GALVANOX™

A Novel Process for the Treatment of Copper Concentrates

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GALVANOX HISTORY

- UBC researchers Dave Dixon and Alain Tshilombo developed a novel process for galvanically-assisted atmospheric leaching of primary copper concentrates in early 2004.

- A preliminary patent application was filed in June 2004.

- Several patent applications were filed in 2005 (US, Chile, Peru, Laos), and successful PCT examination in September 2006 spawned many other national phase applications.

- UBC entered into an exclusive marketing agreement with Bateman Engineering in October 2006, and is working closely with Bateman to identify potential applications of the process.

- Batch testing programs on many candidate concentrates have been initiated or completed, continuous leaching was piloted in May, and three detailed feasibility studies are currently underway, with integrated pilot campaigns planned to begin in November.
GALVANOX FEATURES

- Atmospheric Leach (~80°C)
- No microbes
- Pure sulphate medium (no chloride)
- Conventional materials of construction
- No fine grinding
- Generates elemental sulfur (> 95%), low oxygen demand
- No surfactants
- Selective for chalcopyrite over pyrite (can cost-effectively treat low grade concentrates down to 9% copper or less)
- Complete copper recovery, typically in less than 12 hours, and sometimes in as little as 4 hours
- Fully compatible with conventional SX-EW
GALVANOX CHEMISTRY

- GALVANOX takes advantage of the galvanic effect between chalcopyrite and pyrite.
- Chalcopyrite is a semiconductor, and therefore corrodes electrochemically in oxidizing solutions.
- In ferric sulphate media, the overall leaching reaction is as follows:

  \[ \text{CuFeS}_2 + 2 \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2 \text{S}^0 \]

- This reaction may be represented as a combination of anodic and cathodic half-cell reactions:

  Anodic: \[ \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2 \text{S}^0 + 4 \text{e}^- \]
  Cathodic: \[ 4 \text{Fe}^{3+} + 4 \text{e}^- \rightarrow 4 \text{Fe}^{2+} \]
UNASSISTED CHALCOPYRITE LEACHING

\[
\begin{align*}
&\text{Anodic Site} \\
&\text{Cathodic Site}
\end{align*}
\]
UNASSISTED CHALCOPYRITE LEACHING
GALVANOX CHEMISTRY

- Typically, chalcoprytite surfaces are passivated (i.e., they become resistant to electrochemical breakdown) in ferric sulfate solutions at even modest solution potential levels.

- It is widely held that this results from the formation of some sort of passivating film on the mineral surface that most likely consists of an altered, partially Fe-depleted sulfide layer.

- Because of this, most investigators have assumed that it is the anodic half-cell reaction that limits the overall rate of leaching.

- However, we discovered that it is primarily the cathodic half-cell reaction (i.e., ferric reduction) that is slow on the passivated chalcoprytite surface.
The presence of pyrite facilitates chalcopyrite leaching by providing an alternative surface for ferric reduction.

This essentially eliminates *cathodic* passivation of chalcopyrite in ferric sulfate solutions.

Also, by ensuring rapid chalcopyrite oxidation, the solution potential is easily maintained at levels low enough to prevent *anodic* passivation of the chalcopyrite.

This also prevents anodic breakdown of the pyrite, which remains more or less completely inert.
GALVANICALLY-ASSISTED CHALCOPYRITE LEACHING
GALVANICALLY-ASSISTED CHALCOPYRITE LEACHING

Partially leached particle

Completely leached particles
GALVANOX CHEMISTRY

- The ferric required for GALVANOX leaching is regenerated in situ with oxygen gas.

Ferric leaching of chalcopyrite:

\[
\text{CuFeS}_2 + 2 \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{CuSO}_4 + 5 \text{FeSO}_4 + 2 \text{S}^0
\]

Oxidation of ferrous with dissolved oxygen gas:

\[
4 \text{FeSO}_4 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{O}
\]

Overall leaching reaction:

\[
\text{CuFeS}_2 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2 \text{S}^0 + 2 \text{H}_2\text{O}
\]
GALVANOX CHEMISTRY

- GALVANOX leaching is followed by conventional solvent extraction and electrowinning to recover LME Grade A pure copper cathodes.

Copper electrowinning:

\[
\text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu}^0 + \frac{1}{2} \text{O}_2 \uparrow + \text{H}_2\text{SO}_4
\]
Iron is rejected from the Galvanox circuit by oxyhydrolysis in an autoclave at ~220°C to make hematite, which is easy to filter and perfectly suitable for disposal.

Iron oxyhydrolysis:

\[
4 \text{FeSO}_4 + \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 2 \text{Fe}_2\text{O}_3 (s) + 4 \text{H}_2\text{SO}_4
\]

This autoclave also treats a portion of the concentrate feed, in order to generate the heat required for the atmospheric leach circuit, and also to generate extra acid as required for secondary sulfides or acid-consuming gangue minerals in the concentrate.
In summary, the overall GALVANOX process chemistry is as follows:

Galvanically-assisted atmospheric leaching of chalcopyrite:

$$\text{CuFeS}_2 + \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{FeSO}_4 + 2 \text{S}^0 + 2 \text{H}_2\text{O}$$

Iron oxyhydrolysis:

$$\text{FeSO}_4 + \frac{1}{4} \text{O}_2 + \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{Fe}_2\text{O}_3 (s) + \text{H}_2\text{SO}_4$$

Copper electrowinning:

$$\text{CuSO}_4 + \text{H}_2\text{O} \rightarrow \text{Cu}^0 + \frac{1}{2} \text{O}_2 \uparrow + \text{H}_2\text{SO}_4$$

Overall process chemistry:

$$\text{CuFeS}_2 + \frac{5}{4} \text{O}_2 \rightarrow \text{Cu}^0 + 2 \text{S}^0 + \frac{1}{2} \text{O}_2 \uparrow + \frac{1}{2} \text{Fe}_2\text{O}_3 (s)$$
BATCH TESTING APPARATUS

- Six 3-L jacketed reactors
- Water baths for temperature control
- Digital oxygen mass flow meters for potential control
- Automated data acquisition for potential, pH and temperature
CHALCOPYRITE CONCENTRATE – 35% Cu

Effect of pyrite addition (50 g con, 65 g acid, 470 mV, 80°C)
CHALCOPYRITe CONCENTRATE – 35% Cu

Effect of sulfuric acid addition (50 g con, 100 g Py, 470 mV, 80°C)
CHALCOPYRITE CONCENTRATE – 35% Cu

Effect of solution potential (50 g con, 100 g Py, 90 g acid, 80°C)
CHALCOPYRITE CONCENTRATE – 35% Cu

Effect of solution potential (50 g con, 100 g Py, 90 g acid, 80°C)
CHALCOPYRITE CONCENTRATE – 35% Cu

Effect of temperature (50 g con, 100 g Py, 90 g acid, 470 mV)
CHALCOPYRITE CONCENTRATE – 35% Cu

Effect of pyrite recycle (50 g con, 100 g Py, 90 g acid, 470 mV, 80°C)
CHALCOPYRITE CONCENTRATE – 35% Cu

At constant solution potential, pH is an indicator of reaction progress

![Graph showing Cu recovery and pH over time](image)
CHALCOPYRITE CONC 2 – 23.6% Cu

Effect of pyrite addition (30 g con, 120 g Py, 30 g acid, 480 mV, 80°C)
CHALCOPYRITE CONC 3 – 24.1% Cu

Effect of pyrite addition (10 g con, 40 g Py, 15 g acid, 470 mV, 80°C)
CHALCOPYRITE CONC 4 – 20.1% Cu

Effect of pyrite addition (57 g con, 112 g Py, 60 g acid, 450 mV, 80°C)
CHALCOPYRITE BULK CONC – 10.2% Cu

150 g bulk con @ ~1.21 Py/Cp ratio, 75 g acid, 440 mV, 80°C)
BULK CONC RESIDUE – 22.8 g/t Au

77 g Galvanox residue @ 0.5 g/L NaCN, pH 11, room temp
SUMMARY OF LEACH RESULTS

- GALVANOX is robust (insensitive to the source of chalcopyrite)
- Process optimization is straightforward:
  - Pyrite-to-chalcopyrite ratio (2:1 to 4:1 typically optimal)
  - Acid concentration (stoichiometric + modest excess)
  - Solution potential (> 440 mV)
  - Temperature (> 70°C)
- Recycled pyrite is equally as effective as fresh pyrite
- Under the correct process conditions, GALVANOX leaching is very rapid (limited by the rate of gas-liquid mixing)
- High Au extractions from GALVANOX residues are feasible, with relatively modest cyanide consumption levels
FIRST GALVANOX COPPER
(99.85% Cu directly from PLS at 50 g/L Fe!)
QUESTIONS?

For more information, please visit:

www.GALVANOX.com