Effective Grain Modification in Copper Electrowinning with DXG-F7

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Nodulation is a persistent problem in copper electrowinning, especially where high current densities are used. The resultant porous copper tends to contain impurity levels which are too high for LME quality. A variety of additives have been used in the industry, including starch, various grades of guar gum and modified polysaccharides. These have had mixed success and the more expensive grades of guar have been favoured. Guar is, however, prone to seasonal price fluctuations and, of late, some availability problems as it is being used as an additive in fracking. Guar solutions are also awkward to prepare, as guar tends to gel and form lumps if not given sufficient hydration time.

DXG-F7, developed and produced by G-Process of Chile, is a grain modifier which provides an economical alternative with a number of distinct advantages. The oligosaccharide will dissolve readily at room temperature, requiring no more than 30 minutes of agitation, and there is no tendency to form lumps. The viscosity of the prepared solution is 10 times lower than that of guar solutions and it can be prepared in either water or electrolyte.

DXG-F7 can withstand high current densities and remains effective at values of beyond 450 A/m².

The impact of DXG-F7 on the SX process extensively tested by two major extractant producers and both have confirmed that the additive has no detrimental effects.

The crystal structure of copper deposited in the presence of DXG-F7 is distinctly columnar and dense. By blocking zones of high current density, DXG-F7 forces deposition into the depressions on the cathode surface. This dramatically reduces nodulation and eliminates the occurrence of occlusions and entrainment of electrolyte.

INTRODUCTION

Most copper electrowinning (EW) plants struggle with the formation of nodules on the cathodes. This is in particular the case in EW plants operating with high current densities, above 300 A/m².

The nodulation causes short circuits and resultant loss in current efficiencies. The rough surface of nodular deposits has a tendency to trap suspended solids, which has a negative effect on the
conductivity and ductility of copper deposits. In extreme cases the deposits can become so brittle that the copper sheets break up during stripping, as shown in Figure 1.

Figure 1: Severe nodulation resulting in impure copper and, in extreme cases, brittle copper which breaks up during stripping

Such brittleness not only results in the production of large amounts of scrap copper, but also causes significant delays in stripping as crew struggle to clear the scrap.

Nodular copper also tends to occlude electrolyte in its irregular crystalline structure. This causes increases in impurities such as sulphur, lead and iron, and often makes it impossible to meet the purity requirements for LME grade copper.

A variety of additives have been used in EW plants as smoothing agents or grain modifiers. These include starch, various grades of guar gum and modified polysaccharides. These have had mixed success and the more expensive grades of guar have been favoured. Guar is, however, prone to seasonal price fluctuations and, of late, some availability problems as it is being used as an additive in fracking. Guar solutions are also awkward to prepare, as guar tends to gel and form lumps if not given sufficient hydration time. Guar also has limited usefulness at high current densities.

Some polysaccharide products have proved effective but usually require a dosage which is significantly higher than that of guar, which negates some of the economic benefits of this less expensive product.

DXG-F7, a product developed and produced by Great Process Ltda. (G-Process), of Antofagasta, Chile is a smoothing agent and grain modifier which overcomes many of these problems.

DXG-F7 blocks deposition of copper at prominent points of the copper deposit, thereby preventing growth of dendrites and nodules at the points of higher current density.

At the same time DXG-F7 modifies the crystal growth pattern of copper to form a more columnar crystal as can be seen in Figure 2. This more ordered growth pattern reduces the occurrence of
occlusion. Together these two effects improve not only the surface quality of the copper deposit but also reduce the levels of impurities in the copper.

![Deposit with Guar](image1.png) ![Deposit with DXG-F7](image2.png)

*Figure 2: Cross sectional image of growth pattern of copper deposits with guar vs that with DXG-F7 at Zaldivar, Chile. (100X magnification) Current density 330 A/m²; Dosage 280 g/t; Harvest Cycle 5 days.*

**PREPARATION OF DXG-F7 SOLUTION**

One of the major advantages of DXG-F7 lies in the ease of preparation of the solution for dosing into the electrolyte.

Unlike guar, DXG-F7 dissolved rapidly in water or electrolyte, requiring less than 30 minutes of mixing. There is no need to age the solution to assure hydration. The solution can be used straight after mixing. The product can be dissolved at ambient temperatures down to as low as 5°C. No steam sparging or other means of heating is required.

DXG-F7 forms a low viscosity solution free of gel or lumps, and does not adhere to tank or pipe walls. It has a high solubility, making it possible to dissolve 25 kg in just 3 m³.

No special agitators are required. Even air agitation ensures problem free dissolution.

**OPERATIONAL ADVANTAGES**

In addition to being extremely effective at eliminating nodulation and improving the purity of the copper, DXG-F7 provides a number of additional advantages.

- It is very tolerant of high current densities, staying effective at densities of over 450 A/m².
- The required addition rate is typically 25% lower than that of high grade Guar.
- DXG-F7 can be quantitatively analyzed in the electrolyte, down to concentrations as low as 3 ppm.
EFFECT ON SX CIRCUIT

Detailed studies have been conducted by both Cytec (Maldonado, G.R. 2010) and Cognis (now BASF) (Ardiles H, L. 2007) to ascertain if DXG-F7 has any negative effects on the SX circuit. Both studies showed conclusive that DXG-F7, even at extremely high level, does not affect the SX circuit.

DXG-F7 is currently in use in 26 EW plants around the world, and none have experienced any problems in their SX circuit as a result of using DXG-F7.

PLANT TRIAL DATA

As is the norm in the industry, before introducing any new product to their circuit, most of G-Process’ customers have carried out extensive plant trials, prior to adopting the use of DXG-F7 in their EW operations. Some of these customers have been kind enough to share the results with G-Process. The following is a short summary of the data.

Zaldivar

Barrick’s Zaldivar was one of the first EW plants to try DXG-F7 in their EW circuit. The plant layout permitted them to operate tankhouse sections AB and CD in parallel, using DXG-F7 in AB and guar in CD, while feeding the same electrolyte to both sections, and operating both sections under the same current density. For a period of three months the sulphur levels were monitored in the copper cathodes produced. The average sulphur analyses are shown in Figure 3. Zaldivar also reported a 15% decrease in acid mist when using DXG-F7. This claim has, however, not been independently verified.

\[\text{Cathode chemical Analysis Sector AB vs CD (ppm S)}\]

\[
\begin{array}{cccccc}
\text{S (ppm)} & 5.16 & 6.72 & 6.93 & 5.75 \\
\text{AB} & \text{CD} & \text{AB} & \text{CD} & \text{AB} & \text{CD} \\
\text{DXG-F7} & \text{Guar} & \text{DXG-F7} & \text{Guar} & \text{DXG-F7} & \text{Guar} \\
\text{December 2008} & & & & \text{January 2009} & \\
\end{array}
\]

*Figure 3: Effect of DXG-F7 on cathode sulphur content at Barrick’s Zaldivar EW plant. DXG-F7 added to sector AB; Guar added to sector CD; both sectors operated under the same current density and with the same electrolyte*

Lomas Bayas

At Glencore’s Lomas Bayas the copper quality started deteriorating in June 2010, concurrent with an increase in the copper tenor and current density. Introduction of DXG-F7 significantly reduced the concentration of sulphur in their copper cathodes, permitting them to consistently attain sulphur...
concentrations of below 3 ppm. This contributed significantly to the plant producing in excess of 97% of their copper at LME grade.

Figure 4 illustrates the changes in sulphur content and cathodes quality following the introduction of DXG-F7 in October 2010. DXG-F7 was gradually introduced in increasing proportion to guar. The EW plant now operates on a mixture of 70% DXG-F7 and 30% Guar.

![Figure 4: Drop in sulphur concentration and resultant increase in A Grade copper at Lomas Bayas following the introduction of DXG-F7](image)

**El Tesoro**

In January 2011 the cathode quality at Antofagasta Minerals S.A.’s El Tesoro facility started to deteriorate to such an extent that by August almost all cathodes had to be rejected. DXG-F7 was introduced in stages, starting in August 2011 as illustrated in Table 1.

**Table I: Trend of decreasing quality with increasing current density at Los Bronces**

<table>
<thead>
<tr>
<th>Period</th>
<th>Dosage of DXG-F7 (g/t Cu)</th>
<th>Current Density (A/m²)</th>
</tr>
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<tbody>
<tr>
<td>Feb 2011</td>
<td>0</td>
<td>280</td>
</tr>
<tr>
<td>Mar 2011</td>
<td>0</td>
<td>242</td>
</tr>
<tr>
<td>Apr 2011</td>
<td>0</td>
<td>307</td>
</tr>
<tr>
<td>May 2011</td>
<td>0</td>
<td>342</td>
</tr>
<tr>
<td>Jun 2011</td>
<td>0</td>
<td>341</td>
</tr>
<tr>
<td>Jul 2011</td>
<td>0</td>
<td>325</td>
</tr>
<tr>
<td>8 Aug – 8 Sep 2011</td>
<td>30</td>
<td>305</td>
</tr>
<tr>
<td>9 Sep – 11 Oct 2011</td>
<td>40</td>
<td>349</td>
</tr>
<tr>
<td>12 Oct – 16 Oct 2011</td>
<td>50</td>
<td>354</td>
</tr>
<tr>
<td>26 Oct - 31 Oct 2011</td>
<td>100</td>
<td>354</td>
</tr>
<tr>
<td>1 Nov – 14 Nov 2011</td>
<td>120</td>
<td>355</td>
</tr>
<tr>
<td>15 Nov – 22 Nov 2011</td>
<td>140</td>
<td>375</td>
</tr>
<tr>
<td>23 Nov – 6 Dec 2011</td>
<td>160</td>
<td>371</td>
</tr>
<tr>
<td>07 Dec – 12 Dec 2011</td>
<td>180</td>
<td>362</td>
</tr>
</tbody>
</table>
The quality started improving. Figure 5 illustrates the turn-around in quality. El Tesoro is now operating on a mix of 60% DXG-F7 and 40% guar, and consistently produces in excess of 90% of its copper as A-Grade cathodes.

![Cathode quality at El Tesoro before & after introduction of DXG-F7](image)

**Figure 5: Turn around in cathode quality with the introduction of DXG-F7 at El Tesoro in August 2011**

**Los Bronces**

In 2005 Anglo American’s Los Bronces decided to increase current density in order to achieve higher production. This program of gradual increase was continued until 2010, when current density reached 460 A/m². The increased current density led to decreasing cathode quality. This trends is illustrated in Table II.

<table>
<thead>
<tr>
<th>Year</th>
<th>% Off-Grade Cathodes</th>
<th>Current Density (A/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>19.0</td>
<td>363.0</td>
</tr>
<tr>
<td>2006</td>
<td>27.0</td>
<td>393.0</td>
</tr>
<tr>
<td>2007</td>
<td>28.0</td>
<td>406.0</td>
</tr>
<tr>
<td>2008</td>
<td>53.0</td>
<td>384.0</td>
</tr>
<tr>
<td>2009</td>
<td>60.0</td>
<td>430.0</td>
</tr>
<tr>
<td>2010</td>
<td>80.0</td>
<td>460.0</td>
</tr>
</tbody>
</table>

In April 2010 Los Bronces started introducing DXG-F7, gradually increasing the proportion of DXG-F7 to guar over a 4 week period, until in May 2010 the plant was operating on only DXG-F7. Figure 6 shows how the introduction of DXG-F7 affected the average sulphur content in the cathodes, reducing it from a mean value of 14.0 ppm to around a mean value of 6.3 ppm.
Figure 6: Reduction in sulphur levels in the copper cathodes at Los Bronces following introduction of DXG-F7 in April 2010.

Figure 7 illustrates the change in copper quality, following the introduction of DXG-F7 in April of 2010.

Figure 7: Improvement in copper quality at Los Bronces, following introduction of DXG-F7 in April 2010. ("Special Grade" is an in-house designator for cathodes of better quality than A-Grade)
CONCLUSION

DXG-F7 is being used in 26 EW plants around the world, all of which have realised significant improvements in copper quality. None of these plants have had any negative effects in their SX operations as a result of DXG-F7 being introduced. The effectiveness of the product in reducing nodulation and impurities, in conjunction with the ease of preparation, make DXG-F7 an attractive alternative to other smoothing agents. Its tolerance for high current densities makes it a particularly useful grain modifier in EW plants running at current densities above 300 A/m².

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