ABSTRACT

The design of entrainment control processes in copper SX plants has been studied by use of models based on achievable plant performance. A number of alternatives have been assessed for their suitability in minimising the transfer of deleterious species from PLS into the electrolyte.

The position of the wash (scrub) stage in the circuit, either before or after the loaded organic tank, has been the subject of considerable debate. The modelling shows that at ‘normal’ entrainment levels, the performance of the circuits are very similar. However at high entrainment levels the selection of the wash after the loaded organic storage has significantly lower transfer of contaminants. When considering the inclusion of a loaded organic coalescer the results of the modelling again show that the best circuit has the loaded organic storage / coalescer before the wash stage.

The overall control of EW contaminants includes both a wash stage and an EW bleed flow. The total water use for these two flows is shown to go through an absolute minimum. The minimum flow rate is not greatly dependant on the total entrainment from the SX settlers. This can be a useful operating strategy if the quantity of high quality water for make up is limited by the capacity of the water treatment plant (eg RO). However the minimum cost option is to maximise the flow of water to the wash stage and minimise the EW bleed stream. The main driver for this is the cost of the cobalt sulphate contained in the electrolyte.

Some results from the latest circuit modifications at the Nifty and Girilambone Copper Projects are presented to confirm the benefits of using both coalescing systems and a wash stage. The EW bleed has been reduced to a level that is less than the entrainment loss internally in the SX stage to stage entrainment. There has been an occasional need to add chloride to the EW to maintain sufficient concentration to act as a growth modifier.
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INTRODUCTION

As part of the development process for the Nifty and Girilambone Copper Operations, alternatives have been considered for the increase in the SX plant capacity and operating
efficiency. In the Nifty case an increase in SX capability was required as was a concurrent reduction in the total loss of electrolyte to bleed. The EW chemistry was being controlled to limit the chloride rather than the iron; which resulted in large bleed volumes due to the low [chloride] target in the electrolyte. As part of an overall increase in the SX throughput alternate methods of total entrainment minimisation were needed.

Girilambone on the other hand needed to minimise the total entrainment and resultant electrolyte bleed to maximise current efficiency as well as minimise the bleed volume. A further aim was to minimise the cost of entrainment of organic in the plant raffinate. In this case the existing plant hardware was to be configured in the optimal arrangement. As the plant is in a run down to final closure, minimum cost was also an issue.

THE SX-EW PROCESS AND CONTAMINATION PROBLEMS

A brief description of the SX-EW process is relevant to understand the concepts and details considered in the circuit selection process. A solution containing copper (and some of most of the periodic table - PLS) is treated by solvent extraction to concentrate and purify the copper into an electrolyte for metal deposition by electrowinning.

As a result of the closed cycle nature of the processes there are three main flow loops:
- The PLS from heap leach to SX and return to heap leach
- The SX organic phase, which picks up copper in extraction, has the copper removed in stripping and is returned to the extraction stages.
- The electrolyte, which is enriched in SX, depleted in EW and returned to SX for further enrichment.

The only ‘sink’ for contaminants in the long term is the solution contained in the leached and de-commissioned ore. As such the concentration of all ions reaches equilibrium levels in the leach solution, which generally is at high concentration. Total sulphate for instance can reach 3M while iron is typically 0.2M to 0.5M.

With the high concentration of contaminants in the PLS it is no surprise that they are transferred through the SX process into the EW electrolyte. In EW there are various detrimental effects such as low current efficiency, poor deposition chemistry, generation of high Eh conditions that can degrade the SX organic etc. (Miller 1995). Ions of particular interest are iron, chloride and manganese. Iron (particularly ferric) is transferred chemically as well as physically to EW, while chloride and manganese are transferred by physical entrainment of aqueous PLS in the SX organic advancing to the strip stage.

The build up of contaminants is addressed in a number of ways:
- Minimisation of transfer to EW
- Bleed of electrolyte to PLS to provide a route to transfer the contaminating ions back to the leach cycle.

The cost of the bleed is considerable as it contains cobalt sulphate to reduce EW anode corrosion. As a result attention is given to the minimisation of the total ion transfer to provide low operating costs through minimisation of the EW bleed. Minimisation of transfer is accomplished in a number of ways to address both the physical and chemical transfer mechanisms.
• Physical transfer can arise from entrainment of aqueous in the organic phase, as both crud and unseparated emulsion.
• Crud can be minimised by altering of mixing continuity to produce a compacting variety that accumulates at the settler interface and can be removed by the plant operators (Readett and Miller 1995).

Entrainment can be addressed by improving the operation of the settler with improved feed and discharge geometry (Miller 2001, Giralco et al 1998) or by in-settler materials that promote emulsion separation and reduce circulating flow patterns (Miller et al 1996a, Miller 2001). Other reductions in stream entrainment are obtained with coalescing systems that are applied to the specific flow of interest such as loaded organic coalescing (Miller et al 1996b) and recovery of organic from raffinate streams. (Miller et al 1996a)

The chemical transfer mechanism is primarily related to iron, and chloride to a lesser extent. This is addressed by use of a wash stage (or often called scrub stage) to physically and chemically remove the iron (and chloride) from the loaded organic before it is stripped of the copper. The chemical process is undertaken with a dilute acid solution with some copper to replace the removed iron. Typically these two species are obtained from the EW electrolyte bleed. The wash stage also serves to provide a reduction in the physical entrainment by replacing the high concentration PLS with a lower concentration entrainment from the wash stage aqueous.

Selection of the entrainment control methods to be used, and the configurations in which they are placed, is a significant process decision that has not previously been published in any great detail. This decision can have a major impact on the ability of the plant to cope with process upset conditions and to minimise the operating cost incurred.

**SELECTION OF WASH STAGE POSITION IN THE CIRCUIT**

There has been a significant debate about the merits or otherwise of putting the wash stage before or after the loaded organic storage (and / or coalescing stage). The arguments have generally been centred on the philosophical considerations of the merits of one operating regime over the other. The major alternatives are:

- A wash stage alone
- A loaded organic coalescer alone (LOC)
- Both wash and LO coalescer in configuration E1 => LOC => wash
- Both wash and LO coalescer in configuration E1 => wash => LOC

The choice of either unit is one that can be based on the perceived need of the circuit. This could be a need to be tolerant of fluffy silica crud or one that needs to operate in organic continuity to create compacting interfacial crud. If organic continuity is needed then some method of controlling the resultant high aqueous entrainment in the organic is needed. This can be most efficiently done using some coalescing device; which does not need the costs of a separate mixer-settler unit nor of the wash water to operate it.

If the circuit need is to minimise ion transfer to the EW for control of high current efficiency (iron), corrosion (chloride) or Eh (manganese) then a wash stage is the appropriate choice. However if the objective is to minimise the total cost of the EW bleed, control the EW conditions and to be tolerant of a high silica PLS then a combination of the two unit
operations is appropriate. The question then to be addressed is the configuration that provides the most effective operation with the lowest process upset risk profile.

CIRCUIT MODELLING

The two possible circuits which incorporate both washing and loaded organic coalescing, were modelled under various entrainment assumptions. This allowed assessment of the merits or otherwise of the one circuit over the other. The results were used to make decisions regarding the potential cost / benefits of the circuit alternatives. Figure 1.0 shows typical results from the modelling under a number of entrainment levels.

The wash bleed in this particular model was selected at close to the minimum as discussed later. With typical entrainment of 500 ppm to 1000 ppm aqueous in the loaded organic there is little difference between the two circuits. However at high (2000 ppm) and extreme entrainments (25,000 ppm) there is a significant difference between the circuits. The E1 => LOC => WASH circuit transfers much less contamination to the electrolyte than the alternate configuration.

It is thought that the majority of large transfers of contamination to electrolyte occur during these ‘short’ term, extreme upset conditions (Miller 1995, Miller et al 1996a). Generally the incidence of high chloride in electrolyte can be correlated with an incident of poor phase separation or high crud production in the SX plant. From the point of view of minimising the risk of transfer of contaminants, the circuit selection is relatively straightforward. However other factors can indicate that the benefit of the lower risk is not sufficient to justify the costs of changing the configuration of an existing plant.

TOTAL CIRCUIT BLEED WATER VOLUMES

When considering the overall contamination control in the circuit there are two bleed flows. The most obvious is the EW bleed for direct control of electrolyte chemistry and the other is the wash stage bleed necessary to eliminate the ions removed in this process. The effective
EW bleed is the sum of the controlled bleed and the entrainment of electrolyte in the stripped organic entering the extraction section.

An analysis of the interaction between the individual and total bleed volumes was prepared to address the particular situation at Nifty where the total capacity of the reverse osmosis (RO) plant is limited. The objective was to identify if there was a minimum bleed volume and if it was also the minimum operating cost point. Figure 2.0 shows that for all levels of entrainment from E1 there is a minimum total bleed flow rate. This is true whether the circuit is E1=>LOC => WASH or E1=>WASH =>LOC. In both cases the minimum bleed flow is not very sensitive to changes in the E1 entrainment, nor to the circuit selected.

![Figure 2.0](image)

The cost of the bleed is made up of the cost of preparing the RO water and of the cobalt sulphate in the electrolyte. Figure 3.0 shows that the greater the wash bleed flow the lower is the total cost of the combined bleeds. This assumes that the acid and copper in the electrolyte bleed are not losses but are recovered in the process. Thus for any given process condition it is most economic to run the wash bleed flow up to the limit of the available water supply. Under these conditions the EW bleed will need to be balanced against the wash bleed to ensure that the wash chemistry maintains the necessary concentration of acid and copper for effective operation. For an electrolyte acid concentration of 180 g/L and a wash aqueous concentration of 10 g/L, the flow ratio of EW bleed to wash bleed can be as high as 18:1.
EXPERIENCE FROM NIFTY COPPER OPERATIONS

The Nifty Copper Operation has an existing Krebs SX plant configured as 2 series extract, one parallel extract, one wash stage and one strip stage. The wash stage is directly between E1s and the loaded organic tank, ie the non preferred configuration for the lowest risk of EW contamination. However due to constraints in the proposed shut down programme it was decided to leave the circuit configuration without change.

Another small SX plant consisting of two series extraction plus one strip has been integrated with the existing plant. This plant was sourced from the MIM pilot plant installed in 1989 (Miller and Readett 1992). The two loaded organic streams (one after washing and one directly from MIM E1) are combined and treated in a new loaded organic coalescer. The combined loaded organic is split between the two independent strip stages for production of two electrolytes which are re-combined for delivery to the EW. This circuit has been described and modelled in detail (Readett and Dudley 2001).

The proposed circuit was modelled to provide confidence that the combined effect of the PLS transfer to EW would be within the capability of the RO plant to cope with the wash and EW bleeds. The organic flow is split 2.2:1 between the old and new SX plants (with the old plant washing the loaded organic) and the total flow passes through the loaded organic coalescer. It was apparent that over 90% of the total resultant entrainment arose from the new plant, which relied only on the coalescer for removal. As a result attention was paid to the control of entrainment from this train to minimise the overall entrainment.

Modifications were made to the MIM plant to improve the settler performance. These included the provision of two additional picket fence distributors and filling the space between them with coalescing media. The settler performance had been historically poorer than design and methods of reducing the level of entrainment and the risk of extreme entrainment events were necessary. The option of sending both loaded organic streams to the single wash stage was rejected on the basis that the practical settler flow rate limit would be
exceeded by >50% at the historical O:A ratio required to ensure aqueous continuous operation.

Further modelling of the EW process indicated that the total chloride transfer would be less than the chloride “burn off” at the anode. This is around 1 ppm to 2 ppm (Readett, Miller and Holle 1996) and has been identified as a significant reduction in chloride load in the EW process. As a result it was predicted that the EW bleed control would change from chloride control to manganese control and that the bleed flow rate would be reduced substantially from the previous levels used. A summary of the performance of the coalescing system is provided in Figure 4.

Figure 4 highlights initially the improved performance achieved by similar modifications to the original Train (A) settlers. PLS flow to the settlers was increased and at the same time the entrainment was controlled within a tighter operating window, as evidenced by the EW chloride concentration.

The installation of the Train B and the coalescer allowed for a significant increase in flow but at the same time a significant improvement in entrainment control. Bleed rates from EW were decreased to 0.3 – 0.5m3/hr and were used to control manganese and at times chloride had to be added to electrolyte to maintain it within the required operating window of 24 ppm to 40 ppm.

**EXPERIENCE FROM GIRILAMBONE COPPER OPERATIONS**

In June 2000, the production of ore from the Girilambone pits ceased. Thereafter, the PLS copper content commenced a controlled decline, which impacted upon copper output, and also EW impurity transfer, particularly chloride and iron. The operation is presently undertaking a wind down phase to leach the remaining copper from the leach heaps. As a result there is a great deal of pressure on identifying the minimum operating cost regimes that will provide the greatest economic recovery of copper from the ore.
The plant has already been expanded with a fourth mixer-settler unit as part of the strategy to maximise copper production during changes in leach circuit chemistry (Miller, Readett and Hutchinson 1996b, Readett, Miller and Hutchinson 1996). A loaded organic coalescer was also retrofitted to overcome the effects of silica accumulation on the organic (Readett and Miller 1995, Miller, Readett and Hutchinson 1996a).

Coalescing media was installed into the settlers at GCC to assist with the coalescence of both phases from the mixer emulsion. This media consisted of a series of polypropylene fish net bags filled with short lengths of PVC pipe. As the mixer emulsion exits the settler feed launder, it passes through a conventional picket fence system. The emulsion flows through the coalescing media, which occupies approximately the first quarter of the settler length. The increase in settler flux was in the order of 50 to 60 percent above the operational limits at that time (up to 6m³/m²/hr settler flux rates were achieved) without adverse effects on the exit entrainment levels.

The predominant improvement in solvent extraction performance that was offered by the installation of the coalescing media was the reduction in entrainment at the discharge launder of the settler, both in the aqueous and organic phases. Typical entrainment values, before and after installation of coalescing media, are highlighted in Table 1 (Dudley and Readett 2000). Prior to the installation, typical aqueous entrainment values experienced in the organic phase were in excess of 1000ppm. At times, these were as great as 15000ppm, especially during the winter months when solution temperatures would drop to below 12°C (Dudley and Readett 2000). After the installation, and running at settler fluxes of 5-6m³/m²/hr, typical aqueous entrainment values were less than 120ppm. Again these values are affected by various other parameters, both physical and chemical. It is generally accepted that running deeper organic depths at the overflow launder end of the settler also helps to decrease the entrainment values.

<table>
<thead>
<tr>
<th>Settler Flux (m³/m²/Hr)</th>
<th>Settler</th>
<th>Organic in Aqueous (ppm)</th>
<th>Aqueous in Organic (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>E1</td>
<td>110</td>
<td>40</td>
<td>800</td>
</tr>
<tr>
<td>E2</td>
<td>180</td>
<td>50</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>E3</td>
<td>250</td>
<td>70</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>S1</td>
<td>140</td>
<td>25</td>
<td>250</td>
</tr>
<tr>
<td>E1</td>
<td>80</td>
<td>30</td>
<td>200</td>
</tr>
<tr>
<td>E2</td>
<td>120</td>
<td>40</td>
<td>500</td>
</tr>
<tr>
<td>E3</td>
<td>150</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>S1</td>
<td>100</td>
<td>15</td>
<td>80</td>
</tr>
</tbody>
</table>

Circuit modelling was conducted on integrated leaching, SX and EW operations to identify the likely operating scenarios during the production run down. In line with the results identified from the Nifty modelling a scenario that minimised EW electrolyte bleed would provide the minimum cost for this aspect. Similarly the minimum SX reagent concentration would provide the lowest cost from organic lost as entrainment in raffinate. There is also a significant amount of available pumping capacity in the leach area to provide a large ILS:PLS flow ratio for managing the PLS grade.
In pilot plant tests conducted on site, a number of extractant and circuit combinations were evaluated with the aim of minimising impurity transfer. The most effective solution was found to be a conversion of one of the extract stages to an organic wash/wash stage (Dudley et al 2002). This was implemented in February 2001. Figure 5 shows the circuit layout and Table 2 shows the operating parameters before and after the conversion.

**Figure 5.0 2P x 1W x 1S SX circuit**

![Flow diagram](image_url)

**Table 2. Operational Parameters of 2P x 1W x 1S SX Circuit.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>Cu Tenor (g/L)</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Flow (m³/Hr)</td>
<td>700 - 850</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Fe²⁺ / Fe³⁺</td>
<td>5.0 / 11.6</td>
</tr>
<tr>
<td>LIX 984N Conc. (%/v/v)</td>
<td>&gt;11.0</td>
</tr>
<tr>
<td>Flow (m³/Hr)</td>
<td>350 - 400</td>
</tr>
<tr>
<td>Transfer (kg Cu/Hr)</td>
<td>500</td>
</tr>
<tr>
<td>Cu:Fe Selectivity</td>
<td>&lt; 100:1</td>
</tr>
</tbody>
</table>

The circuit selected involved the following main elements:

- Configure the four mixer settler units as series extract + wash + single strip. This provides >92% extraction from all PLS grades with the minimum SX reagent concentration. Under this configuration the total iron transfer to EW will be minimised by max loading the organic as much as possible and removing the iron in the wash stage. The wash stage bleed volume is minimised to a level just sufficient to control chloride and manganese transfer to EW.
- Allow the iron in electrolyte to equilibrate at a level set by the entrainment loss from S1 to E2 plus that needed for wash stage acidification. Accept the lower current efficiency in EW as the cell voltages are low and the total EW kW/tonne is not significantly increased.
Configure the leaching irrigation and reticulation to allow 400 m³/h of PLS to the SX and up to 1200 m³/h of recirculated flow. The 3:1 ILS:PLS ratio allows “preg building” and management of the PLS grade.

The key to the decisions is the combined effectiveness of the in-settler coalescing and the loaded organic coalescer followed by a wash stage. The results of this plant configuration are shown in Table 3. The total amount of EW bleed has been limited to that needed for wash stage acidification. Total EW iron has risen to 8.5g/L but chloride has fallen to a point (<20ppm) where extra salt (NaCl) has been added to ensure the correct copper crystal growth orientation. Manganese and Eh have remained in controlled regions and have not proven to be an issue.

**TABLE 3. EW Conditions Before and After Circuit Changes.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Prior to Changes</th>
<th>Post Changes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range Ave</td>
<td>Range Ave</td>
</tr>
<tr>
<td>Acid to EW - tonnes per day</td>
<td>8-20 12</td>
<td>0-10 2.5</td>
</tr>
<tr>
<td>EW [Cl] - ppm</td>
<td>31-40 33</td>
<td>18-30 24</td>
</tr>
<tr>
<td>EW [Fe] - g/L</td>
<td>4.5-7.5 5.8</td>
<td>--- 8.5</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

The use of a wash stage in an SX circuit can provide maximum benefit when placed after the loaded organic storage and/or coalescing system. The circuit performance under good operating conditions is better than the alternate arrangement (with the wash stage before the loaded organic tanks). However under upset conditions the preferred circuit provides for a significantly lower transfer of PLS through into the electrolyte.

Use of a loaded organic coalescer provides significantly improved circuit performance in both reduction of entrainment and providing a robust mechanism for dealing with plant upset conditions. Operating results have shown major cost reductions when these units have been included in the process design.

When considerations of total water requirements for control of electrolyte contamination are made, it has been shown that there is a minimum total volume of bleed that can provide the control. This minimum is not particularly sensitive to the level of in-plant entrainment in the SX circuit. As such it provides a stable operating regime that has the benefit of being relatively self regulating under plant upset conditions. However the minimum total cost operating point is with the maximum water flow rate to the wash stage and the minimum electrolyte bleed volume.

The experience with two different plants with very different circuits has shown that the techniques used can be applied under very different circumstances. The economic benefits of combining coalescing with loaded organic washing are very robust.
ACKNOWLEDGMENTS

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REFERENCES


