RECENT EXPERIENCE WITH MANGANESE AND ITS EFFECTS ON COPPER SX-EW OPERATIONS

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ABSTRACT

The occurrence of significant concentrations of manganese in copper SX feed solutions is uncommon but not rare. The literature on its effects on industrial scale plants has however, been extremely sparse until the mid 1990’s. Codelco, Chuquicamata Division, has published a short discussion on manganese effects in their SX operation. Other North American operations have kept their experience in-house. Miller published an account of the experience at Girilambone in 1996. Current experience at many operations which have suffered severe manganese effects, has allowed a study of methods of control of the effects which attend an uncontrolled introduction of manganese into an SX-EW circuit.

Manganese has both direct and consequential effects on the operation of both the SX and EW circuits, as well as some other unit processes. These in turn generate further symptoms which can form positive feedback loops and can very quickly lead to catastrophic reductions in plant performance. Up to four levels of symptoms have been identified, along with combined effects from the presence of chloride and low operating temperatures.

Many of the uncontrolled manganese incidents have been the result of a primary issue with polymerisable silica in the PLS. This has caused the uncontrolled transfer of PLS into the electrolyte with all the subsequent effects previously identified.

Mechanisms for the treatment of symptoms and reduction of primary effects have been identified, along with rehabilitation strategies for the main process operations. These are reinforced by plant experience in implementing the strategies adopted. A number of case studies have been described. Changes have been made to the primary design paradigm approach for new SX plants. There is a greater emphasis on identification of potential problems and implementation of engineering contingency plans to address the issue should it arise.

KEY WORDS
Copper, Solvent extraction, Manganese, silica, Crud, Organic Degradation, Entrainment, Anode Corrosion, coalescing, cobalt.
INTRODUCTION

The incidence of SX-EW operational problems due to the presence of manganese has been poorly reported in the technical literature except very recently (1, 2, 3). The range of manganese induced problems has likewise had no coverage outside the paper by Miller (1). Anecdotal evidence of these problems has tended to become scarce as plant personnel transfer positions and the results of short term problems and solutions are submerged in the new "normal" operating conditions, Robinson (4) and Olafson (5).

Since the original Miller paper (1) a number of operations have had occurrences of manganese issues with various levels of process and production collapse. The primary initiating mechanisms are reasonably diverse and it is these that must be identified and addressed as part of the overall

OCCURRENCE OF MANGANESE PROBLEMS

The occurrence of manganese problems has tended to have been recognised only from a catastrophic degradation of the SX organic chemical and phase disengagement kinetics. As of 1994 only four operations have been reported as suffering significantly from the effects of the presence of manganese in the pregnant liquor solution (PLS). These were:

- Phelps Dodge - Tyrone (New Mexico)
- Phelps Dodge - Chino (New Mexico)
- Arimetico - Johnson Camp (Arizona)
- Codelco - Chuquicamata (Chile)

Of these only Codelco has published the results of their experience, Farias and Alvarez (1). In the North American operations mentioned, the manganese is present in the PLS and the electrolyte; but in these instances the present operating personnel did not appear to be aware of previous experience with manganese effects. Subsequent correspondence, Robinson (3), Olafson (4) with earlier operating personnel has shown the dire nature of these effects.

Chuquicamata recognised that manganese was present in the ore and the PLS but did not make design allowance for any adverse affects. The design criteria had been extensively tested through large scale column leaching and pilot SX/EW processes, which did not identify manganese as a particular process risk.

The severity of the problems suffered to date by the plants, have varied from years (Chuquicamata) to months (Tyrone, Arimetco and GCC). This is probably due to the transient nature of the problems.

MECHANISM OF MANGANESE PROBLEMS

Manganous ion Mn$^{2+}$ itself has no affect on the operation of the SX plant. Its presence in the
PLS merely serving to increase the total dissolved solids (TDS). Mn\(^{2+}\) however can be transferred into the electrolyte by aqueous entrainment in the loaded organic stream. Once in the electrolyte, the highly oxidative environment of the EW cells can oxidise the Mn\(^{2+}\) to higher oxidation states. This situation is particularly notable during the early weeks of plant operation, when no electrolyte bleed is being utilised, due to the low iron concentrations in both the PLS and, consequently, the electrolyte. This low iron concentration during early operation has a further consequence in accelerating the buildup of the manganese problem.

When sufficient ferrous ion is present with the manganese, it provides a pathway for the highly oxidised manganese to be reduced by oxidising the ferrous to the Ferric form.

The presence of high oxidation state manganese is visually noticeable in the tankhouse operation. The first indication is the deposition of black MnO\(_2\) solid precipitates inside the cells, on the mist elimination beads (and balls), plastic cathode edge sticks and the darkening of the anode surfaces. A second visible symptom is the colouration of the cell overflow electrolyte. This takes on a deep purple tint and is indicative of the permanganate ion MnO\(_4^-\). This ion is a very powerful oxidant and will react with organic molecules.

With the increasing oxidation of the manganese; and with increasing concentrations of manganese, the chemical reaction potential Eh of the electrolyte, also increases, from a normal level of 400 mV to as high as 900 mV. Under these circumstances the range, and rate of, reactions increase to an extent which causes problems with the reaction products e.g.:

- Chloride, Cl\(^-\), will react to form chlorine gas, Cl\(_2\) which is released into the cell house environment. (Farias et al (2) reports an increased reaction potential and rate for this which could lead to higher Cl\(_2\) levels than otherwise would be the case.)

- The SX reagent (organic) is oxidised and the reaction products accumulate in the organic phase.

- Increased corrosion of stainless steel components occurs which leads to mechanical failures.

**CONSEQUENT EFFECTS OF MANGANESE PROBLEMS**

**General**

Figure 1 shows the cascading effects of manganese once it reaches the electrolyte. There are a number of complex interactions and effects between the various symptoms induced by the manganese. As well a number of positive feedback loops exist, where various primary and secondary symptoms reinforce themselves leading to an accelerating deterioration in the process. These positive feedback loops are the underlying mechanism for the catastrophic process failures which have been experienced at plants subject to manganese incursion.

Two other factors also play a part in the symptoms seen in the plant. These are:
• Low PLS temperature, and
• "High" chloride in the PLS.

Both of these have been included in the flowsheet to show their direct and interactive effects with the manganese.

**Primary Effects of Manganese**

The primary effects of manganese in the electrolyte are caused by the high oxidation potential of Mn$^{7+}$ ions. These ions react with the organic phase in the SX plant giving reaction products which have the following effects:

• A reduction in the chemical reaction kinetics of the extractant.
• A reduction in the reagent capacity to react (chelate) with copper ion ie. reduced "carrying" capacity of the reagent.
• Interference with the surface tension characteristics of the organic phase, reducing the interfacial tension available for coalescence and for settling.
• Direct attack on the anode protective layer (oxidation product). This produces voluminous PbO and Pb(OH)$_2$ rather than PbO$_2$, which flakes off and does not adhere to the anode surface. i.e. accelerated corrosion of the anodes.
• Production of an amorphous MnO$_2$ precipitate in the electrolyte.
• Accelerated oxidation of chloride to chlorine gas in the EW cell and discharge of this gas into the atmosphere in the cell house.

Other than the accelerated anode corrosion, all of these primary manganese affects have follow-on consequential effects which appear in the plant operation. There sometimes may be a third or even fourth level effect as indicated in Figure 1.

**Subsequent Effects of Manganese**

*Reduced Chemical Kinetics*

The subsequent effect of a reduction in chemical kinetics is the loss of copper to raffinate due to decreased recovery by the reagent. Since the mixing time is constant, any decrease in reaction kinetics will give a decrease in recovery.

*Reduced Reagent Capacity*

Once again, the effect of reduced capacity of the reagent will be an increase in the raffinate copper concentration. This will be an interactive effect with the reduced kinetics and can lead to a dramatic reduction in the copper recovery through SX. Typically reductions from 90% to 70% recovery can occur.
Reduction in Surface Tension Characteristics

This effect has many subsequent effects. It also has many interactions with other factors. As a result of this greater complexity, the system dynamics need more detailed analysis than other effects. The degradation reduction of interfacial surface tension has the following effects:

- Increase in phase disengagement times.
- Decreased hydrophobicity of the organic phase.
- Decreased coalescing abilities of the organic phase.

Consequent to these secondary effects, tertiary symptoms that can appear in the plant are:

- Production of a stable "mixed phase" resulting in large stable dispersion bands in the settlers.
- Increased entrainment of aqueous in organic and organic in aqueous. These entrainments can reach extreme proportions, with organic streams carrying 15-20,000 ppm aqueous, from an organic continuous mixer (and vice versa).
- Difficulty in maintaining the required phase continuity in mixing, and a strong tendency to change continuity, especially in the extraction stages.
- Poor recovery of organic from the electrolyte when using process which rely on the hydrophobicity of the organic e.g air flotation. This in turn leads to organic burn on the cathodes and a reduction in the product quality. As well, the stainless steel blanks become difficult to strip, requiring buffing and/or pickling to remove the adhering copper layer.
- Increased loss of organic to raffinate.
- Increased crud production.
- Increased over carry of crud from E1 to the loaded organic tank, and hence to the strip mixer-settler.

Direct Anode Corrosion

The subsequent effect of the change in the anode corrosion product is an increase in product lead levels. This is due to occlusion of the flaky corrosion product in the growing cathode. These particles can also contribute to nodular growth of the cathodes.

Amorphous Precipitate Formation

The oxidation of Mn$^{2+}$ to Mn$^{4+}$ and precipitation as MnO$_2$ entails a nucleation process. As a result precipitates will preferentially form on surface irregularities or on colloidal particles. The latter will be predominantly, silica from the PLS. The result will be a macro non crystalline
structure of mixed MnO₂ and silica, which does not settle readily. This is dispersed throughout the electrolyte and causes nodular growth on the cathodes; as well as contributing to crud formation in the strip circuit. Because of their high specific surface, the particles are absorbed by the organic and serve to further decrease the hydrophobicity of this phase. This in turn will lead to a further reduction in the efficiency of removal of organic by flotation and of the coalescing processes.

Chloride Oxidation

Manganese serves to increase the Eh of the electrolyte to a level where chloride oxidation to chlorine gas is accelerated. This reaction releases the gas into the house cell atmosphere. The high concentration of chlorine in this area leads to redissolution as chlorine based acids and pitting attack of the 316L stainless steel blanks. The chlorine gas also reacts with the copper on the header bars and leads to high contact resistances. The pitting corrosion of the blanks can lead to stripping difficulties and a need to rehabilitate the blanks.

DIRECT MANGANESE CONTROL MEASURES

General

The direct manganese control measures are aimed at:

• Reducing the transfer of manganese into the electrolyte, and

• Providing chemical protection to maintain the manganese in the Mn²⁺ state.

These approaches give the least potential for manganese attack on the organic and on the anodes.

Reduction of Manganese Transfer into Electrolyte

General

These measures aim at reducing the entrainment of PLS into the loaded organic. As such they rely very heavily on the maintenance of good phase disengagement and surface tension characteristics of the organic. The target is to reduce the total manganese transfer to the electrolyte, to equal that lost in the iron control electrolyte bleed. This technique should not be used without also providing chemical inhibition of the manganese.

PLS entrainment is reduced by:

• promoting coalescence of the entrained aqueous

• Replacement of entrained aqueous (scrubbing or washing).

• Reduction in crud production and production of compact interfacial crud.

Coalescing
Promotion of coalescence is readily done within the settlers through further picket fences. The fences increase the stream velocity by 10:1 which results in impingement coalescence. Multiple fences promote flow splitting, mixing and remixing, which has the affect of further improving the coalescence performance. This technique has been successfully applied in many operations that have experienced slow settling and/or coalescence due to other reasons e.g. high viscosities caused by low temperature, or higher than design reagent concentration. In these cases the extra picket fences increased the bubble sizes to promote separation.

Some operations have substituted other media for the picket fences. These include FRP floor grating, coarse mesh netting "tennis nets" and fine mesh netting. Crud accumulation, especially on the finer nets, is a problem which is not apparent with picket fences.

The use of an inert medium has been practised at a number of uranium and copper installations, particularly on raffinate. The common material is glass "Raschig" rings. An alternative developed by Chuquicamata for the loaded organic is the use of high density polyethylene swarf, (Farias et al (2)). This has a high specific surface area, low volume, high void space and large voids to enable crud to be accommodated and readily backwashed. Other techniques have been developed by Miller (5).

**Washing of Loaded Organic**

This is a technique which has been most recently developed for control of chlorides in ISAPROCESS operations for copper EW circuits. It is a technique which, combined with chemical regeneration of the organic reagent, has been used in uranium circuits for many years. The basic concept is to wash the PLS entrained in the organic, with slightly acidified, high quality water in order to minimise the over carry of dissolved solids. This process is mandatory for operations having high chloride in the PLS and even more important for those operations using stainless cathodes. However, for those operations with low chloride in the PLS, a scrub stage is not readily justifiable for manganese control alone.

**Reduced Crud Production**

The effect of crud production, and the type of crud produced, on PLS entrainment in the loaded organic is discussed in great detail in the paper by Farias et al (2). In essence they recommend that the procedure least liable to process upset and total carry over of PLS to the strip section is:

- Run E1 organic continuous to reduce the crud make and ensure that it is a compacted crud. (Aqueous continuity produces more crud which does not compact as readily and carries over into the loaded organic thus entraining PLS.)
- Coalesce the aqueous from the loaded organic prior to pumping it to the strip mixer-settler.
- Be very scrupulous about keeping crud accumulation to a minimum, by daily removal and treatment.
This procedure was used successfully at the Girilambone Copper Company to help reduce and control crud production.

**Chemical Inhibition of Manganese**

*General*

The chemical inhibition of manganese is aimed primarily at reducing the Manganese to $\text{Mn}^{2+}$ and maintaining it in this condition. The two techniques used are:

- Provide a species of lower oxidation potential which will be oxidised by the manganese.
- Provide a species which reduces the manganese to $\text{Mn}^{2+}$.

The other factor to consider is that all chemical species in all the relevant oxidation states must be benign to the organic reagent.

*Provision of Lower Oxidation Potential Species*

The most readily available species is iron in the form of $\text{Fe}^{2+}$ as shown in equation (1).

$$\text{Mn}^{7+} + 5\text{Fe}^{2+} = 5\text{Fe}^{3+} + \text{Mn}^{2+}$$  (1)

In order to obtain low levels of Mn$^{7+}$ high levels of Fe$^{2+}$ (or total Fe) need to be maintained. In practice it has been found that a minimum of 8 or 10:1 is necessary to keep manganese effects under control. This is about twice the stoichiometric and mass ratios. It has also been found that a minimum of 1 g/l of total iron is necessary to prevent high Eh levels in the electrolyte.

The plant at Chuquicamata operates at approximately 0.4-0.5 g/l of total iron, (Farias et al (2)). This is done to maintain high current efficiencies in the cellhouse. Because of this low level of total iron, a very high solution Eh of 900 mV is generated (compared with 400 mV normally). The Eh is reduced by contacting the spent electrolyte with copper scrap in a reduction tower. This reduces the manganese to Mn$^{2+}$ and renders it benign to the organic.

The concentration of manganese in the electrolyte at which adverse effects occur, is dependant on the level of iron maintained. For an operation with 2 g/l iron, the maximum safe level of manganese is 200 ppm. For the Chuquicamata operation, the maximum safe level is 40 ppm of manganese.

*Use of Higher Oxidation Potential Species*

The permanganate ion is one of the strongest oxidants available. The choice of stronger oxidants is therefore quite limited. Further, these stronger oxidants enhance the risk of oxidation of the reagent rather than the manganese. The practical choices based on price and availability are reduced to:

- Sulphur dioxide
• Hydrogen peroxide

Peroxide, however, strongly attacks the reagent and is thus unsuitable.

SO₂ at low dosages is suitable. However, if there is any residual dissolved oxygen, then the SO₂ will react to produce hydrosulphurous acid, HOSO₃⁻; which is itself a strong oxidising agent. Some risk is thus attached to the use of SO₂. Except for the use of SO₂ at Girilambone to obtain a quick reduction of the permanganate inventory, no other use of this reagent has been documented by SX plant operators.

**CONTROL MEASURES FOR CONSEQUENT EFFECTS OF MANGANESE**

**General**

As described previously there are many consequent effects of manganese, which have positive interactions with each other. Once manganese has affected the plant operation it appears that there are residual adverse effects. Ongoing programmes of control/rehabilitation may be required to maintain acceptable operating conditions.

**Control Measures**

*Reduced Chemical Kinetics and Reagent Capacity*

Treatment of the degraded organic by contact with an acid activated montmorillonite clay has been developed by Henkel Corp, (6) and used by Magma San Manuel, Jenkins (7) to rehabilitate the circuit organic. Large scale clay treatment of the whole organic inventory has been practised by Girilambone Copper Company at Girilambone and by Western Mining Corporation at Nifty Copper Operations.

The clay treatment returns the reagent to "original" chemical condition, within the accuracy of measurement (+5%). There might well be a slight permanent reduction on the copper capacity of the reagent, which would not be measurable by the techniques used. Ongoing clay treatment of the organic is recommended as a normal operating procedure. San Manual treat a side stream of the organic to improve coalescence and phase separation, particularly during winter.

*Reduced Surface Tension Characteristics*

The main method of overcoming the reduced surface tension characteristics of the organic is to clay treat the organic. Multiple treatments may be necessary to restore the reagent to near original condition.

As noted above, there may be up to 1% of the organic not rehabilitated by the clay treatment. In a 16.5% solution this would correspond to 1650 ppm of degraded reagent in the organic phase. The degradation products are, in the main, polar molecules which will decrease the surface tension. This level of surface active agent is well above those generally used in mineral flotation where 200-300 ppm of surface active agents can completely alter the hydrophobic/hydrophilic nature of separation. Thus even ½% or 1% of degraded reagent will
have significant effects on coalescence and phase separation. It is for this reason that multiple treatments and slow recovery from the badly degraded condition are experienced. Experience with a fluorocarbon frother (FC100) in an air-sparged organic flotation column, has shown that 5 ppm of this surfactant will decrease the organic recovery to zero.

Further effects of the poor surface characteristics can be treated as they arise in the following ways:

*Production of Stable Mixed Phase in the Settlers*

Mechanical enhancement of coalescence can be done by adding extra picket fences, or other coalescing devices, into the settlers. These serve to split and re mix the flow and act as coalescers in the production of larger bubbles, which then separate faster, (Miller et al (5)).

*Increased Phase Entrainment*

This is a further, downstream, effect seen in the exit streams of the settler. Again, extra picket fences or other media will assist in coalescence and separation thus minimising the carryover. Other measures can be used to treat the symptom directly in the relevant process stream, such as for:

*Loaded Organic:*

The loaded organic can be treated by an extra coalescence step using a "deep bed" type coalescer. Such a unit has been developed by Chuquicamata in their own plant and has proved effective in reducing aqueous carryover from 15,000 ppm to 400 ppm, (Farias et al (2)). A similar unit, using different media and hydraulic flow patterns, has been developed by CMPS&F, (Miller et al (5)). This has been successfully implemented at both the Girilambone and Nifty operations with up to 98% removal of entrained aqueous from the loaded organic.

*Strong Electrolyte:*

The strong electrolyte can also be treated by a "deep bed" type coalescer (2). An 85-90% recovery of organic from the electrolyte has been achieved by this method.

*Difficulty in Maintaining Mixer Continuity*

The difficulty in maintaining mixer continuity is related to a number of factors including interphase entrainment, solids presence, air entrainment, O:A ratio, degree of degradation and crud presence. No direct control method is available except the O:A ratio. This may be varied within limits set by the volumetric throughput and control is limited to a small range of O:A. This is reinforced by Chuquicamata's operating technique of shutting down the plant when continuity of choice is lost in order to re-establish the proper operating regime, (2).

*Poor Recovery of Organic from Electrolyte*

Poor organic recovery from the electrolyte is seen as a reduction in the ability of surface tension
or coalescence processes to remove the entrained organic from the rich electrolyte. Conventional multimedia filters perform poorly and at reduced throughput compared to plants with undegraded organic. Processes which use air bubble attachment for organic removal are most prone to being adversely effected by the presence of polar molecules. The polar organic molecules are attracted to the aqueous phase. As such they concentrate at the organic bubble interface and reduce the surface tension. A monomolecular layer around the organic bubble is all that is required to adversely effect the bubble contact angles and the flotation response.

For a bubble of average size 4 microns, the concentration of polar molecules would be about 1000 ppm for complete encapsulation of the rest of the organic (based on a molecular length of 1 Armstrong unit)

Control measures available are therefore very limited, consisting of:

- Accepting low unit rates and recovery in multimedia filters.
- Reactivating the organic, by clay treatment.

Other processes are available for removing the unresponsive entrained organic from the electrolyte.

- Deep bed coalescence developed by Chuquicamata using a packed bed of polypropylene mesh about 4.0 m high, (Farias et al (2)).
- Filtering using media of ultra high specific surface area e.g.
  - cellulose fibre
  - diatomaceous earth.

These two filter media have been used to remove the organic from electrolyte at GCC, to good effect. The drawback to this technique is that the organic removed is not recovered for re-use in the process. This is a significant cost penalty and may justify alternative processes which recover organic in a form suitable for reuse after clay treatment.

*Increased Loss of Organic to Raffinate*

Once the organic leaves the final extract settler in the raffinate, only a post settler will recover it. This could take the form of a separate process pond, or vessel, or suitably baffled raffinate pond.

A number of operations have raffinate after settlers, E1 Teniente, Chuquicamata and Olympic Dam (both subsequently modified to scrub stages). These, however, have been reported to be of little benefit with degraded organic. Far more widespread is the use of the raffinate pond to recover organic. The settling time of 8-24 hours is 15 to 50 times longer than available in conventionally sized after settlers. Recovery from the pond needs a floating skimmer and decant system to remove excess raffinate from the recovered organic. This organic must be clay treated before it's return to the circuit; as it has been further degraded by the combined action of both
UV radiation and atmospheric oxygen.

**Increased Crud Production**

When operating the SX mixers in aqueous continuity, increased quantities of light fluffy crud will be produced due to the lower surface tension of degraded organic and the amorphous Mn/SiO$_2$ precipitate from the electrolyte. As well, clay from the organic treatment process can escape and concentrate in the strip stages producing further crud. In the extreme, the presence of large amounts of fluffy crud can lead to major entrainment. Once the settler is full of crud, the phase residence times are dramatically reduced. In these situations entrainments are minimised by operating with organic continuity in all mixer stages. This technique is practised at Chuquicamata, MIM and at Olympic Dam.

Control consists in removing, as far as possible, the factors leading to crud production:

- Where possible operate mixers in organic continuity to produce compacted crud.
- Reduce PLS solids content (this was important in stabilising the operation at Chuquicamata)
- Reduce air entrainment
- Reduce clay escape from the organic treatment process
- Reduce amorphous precipitate formation by minimising the Manganese and silica content of the electrolyte.

**Increased Crud Carryover to Loaded Organic**

Operation of the E1 mixers in organic continuity will produce a compacted crud which will settle at the interface. The fluffy crud produced by aqueous continuous operation has a tendency to overflow the organic weir and entrain large quantities of aqueous. Control strategies revolve around:

- Reduction in fluffy crud production.
- Use of a loaded organic coalescer to trap and remove the crud from the loaded organic before transfer to the strip mixer settler.

**Direct Anode Corrosion**

With the accelerated anode corrosion, and the altered morphology, more lead oxide flakes are released into the electrolyte. These co-deposit and contaminate the cathode. Two control measures are practised to help reduce this effect:

- More regular cleaning of cells and descaling of the anodes.
- Use of a Guartec (flocculating agent) to settle fine particulates to the base of the cells.
Elimination of fine suspended solids reduces the nodular growth of the cathodes.

The anode corrosion is inhibited by the addition of cobalt sulphate. It also keeps the lead oxide in the correct morphology. Under manganese conditions higher levels of cobalt sulphate are required to minimise the manganese attack. Up to 200 ppm Co has been used, with 150-170 ppm the norm in plants with manganese under control.

*Amorphous Precipitate Formation*

These semi-colloidal precipitates contribute to nodular growth on the cathodes and to crud formation; particularly in the strip stage(s). Again use of Guartec has a three-pronged effect by:

- Removing precipitates as flocs.
- Reducing nodular growth caused by the solid particles settling on the cathode,
- Reduction in crud formation by removal of particulates.

**DISCUSSION OF GIRILAMBONE SITUATION DEVELOPMENT**

**General**

The development of the manganese problem at Girilambone occurred quickly. By the time the problem was properly recognised a catastrophic situation had developed which entailed:

- Loss of kinetics and capacity of the organic reagent
- Extreme raffinate copper levels
- "Mixed phase" filling E2 settler
- Long breaktimes in both field and laboratory testing
- 10-15 000 ppm entrainment leaving all stages
- Minimal recovery of organic by the flotation columns
- Extremely poor product quality in scavenger EW cells
- Deteriorating product quality in commercial EW cells
- Deep layers of organic in scavenger cells
- Black discolouration of mist suppressing beads, cathode edge sticks and EW cells.
- Presence of colloidal solids in circulating electrolyte streams
- Nodular growth on cathodes
• High organic loss to raffinate
• Electrolyte loss to E2 via entrainment in stripped organic
• Very sticky cathodes in scavenger EW cells
• Increasingly sticky cathodes in commercial cells
• Copper chloride formation on copper hanger bars
• Purple colouration of the spent electrolyte

All the entrainment losses increased as the plant operation entered winter and the PLS temperature dropped.

Rehabilitation Programme

The rehabilitation programme started with the identification of clay treatment of the organic as being required to recover the activity and reagent capacity. Initial treatment was by means of mixing in the crud tank, settling, and decanting treated organic back into the circuit. This method suffered from the following problems:

• Not all clay was removed by settlement, and clay returned to the circuit substantially increased crud production.
• An accumulation of clay-organic mixtures that had no available treatment.
• Very slow batch rates of 24-36 hours per 15-20 m³ of treated organic.
• Short time of improved operation. A batch of treated organic, when returned to the circuit, would provide a period of 6-18 hours of improved phase separation, before the circuit reverted back to poor operation.

The initial moves to control the electrolyte permanganate levels were also taken during this period.

• The electrolyte was dosed with ferrous sulphate to a level of 1 g/l of Fe^{2+}. This began to reduce the permanganate levels slowly. SO₂ injection into the spent electrolyte tank was sufficient to remove the bulk of the permanganate in 2-3 days.

• Continuing addition of ferrous sulphate was required to maintain the Fe^{2+} levels due to high losses of electrolyte to E-2. These losses were reduced by installation of "tennis nets" across the strip settler. Five nets were finally installed in an effort to improve the coalescence and to reduce entrainment. Further nets were installed in E1 and E2 to attempt to reduce entrainments from these settlers as well. These "tennis nets" eventually became ineffective as the fine mesh became blocked with crud.
Major advances in organic rehabilitation were made with the commissioning of a plate and frame pressure filter for filtering of the organic, after clay treatment. This gave a much reduced batch time and allowed the individual batch gains to be built upon before the reduction in performance became irreversible. Noticeable improvements in SX physical performance were evident after a short period of operation. Overall the organic inventory has been treated about 5 times to recover SX operation to an acceptable level. This is the first time that such a process has been applied on such a large scale and to have treated the entire inventory.

The cellhouse operation had deteriorated with the scavenger cell product becoming extremely porous and all cathodes showing signs of becoming sticky. A programme of pickling cathodes was undertaken when only 2/3 of the cathodes installed were in use. However this was discontinued when production increases required the use of the full cathode inventory. At this time a programme of mechanical buffing of the cathodes was initiated.

All of the tankhouse effects were the result of high levels of organic in the electrolyte. Clay treatment of the organic had not improved the operation of the two air bubble organic flotation columns. As a result generally about 90% of organic entrained in the electrolyte was advancing to the cellhouse. Resolution of this situation is covered by Readett (8) and Miller et al (5).

Ongoing Operation

At this point the plant operation had recovered sufficiently to enable "normal" production and other work to continue eg

- Measurement of electrolyte Eh showed no signs of excessive levels and cobalt levels were lowered to 150 ppm.
- EW cell cleanout began with removal of accumulated dust, precipitate and anode flakes.
- Cathode buffing was discontinued.

CONCLUSIONS

A number of SX-EW plants have suffered a catastrophic collapse of the process circuit due to degradation of the SX reagent by permanganate attack. The consequent effects of this attack are the appearance of many interacting symptoms, some giving feedback loops which accelerated the decline in plant performance.

The cause of this situation is the presence of manganese in the PLS and its carry over into the electrolyte. Production of permanganate creates an oxidant which denatures the SX reagent, causing chemical and physical problems in the plant.

The effects of manganese can be seen at low concentrations in the electrolyte, if insufficient iron is present. For operations having manganese in the PLS; during commissioning the electrolyte should be loaded with iron to 1g/l, to protect the SX regent from permanganate attack.

Regeneration of the organic reagent by clay treatment restores the chemical activity to previous
levels. The physical problems have improved but have not returned to previous levels of performance.

RECOMMENDATIONS

The following recommendations were made to enable long term stable operation of the GCC SX plant. They were aimed at achieving reliability of process flow and cathode quality. Implementation and maintenance of the full range of hardware and procedures generated a pro-active response mode which served to minimise any process upsets.

• Maintain Fe:Mn ratios in electrolyte above 10:1 with a minimum of 1 g/l Fe.
• Operate the EW bleed to obtain an electrolyte having minimum manganese.
• Maintain low chloride levels in EW make up water.
• Continuous clay treatment of organic:
  - intensively in the short term to improve break times
  - less intensively in the longer term to maintain the improved break times.
• Install coalescing systems in settlers to improve coalescence.
• Install coalescing medium in No.1 loaded organic tank to remove entrained aqueous. Miller et al (5).
• Continuously monitor:
  - spent electrolyte Eh
  - circuit organic break times
• Maintain cobalt levels to 150 ppm or above.
• Remove crud regularly from settlers.
• Operate all extract mixers organic continuous. Readett (8)
• Increase settler organic depths to minimise interphase shear effects.

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