heap leach gangue silicate reaction products arranged by reaction type, i.e. according to whether the reaction is silicate breakdown, limonite breakdown, copper oxide breakdown, precipitate product formation, silicate alteration product formation or mineral alteration reaction. Feed and reaction products are shown and reaction products are classified as precipitation product, alteration product or solution product.

As an example, in limonite breakdown hematite reacts with sulphuric acid to form ferric ions in solution. No precipitation or alteration products are formed. In another example, in precipitate product formation Ca\(^{2+}\) and SO\(^{4\,-2}\) ions already in solution react with each to form gypsum as a precipitate. In a third example, in silicate breakdown product formation the soluble solution reaction products silicic acid and Al\(^{3+}\) react with each other to form pyrophyllite as a precipitation product and sulphuric acid as a solution product.

Table 2B summarizes heap leach gangue silicate reaction options arranged by gangue mineral type i.e. according to whether the mineral being leached is biotite, K feldspar, Na feldspar, or Ca plagioclase. Three leach options are indicated for each mineral being leached including option 1 involving sequential mineral breakdown, subsequent precipitation and/or alteration and options 2 and 3 involving direct mineral alteration.

As an example, biotite is converted by option 1 reaction involving a combination of successive mineral breakdown, precipitation and alteration initially to produce soluble reaction products, silicic acid, Ca\(^{2+}\), Fe\(^{3+}\), Mg\(^{2+}\) and Al\(^{3+}\) and subsequently to produce precipitation products, silica and gypsum, as well as alteration solid products, magadiite, pyrophyllite, kaolinite, allophane, vermiculite and chlorite, and an alteration solution product, sulphuric acid. In option 2 reaction, biotite is converted to both precipitation products jarosite and silica and a silicate alteration product vermiculite. No solution products are formed. In option 3 reaction, biotite is converted to a silicate alteration solid product, vermiculite, and silicate alteration solution products, silicic acid and ferric ion.
8. GANGUE SILICATE MINERAL GROUPS

Table 3 presents a summary of the following gangue silicate and iron mineral groups with corresponding formulae, where available:

- Mica (including muscovite, phlogopite, biotite and vermiculite)
- Feldspar (including orthoclase, microcline, soda spar, lime spar, soda lime, felspathoid and felspathoid minerals)
- Clays (kaolinite, beidellite, montmorillonite, halloysite, hydromica, bentonite, china clay and ball clay)
- Iron oxidation (hematite, limonite, goethite)
- Other potential silicate minerals or alteration products (chlorite, chrysolite, chrysothile, cinchotine, epidote, glauconite, glaucophane, grossularite, halloysite, haunyrite, heulandite, hornblende, laumontite, leucite, natrolite, nephelite, pyrope, pyrophyllite, staurolite, stilbite, talc, tremolite, wollastonite and zoisite).

Acid reactivity issues include:

- Some minerals are close to equilibrium with the leach solution and will therefore have limited reactivity.
- Acid consumption in high biotite and high chlorite ores is proportional to wt% acid
- Iron minerals, especially those producing ferric iron, have a major impact on acid consumption
- Chlorites are powerful long term acid consumers
- Epidote alteration can drastically increase acid consumption when long leach times are involved
Fig 1 is a simplified schematic of the geochemical cycle for a typical oxide copper ore heap leach process. Acid consumption and liberation reactions are shown in separate stages. Acid consumption occurs in the initial heap leach reactions. Acid liberation occurs in both the initial leach process and final heap precipitation and alteration stages as well as in the solvent extraction stage. Examples of the types of minerals that dissolve in the initial heap reaction stage and precipitate or alter in the initial or final heap reaction stages are shown. The liberation and/or consumption of different metal ions in the different reaction stages are also shown. The main point the figure is to show that a broad range of different solid products and solution products either form or are removed from solution as the reactions proceed.

9. GEOCHEMICAL LEACH CYCLE
Fig 1: Simplified Schematic of Geochemical Cycle of Typical Oxide Copper Ore Heap Leach

**Heap reactions (initial)**

- Acid Consumption
- H^+
- Solids Dissolving
  - NaFelspar NaAlSiO_4
  - K Feldspar KAlSiO_4
  - Bottle (H.5K).Mg.Fe.Al(SiO_4)_2
  - Chlorite H_2O(Mg,Fek,Fe)SiO_3
  - Magnesite FeO.Si_2
  - Chrysocolla CuSiO_3
  - Tenorile CuO
  - Goethite FeO(OH)
  - Hematite FeO.
  - Carbonate CaCO_3
  - Calcic Plagioclase CaAl_2Si_2O_6
  - Amphiboles
  - Montmorillonite H_2Al_2Si_4O_12+nH_2O
  - Pyroxenes

- Ion Liberation
  - Cu^{2+}
  - K^+
  - Na^+
  - Ca^{2+}
  - Fe^{2+}
  - Fe^{3+}
  - Al^{3+}
  - Mg^{2+}
  - Mn^{2+}
  - SiO_2
  - OH

- Solution Make-Up
  - Water

**Heap precipitation/alteration (initial)**

- Acid Consumption
- H^+
- Solids Precipitation
  - Illite HA(SiO_3)_2
  - Silica SO_2
  - Vermiculite MgAl_2SiO_5(OH)_2
  - Chalumite H_2O(Mg,Fe)_2SiO_3
  - Kaolinite H_4Al_2Si_2O_9
  - Magadellite NaSiO_3(OH)_2.3H_2O

- Ion Consumption
  - Na^+
  - Fe^{2+}
  - Fe^{3+}
  - Al^{3+}
  - Mg^{2+}
  - Mn^{2+}
  - SiO_2

**SXEW plant**

- Acid Consumption
- H^+
- Solids Precipitation
  - Goethite FeO(OH)
  - Jarosite KFe_2(SO_4)_3(OH)_6
  - Alumite KAl(SO_4)_4(OH)_6
  - Gypsum CaSO_4.2H_2O
  - MnHPO_4.2H_2O
  - Al(OH)_3

- Ion Consumption
  - Cu^{2+}
  - K^+
  - Ca^{2+}
  - Fe^{3+}
  - Al^{3+}
  - Mn^{2+}
  - OH

**Heap precipitation/alteration (final)**

- Acid Consumption
- H^+
- Solids Precipitation
  - Goethite FeO(OH)
  - Jarosite KFe_2(SO_4)_3(OH)_6
  - Alumite KAl(SO_4)_4(OH)_6
  - Gypsum CaSO_4.2H_2O
  - MnHPO_4.2H_2O
  - Al(OH)_3

Reference: Geochemical Aspects of Leaching, Copper Heap Leach, Arizona 1992, John Dreier

* indicates IPDS addition of alteration products based on text of Dreier reference
10. GANGUE SILICATE REACTION PATHS

Fig 2 shows idealized mineral reaction paths for the acid leaching of oxide and gangue silicate minerals during heap leaching. The original silicate feed minerals are assumed to be K feldspar, Na feldspar, Ca plagioclase and biotite. The other minerals present are assumed to be limonite and oxide copper minerals. As in Fig 1, the figure shows that a wide variety of different solid products (in this case 11) can form from the breakdown and/or alteration of just four original silicate minerals during acid leaching. The figure also shows that the pregnant leach solution to SX would be expected to contain silicic acid, sulphuric acid and a wide variety of metal ions from silicate and limonite mineral breakdown during leaching. It would appear that aeration would be necessary to ensure jarosite formation during alteration of iron rich biotite during oxide copper leaching.

Notes:
1) Fig 2 shows conversion of gangue silicate (K Feldspar, Na Feldspar, Ca Plagioclase & Biotite) to other solid and solution products
2) Reaction details shown on Reaction Worksheet, Table 2
3) Solid and solution species assumed at equilibrium conditions
4) Ion generation and consumption shown in Geochemical Cycle Fig 1
5) Reactions from John Dreier, Copper Heap Leach, Arizona, Feb 1992, "Geochemical Aspects of Copper Heap Leaching"
6) Silicic acid is $\text{H}_4\text{SiO}_4$
Farlas and co-workers\textsuperscript{6} point out that acid curing can avoid the problems of silica dissolution and control that can otherwise often occur in heap leaching. The mechanism proposed for acid cure is that it dehydrates the surface of aluminium silicate minerals in the ore, by partial removal of a monolayer of hydroxide groups that cover the surface of silica and silicates, rendering the surface hydrophobic and virtually insoluble in aqueous solutions. It can also encourage chemical cementation of neighbouring interlayers of sheet and chain silicates.

Data presented for industrial vat leaching shows that acid cure not only assures an even distribution of the leaching agent with a strong sulphation effect but also improves the mechanical characteristics of the ore, the overall hydraulic behaviour, copper recovery and leads to reduced acid consumption.

11. DIAGNOSTIC OR SEQUENTIAL LEACHING

Diagnostic leaches are empirical relatively low cost methods that are used to estimate the type of copper species present in leach feed and leach residue materials. The diagnostic leaches determine firstly the acid-soluble copper content, secondly the cyanide soluble copper content in residue from the preceding acid soluble determination and thirdly the non-acid soluble and non-cyanide soluble copper content remaining in the cyanide soluble determination residue. The results are then analyzed to infer the extent of acid-soluble copper and slow-leaching oxide or potentially sulphide copper. Fig 3 shows a schematic of a typical diagnostic leaching assay method. (In a number of cases it has been found that a hot acid procedure at 50°C is more reliable, and that a cold acid technique may understate the acid soluble copper content.)

The acid-soluble copper assay is normally expected to leach 100% of the copper present in the following minerals: chrysocolla, malachite/azurite, brochantite, chalcocite, atacamite, antlerite, tenorite, pseudomalachite, copper pitch and neotosite. It is also meant to leach the order of 20% native copper, 50% cuprite, 5-40% cupriferous iron oxide, 5-60% of cupriferous clay, 10-50% of delafossite and 10-80% of copper wad. In some instances it can also leach a minor portion of the more soluble sulphides, for example up to approximately 20% of the chalcocite.

The subsequent cyanide-soluble copper assay is usually expected to leach 100% of the copper present in chalcocite, covellite, native copper, brochantite, antlerite, atacamite, pseudomalachite, cuprite, tenorite and malachite/azurite. It is also expected to leach in the order of 40-60% cupriferous iron oxide, 20-60% cupriferous clay, 10-12% hematite, 10-80% copper wad, 5-10% turquoise, and for sulphides present 100% chalcocite and covellite, 80% bornite, 60-80% enargite, 20-30% tetrahedrite and 10-20% chalcopyrite.

The cyanide leach residue is expected to indicate the extent of the residual copper still present in clays, feldspars, iron oxides, turquoise, sulphosalts, oxide copper in silicates and partially soluble sulphides.

There can be variations from the above figures due to complex mineral intergrowth.

One benefit of the above sequential procedure is that chrysocolla is accounted for in the initial acid-soluble step. If a cyanide-soluble assay is undertaken without a preceding acid-soluble step, the soluble copper present as chrysocolla will be underestimated, as chrysocolla is only partly soluble in cyanide.

Without a through understanding of the ore mineralogy, it can be seen that diagnostic leaches can readily lead to misinterpretation of leach data in terms of copper mineralogy. Further limitations include the possibilities of complex locking and occurrence of copper, readsoption of copper from solution after leaching and changes in extraction efficiencies of a given mineral with changes in mineralogical composition of the ore. It would seem that
diagnostic leaching should preferably be used where the ore mineralogy is generally known.

The data from the mineralogy and diagnostic leaching methods can be usefully used to specify the soluble copper assay methods to be applied to the drilling program and the subsequent metallurgical test program. A much clearer picture of the orebody can be obtained by utilizing the soluble copper assay rather than the total copper assay in orebody modeling. In addition the assessment of leaching performance is more meaningful when expressed in terms of soluble copper rather than total copper.

### 12. MINERALOGICAL STUDY

A relatively inexpensive polished section study, supplemented as appropriate by XRD analyses, can provide valuable information on the extent of potential acid-consuming gangue silicate, iron or calcite minerals present and the relative amounts of different oxide copper minerals and slower leaching sulphide minerals. In some case, microprobe work may be needed to resolve specific issues. Ideally such a study is carried out on representative ore type samples, well before commencement of the metallurgical test program.

The results of the initial mineralogy study are a key to understanding future potential leach performance and in building up a reliable database for future development work including planning of testwork. Without suitable initial mineralogy work, leach results are potentially subject to misinterpretation.
For example, a new resource could conceivably be prematurely rejected from further evaluation due to inadequate understanding of mineralogical reasons for low recoveries in early exploratory leach tests. Conversely, a new resource might be prematurely adopted for a major development program based on unduly optimistic leach test results on ore samples that are only partially representative of the resource. Only after further more extensive testwork has been carried out might any problems of major mineralogical variability and related recovery variability recoveries become better defined.

Careful mineralogy studies, on samples of established representivity, at the outset should help avoid misclassification of prospective heap leach projects.

13. CONCLUSIONS

Acid consumption in oxide copper heap leaching is due to the presence of silicate and limonite gangue as well as more obvious acid consuming carbonate minerals. Acid consumption in closed circuits can be significantly lower than in open circuits because of equilibrium effects. Also, the acid solubility of copper minerals varies widely. Thus, greater attention to relatively low cost mineralogy work on carefully selected samples, early in the project development program can be expected to provide significant cost and planning benefits in later testwork, plant design and operations of new leach projects. Particular benefits are likely to include improved definition and characterization of ore types, better understanding of potential variability in copper recovery and acid consumption within the resource, a probable reduction in the number and cost of leach tests needed for project feasibility assessment, more reliable plant design criteria and more predictable commercial heap performance. Insufficient attention to mineralogy can lead to inadequate understanding of the reasons for variable ore performance and to much higher risks in plant design and commercial heap performance.

14. REFERENCES

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