

Project Proposal

Carmacks Copper Project Yukon Territory

Appendix E2

Fate of lead at the anode of the electrowinning circuit – Carmacks Copper (August 2006)



To: Dan Cornett, Access Consulting Group From: Joseph G. Harrington, Green World Science, Inc. Re: Fate of lead at the anode of the electrowinning circuit – Carmacks Copper

Summary:

It is understood that an outstanding question has been raised regarding the solvent extraction/electrowinning process (SX/EW) proposed for the Carmacks Copper project heap leach. Specifically the question relates to the potential for lead dissolving from the electrowinning anodes in the process and ending up on the heap as part of solution distribution.

Given that lead sulfate is very insoluble, the soluble amount of this lead would be less than a part per billion. The incremental environmental risk posed from the use of tincalcium-lead anodes is very small.

Review:

Anodes made of lead alloys are used in the electrowinning and plating of metals such as manganese, copper, nickel, and zinc. Rolled lead-calcium-tin and lead-silver alloys are the preferred anode materials in these applications, because of their high resistance to corrosion in the sulfuric acid used in electrolytic solutions.

The use of lead and lead-alloys in such applications is based upon their general ability to withstand prolonged exposure to sulfuric acid under highly oxidizing conditions. Lead and lead-alloy electrodes, usually in the form of cast plates and typically containing alloying constituents such as Ag, Ca, Sn and Sb, are expected to endure periods of up to 4 years under such harsh acidic conditions. The degradation of these electrodes is primarily due to intergranular corrosion, which occurs as a result of local volumetric changes associated with lead-sulfuric to lead-oxide transitions at the intersection of internal grain boundaries with the free surface of the electrodes. This results in a local compromise of the protective lead-oxide film, and subsequent propagation of corrosive attack into the grain boundaries, and ultimately, general loss of electrode metal via spalling and grain dropping. Such loss of electrode material, in addition to compromising the structural integrity of the electrode, results in contamination of the electrolyte by lead and other electrode alloying constituents, which ultimately limits the purity of the metal deposit which can be achieved during the electrowinning process.

Electrowinning conditions of high-temperature and strongly acidic electrolyte combined with the anodic half-cell reaction, the decomposition of water to hydrogen cations and oxygen gas, produce a corrosive environment for the insoluble lead anodes. Although lead ions should not co-deposit with the electrowon metal at the cathodic potential at which the metals is deposited, electrowon copper is often contaminated with up to 10



PPM lead. This is a significant problem because the corrosion products become trapped on the surface of adjacent cathodes, impairing cathode product quality and market grade. The anode corrosion rate can also be reduced by the use of different alloying agents and alternate methods of anode production. The use of rolled lead-calcium-tin anodes reduces the rate of chemical corrosion, but the corrosion products adhere less, which may increase the rate of particulate inclusion on the cathode surface and cause nodular copper growth. The reduction in corrosion rates and loss of corrosion product adhesion is attributed to the fine-grained structure of the anodes.

In conventional copper electrowinning practice, operators add cobalt to the electrolyte to reduce the rate of corrosion. Cobalt is believed to catalyze the oxygen discharge reaction and thus depolarizes the anode thereby reducing the corrosion rate. Modern copper electrowinning facilities employ cold rolled Pb-Ca-Sn anodes. These anodes address the shortcomings of traditional lead alloy anodes in reducing corrosion while possessing good mechanical properties, and ultimately they also have low production costs.

Because of the high voltage potential difference at the cathode, it is very unlikely that lead could be solubilized from the anode into solution, and then makes it back into the solvent and re-enter the leaching circuit. Because of this, the only environmental concerns should be focused on the disposal of the sludge which might need to be cleaned out of the tank house bottoms periodically.

At a lifetime of 4 years or more, and with at least 90% of the lead lost at the anode making its way to the cathode as a part of the process, 10 PPM lead potentially in the cathode copper product, the amount of lead in the sludge is very likely miniscule. Furthermore, because gold and silver also report to the same location – at the sludge bottoms – the value of the sludge is likely high enough to justify recycling.

If 100,000 pounds of lead were in anode inventory, and 10% of this amount were to enter the heap leach circuit over a 4 year period, during which 2 MM tons of rock were leached each year, the concentration of lead left in the heap from this source could at most be 10,000 pounds into 8 million tons, or 5 tons per 8 million tons. This would be less than 0.6 PPM in the rock on the heap.

Given that lead sulfate is very insoluble – otherwise lead-sulfuric acid car batteries would not be able to discharge (forming lead sulfate) and be recharged (reforming lead and sulfuric acid) hundreds of times – the soluble amount of this lead would be less than a part per billion.

Ksp (PbSO₄) = 1.7×10^{-8}

 $Pb^{2+} + SO_4^{2-} \leftarrow \rightarrow PbSO4(s);$ Ksp (by definition) = [PbSO4] / [Pb²⁺][SO₄²⁻];



With lead sulfate at unit concentration at its surface, and with sulfate concentrations dictated by the leaching chemistry at 50 - 100 grams per liter – or nearly 1 molar, the concentration of lead in solution will be about equal to the solubility product of about 10^{-8} molar, prior to any scavenging by iron oxides or iron oxy-hydroxides.

These mechanisms, along with the isolation of the lead anodes from the leaching circuit by the intermediate organic extraction separation circuit, make the incremental environmental risk posed from the use of tin-calcium-lead anodes very small.