

The link between operational practice and maximising the life of stainless steel electrodes in electrowinning and electrorefining applications

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ABSTRACT

The use of a permanent stainless steel cathode plate in both electrowinning and electrorefining applications has long been accepted as a proven technology for cathode copper production. Mount Isa Mines Limited is the original inventor of this technology and experience has shown these cathodes can have a life of more than fifteen years in electrorefining and ten years in electrowinning.

Correct management of the operating system and attention to detail will ensure the life of the electrode in both applications. Chloride levels in electrolyte, current density, the use of shorting frames, current distribution, harvesting patterns, and cathode-plating cycles all affect cathode plate life.

The aim of this paper is to discuss common problems encountered with electrode management, with a particular focus on electrowinning plants. Proven practical control measures, possible management solutions and operating parameters that extend the cathode operating life will be discussed. These recommendations are based on test work conducted by the ISA PROCESSTM, operating experience and knowledge gained through cooperation with licensees.

INTRODUCTION

The introduction of the permanent stainless steel cathode plate in 1978 was a revolutionary development in the copper industry. This occurred in 1978 when Mount Isa Mines (MIM) undertook a complete modernisation from starter sheet to permanent cathode technology in their Townsville Copper Refinery.

The ISA PROCESSTM Technology is based upon a superior cathode plate design and cathode-stripping machine. The ISA cathode plate consists of a stainless steel hanger bar that is stitch welded to a stainless steel blade. The hanger bar and part of the blade are then electroplated with copper to provide maximum electrical conductivity and corrosion resistance.

Currently ISA PROCESSTM has fifty-six licensees, of which thirty-five are electrowinning plants and twenty-one are electrorefining plants. Approximately 33% of the world's copper production is produced using the ISA PROCESSTM. The ISA cathode plate has applications in both electrowinning (EW) and electrorefining (ER) applications. Cathode plate longevity is directly related to operating conditions.

Operators of both electrowinning and electrorefining plants are facing similar challenges, including:

- Achieving and maintaining target copper production levels.
- Ensuring chemical and physical cathode copper quality.
- Ensuring a safe working environment for all employees.

The operational methodology to achieve these goals can at times be detrimental to the long-term service life of the cathode plate.

THE STAINLESS STEEL PERMANENT CATHODE PLATE

The latest ISA PROCESSTM cathode plate design is the ISA Cathode BRTM and is the lowest resistance cathode plate available in the market. The ISA Cathode BRTM is based on the proven ISA design. The copper coating is thicker to provide greater corrosion resistance and the plating has been extended to the base of the lifting windows to significantly reduce electrical resistance. These improvements will provide a greater service life, but only good management practice will ensure the extended operating life of the permanent cathode plates.

LIFE EXPECTANCY OF THE ISA PROCESS™ CATHODE PLATE

The ISA PROCESS™ is based on the premise that stainless steel cathode plates are a capital item not a consumable. Cell house management in both electrowinning and electrorefining will influence the effective life of this capital investment. It has been proven that ISA PROCESS™ cathodes will perform without significant repair, for greater than ten years in electrowinning and in excess of fifteen years under electrorefining conditions.

Cathode plate life may be defined as the operating period in which the cathode plate will produce LME grade A copper at high operational efficiency. The integrity of the cathode plate assembly must be maintained. This requires attention to plate straightness, verticality, integrity of the welded joints, condition of the copper coating, stripability and overall electrical performance.

The life expectancy of the standard ISA PROCESS™ plate in electrorefining is currently beyond fifteen years in well-managed refineries. These plants do not commit to major cathode repairs except through unusual misadventure.

This is not the case in electrowinning plants because the ability to maintain a stable, ongoing production regime within the cell house is often compromised. The solvent extraction plant, heap leaching operation and in some cases the mining operations have a significant impact of the ability to operate the electrowinning plant. Subsequently the condition of the cathode plate can be compromised. The life expectancy of an ISA PROCESS™ cathode plate is up to ten years without repair compared to less than three with other cathode types.

EXTERNAL FACTORS INFLUENCING ELECTROWINNING OPERATIONS

Mining, leaching and solvent extraction processes can have overflow effects on the electrowinning operations that are not within the direct control of the EW operators. These effects can be transient, whilst others may be longer term and site specific. Failure to react promptly to such occurrences can impact on cell house operations, which may affect the integrity of the cathode plates.

Mining operations

The impact of variable mineralogy and ore grades is well recognised. Experience at Girilambone Copper Company in NSW showed that a change in crushing, stacking and heap leach irrigation methods was necessary to optimise recovery from lower grade ores with the changing ore types (Dudley, Bos & Readett, 3).

Variability of gangue minerals in heap leaching operations can be just as significant. Gangue materials may contain higher silicates, a larger percentage of fines or produce more fines in crushing (due to lower mechanical strength), higher chlorides and iron minerals (for example pyrite). These characteristics may result in:

- Reduced recovery rates and overall recovery, resulting from lower heap permeability.
- Lower heap permeability can also lead to leach solution ponding, wash outs resulting in higher suspended solids in the PLS.
- High chloride and iron levels in the PLS.

These changes can affect crud build up and impurity transfer (Cl, Mn & ferrous) to the cell house. Elevated chlorides in the cell house will increase the potential for corrosion of the cathode plate and high iron transfer will reduce the current efficiency.

Heap leaching operations

Management of the heap leaching operations is crucial in maintaining the quantity and quality of the PLS solution being delivered to the solvent extraction plant. The composition of soluble salts (other than copper) in the PLS can vary and is generally site specific. The heap leach system can be used to "filter" out many of the unwanted suspended solids in the leach solution prior to the solvent extraction plant.

Close monitoring of the heap leach system to reduce the amount of solids entering the SX plant and achieve the desired recovery rates is required. Below are general areas which require attention to achieve these targets:

- Irrigation methods - wobbler versus dripper irrigation for temperature control and recovery.
- Application rates should match heap permeability in order to reduce the occurrence of ponding and the likelihood of wash outs.
- Heap maintenance to detect quickly any problems with application rates, line failures, washouts.

Suspended solids and low copper grades in the PLS increase the difficulty of the solvent extraction operation. Suspended solids generally result in crud formation, increasing the phase break times and ultimately lead to higher entrainment levels passing through to the cell house.

Solvent extraction plant

The copper grade of the PLS can be utilised to maintain production, reduce iron transfer, organic losses, crud build up and the loads on the electrolyte filters. High copper grades in the PLS combined with low extraction rates (provided production targets are achieved) will:

- Allow lower PLS flow rates - resulting in reduced aqueous and organic entrainment due to more effective phase disengagement.
- Minimise ferric iron transfer, therefore maximising current efficiency.

- Result in longer residence times in PLS, ILS ponds which reduces suspended solids and therefore crud formation.

Crud formation can lead to increased aqueous entrainment. This can result in increased chloride levels in the electrolyte feeding the tankhouse which at elevated levels can lead to pitting corrosion of the stainless steel blade.

Increased sulphuric acid concentrations and high levels of organic entrainment in the electrolyte can be detrimental to the cathode plate, resulting in increased levels of corrosion. Higher primary flow rates can lead to larger organic losses to both the raffinate stream and to the strong electrolyte phase also increasing the likelihood of corrosion. In plants that are operated at high extraction efficiencies with low copper PLS grades, ferric iron transfer can become a significant operational problem for the electrowinning plant

SOME PROBLEMS EXPERIENCED IN ELECTROWINNING PLANTS

Repair of mechanical damage to the cathode plate is a common problem for both electrowinning and refining operator's. Problems in EW plants tend to be more severe than those of an ER plant and as a result their cathode plates generally last longer.

Problems experienced in some operations include corrosion of the stainless steel blade, corrosion of the copper coating on the hanger bar, corrosion of brazed copper to stainless joints, solution line corrosion and maintaining plate geometry.

Corrosion of copper plating and brazed copper to steel joints

Experience and plant data indicates that two of the most common problems experienced in electrowinning plants are:

- Corrosion of the brazed joints of solid copper hanger bar system
- Corrosion of the copper of the hanger bars

It is common to experience failure of the braze between the solid copper hanger bar and the plate after a relatively short time (as illustrated in Figure 1). When the hanger bar is bent and cracking of the braze occurs, crevice corrosion is accelerated through the crack. The braze material becomes anodic and corrodes, where rapid failure is possible.

The rate of corrosion of this type will be dependent upon weld quality and material choice. Corrosion of this joint results in higher resistances and poor cathode efficiency. Re-brazing of the solid copper hanger bar to the blade will repair this poor performance and prevent ultimate failure of this joint. ISA PROCESSTM cathodes are not subjected to this type of failure.

Plate is
beginning to
detach from the
hanger bar

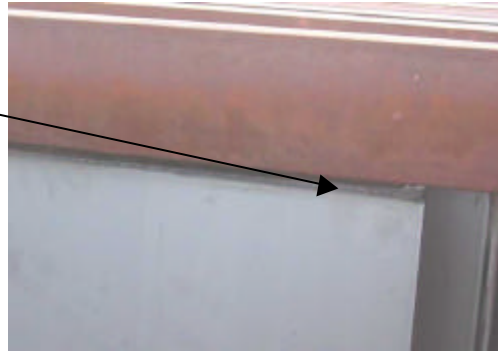


Figure 1: Corrosion of brazed joint between solid Cu bar and stainless steel plate

In some environments ISA cathodes may experience corrosion of the copper coating. This can be accelerated if the coating has been mechanically damaged in some way. The corrosion mechanism is galvanic. Often incorrect use of shorting frames can initiate this type of corrosion. This is illustrated in Figure 2 where the shorting frame has damaged the hanger bar and corrosion of the copper coating has resulted.

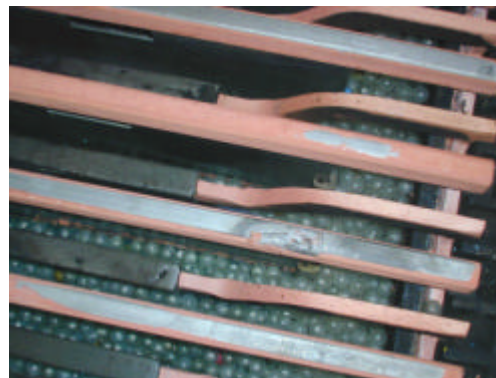


Figure 2: Corrosion of copper coating after 7 years operation

Galvanic corrosion

A review of the mechanism of galvanic corrosion, illustrates that it will occur when two dissimilar metals are connected in an electric circuit and immersed in electrolyte (Hayes, 4). The point at which the two dissimilar metals are joined is generally where the corrosion will occur first. Copper is more reactive and will act as an anode compared to the passive 316 stainless steel will take the part of the cathode (Craig and Pohlman, 2).

Corrosion of the stainless steel blades

The superior corrosion resistance of stainless steel is a result of the formation of a thin passive layer on the surface of the cathode plate. This passive layer mainly comprises of chromium oxide. If this layer is damaged and unable to rebuild itself, corrosion will occur in the unprotected areas (Hayes, 4). Great effort is then required to remove copper from corroded blades often resulting in damage to the cathode plate. Following copper removal, cathode plates are re-straightened and buffed to restore a useable surface. Figure 3 illustrates surface corrosion of the stainless steel blade.

316 stainless steel is corrosion resistant within a range of electrolyte conditions. Temperature, acid concentration and chloride levels are the key factors when considering the corrosion resistance of 316 stainless steel.



Figure 3: Surface corrosion of the cathode mother plate

Pitting and crevice corrosion

Pitting and crevice corrosion are a type of localised corrosion, where there has been a localised breakdown of the passive film. Pits are formed that are very small in comparison with the overall surface, and subsequently corrode very quickly (Aspahani & Silence, 1). Once the localised breakdown of the protective film occurs an electrolytic cell is effectively created. The anode is the pit (small area) and the surrounding larger protected surface acts as the cathode. As the corrosion continues down the pit it is less likely that the surface in the pit is able to re-passivate.

Pitting corrosion is common in neutral and acid solutions that contain chlorides (and bromides). The chloride ions facilitate the pits by breaking down the passive film in localised areas, this is particularly so in the presence of surface imperfections. These imperfections could include such things as suspended solids, sulphides and micro crevice imperfections (Hayes, 2001).

Crevice corrosion occurs under the same conditions as pitting corrosion but only requires a small crevice for corrosion to be initiated. This is because capillary forces apply, and solution is drawn into the crevice creating an environment with stagnant solution. The supply of oxygen to the surface of the plate is restricted and the passive oxide layer is not replenished and corrosion continues to occur.

Low pH's, high chlorides, high temperatures and stagnant solutions are conducive to pitting and crevice corrosion.

Solution line corrosion

Solution line corrosion is often characterised by pits above and around the solution line (illustrated in figure 4). Pitting may be due to chlorides and organic transferred from the SX plant. It may also be due to incorrect addition of chlorides for reagent purposes, further exaggerated by the presence of organic residue in the electrolyte.

Unnecessary buffing of the entire cathode plate to overcome this 'tightness' is frequently undertaken. This practice can accelerate the surface corrosion and may result in 'prestripping' of the newly buffed plates.



Figure 4: Solution line corrosion

Pre-stripping of the copper cathode

The ISA PROCESSTM cathodes have a surface finish that will allow for the necessary mechanical handling of the cathodes without pre-stripping. It will also enable the easy separation of the copper in the cathode-stripping machine that has been specifically designed for that purpose.

When cathode plates are buffed excessively, pre-stripping may occur. ISA PROCESS™ recommends a standard surface finish for refurbished blades, which is different to that of a brand new plate. The tendency to polish the plate to a 'mirror like' surface must be avoided. It should be noted that cathodes up to 110kg per side are routinely produced in ISA PROCESS™ plants without any pre-stripping problems.

Difficult to strip copper - "sticky copper"

At times it is difficult to strip the copper successfully from the cathode mother plate. This can be due to pitting corrosion of the blade or thin copper deposits. ISA PROCESS™ recommends an average copper cathode weight in excess of 40kg to ensure easy stripping. Without sufficient weight and thickness it may be extremely difficult to flex the copper from the plate. The copper tends to simply bend and flex with the stainless steel plate.

Sticky cathodes are often removed by manual or more aggressive mechanical means. These techniques can result in dents, bends and severe scratching of the blades. All of which will affect the plate verticality and future corrosion resistance.

INTERNAL CELLHOUSE OPERATING PARAMETERS

Within the cell house there are opportunities for operational choices that can extend the service life of the cathode plate. Where possible these practices should be employed. Those that result from limitations of the original design need to be compensated for where practical.

Harvesting sequences in electrowinning operations - current density

The operating current density at the time of copper initiation and nucleation has a significant effect on the copper quality and stripability. The chosen harvesting cycle will determine the initiation current density. There are two types of live harvesting sequences commonly employed in electrowinning:

- Harvesting the cells by lifting every third cathode
- Harvesting the cells in blocks of cathodes in thirds

Harvesting by lifting every third cathode

This harvesting sequence ensures that current is maintained through each anode and the subsequent current density of the cathode plates is not excessively high. Cathode currents in adjacent cells are virtually unaffected, anode currents are maintained, easy access for above cell inspection and wash down of cathodes and contacts. The results of which is a much higher cathode quality and the life of the lead anode is prolonged by a more steady and constant method of operation.

Harvesting in one third blocks

The difference lies within the current distribution of the anodes. In effect every time that one third of the cathodes are removed from the cell for stripping, that block of anodes is effectively turned off. Consequently the anodes are frequently cycled which can lead to premature spalling of the anode. This will result in reduced anode life and a greater potential for lead contamination in the cathode copper. Once lead contamination of the cathode is detected the logical step is to remove the lead from the bottom of the cells or clean individual anodes. To remove lead from the cells a shorting frame is required which leads to further anode cycling.

This method utilises a smaller crane bale and enables a shorter inlet and outlet conveyor. Loading and unloading of electrodes into the cell is simplified, resulting in a more rapid turnaround of electrodes through the cell house.

Stripping cycles

The initiation current density on bare stainless steel is extremely important when choosing stripping schedules. At high current densities in excess of the normal operating range it is possible to form nascent hydrogen. This occurs when the limiting current density for cupric ions has been exceeded. This highly reactive form of hydrogen can react with the chromium oxide film that protects the stainless steel. Once this occurs corrosion of the plate is possible, resulting in "sticky" cathodes.

If one entire cell load of cathodes is stripped one after the other in blocks, bare stainless steel is exposed to much higher current densities. It is preferable to strip one group (every third cathode) moving around the cell house, then stripping the next group the following day and so on. With this approach no bare stainless steel is exposed to the higher current densities while one group is out of the cell being stripped. In this situation if the limiting current density for cupric is exceeded and nascent hydrogen is formed, the stainless steel blade cannot be corroded because it will already have a skin of copper over it. It may be possible that the copper will be slightly corroded and perhaps result in a rougher copper deposit.

The harvesting method and stripping sequence determine the initiation current density. At lower current densities corrosion of the stainless steel blade is unlikely and the possibility of rough copper deposits is reduced.

Use of shorting frames

Shorting frames are commonly used in electrowinning operations, to take cells off line for lead scale removal and anode cleaning. The correct choice, design and proper use of the shorting frame is important in avoiding damage to the cathode plate's hanger bar.

Uniform current distribution is critical during the operation of a shorting frame. Significant damage can result from uneven current distribution resulting in elevated temperatures and melting of the bar at the point of contact. Subsequently, penetration of the copper coating will accelerate the corrosion and this is illustrated in figure 5. Extreme temperatures may also soften and weaken the braze of the solid copper hanger bar systems, making them susceptible to corrosion attack at the joint.

Certain types of shorting frames are able to compensate for variation in cathode type where the bars do not sit at the same height and should be used.



Figure 5 Damage caused to hanger bar from incorrect use of shorting frame

Frequent use of shorting frames increases the rate of anode cycling, the likelihood of lead contamination of the copper cathode and damage to the hanger bar.

Choice of acid mist control systems

There are various types of acid mist suppression systems employed by EW operators throughout the world. These include, cell covers, ventilation systems, mist suppressant reagents, bb's and balls and hoods. Associated with each of these are elements that can cause some damage to the cathode mother plate in the form of corrosion. The extent of these problems will be dependent on the specific management practices within the cell house.

Cell covers tend to limit the operation of the cell house by dictating harvesting sequencing due to the necessary removal and placement of the cell cover/hoods. The longer cathodes are out of the cell means the remaining cathodes are subjected to higher current densities for extended periods. This can result in corrosion of the stainless steel and rough copper deposits.

The use of Bb's or balls in scavenger cells requires constant cleaning to remove organic carryover. Failure to do so may result in corrosion of the stainless steel at the solution line. Organic carryover can result in an increase in acid concentration, copper depleted solution in this region that is conducive to corrosion. A thick layer of bb's/balls in the presence of high chlorides can also result in solution line corrosion.

Cathode plate maintenance

Plate straightness and verticality is of utmost importance in maintaining uniform current distribution and efficiency. A cathode plate that is not hanging vertical will result in uneven current distribution, which can lead to further problems with short-circuiting and cathode quality. Significant damage to the plates can occur if these are not straightened correctly.

Surface finish is the key factor affecting stripping performance. The initial 2B finish provides sufficient adhesion so that the cathode can be transported safely throughout the tankhouse but easily stripped by ISA PROCESSTM cathode stripping machines. Only when the copper is proving to be too difficult to strip by the normal means, should buffing of the plates to restore the surface condition be considered. As a general rule it is said that plates which do not machine strip, but are able to be hand stripped do not require surface conditioning.

The reason some plates do not machine strip is due to thin copper deposits rather than poor surface condition. In the case of thin deposits, rather than the copper flexing (shearing) off the cathode plate the copper moves with the stainless steel blade. Aging anodes, poorly maintained electrode geometry, poor current distribution and high current densities all contribute to poor physical quality cathode and may necessitate early cathode stripping.

The correct refurbishment methods are crucial. Buffing should be conducted with the appropriate buffing media, fitted to the correct machines and operated at the recommended speeds for which the media was designed. Only those areas that have a damaged surface should be buffed.

Over polishing can often result in pre-stripping of electrodes, creating a serious safety concern in the tankhouse and repercussions in current distribution. If buffing is conducted at machine speeds that are too high there is a tendency to scratch the plate. This can lead to crevice corrosion of the stainless steel blade.

Copper deposit quality

As current density and anode age increases the ability to maintain even current densities is compromised. Poor current distribution can lead rough copper deposits, increasing the probability of lead contamination and the formation of direct shorts.

Direct shorts will result in anode distortion and increase spalling of the lead anode. Subsequently, lead contamination in the cathode will increase. To overcome this problem, operators may choose to produce lighter cathodes.

Light cathodes are not as easily stripped and subsequently stripping performance may deteriorate. This deterioration may result in the perception that the plates require buffing. The amount of cathode buffing increases, which can then result in pre-stripping.

MACHINE AND DESIGN CONSIDERATIONS FOR EW PLANTS

Machine reliability, crane cycles and stripping cycle times are crucial to the successful operation of a cell house and maintaining the integrity of the stainless steel cathodes. It is important that all of the equipment operates in sequence with one another, so that one piece of element does not delay the entire process. Cell turnaround requirements and work scheduling ultimately dictates the machine capacity in the design for a new EW plant.

The crane must provide a continuous supply of cathodes to the stripping machine so that it can operate at design capacity. If the crane is unable to keep up with the stripping machines, cathodes will spend longer out of the cells than necessary. Cycle times need to compliment one another to ensure this does not occur and that cathodes have adequate time in the wash chamber. On the other hand the crane should not wait over the inlet conveyor with a rack of cathodes if the machine is not coping with the throughput. It should wait over the cell and remove the cathodes when the conveyor is able to fit another rack of cathodes. This will also ensure that cathodes are out of the cells for the shortest time possible.

Regular machine and equipment maintenance is absolutely critical for the smooth operation of the cell house and service life of the cathode plate. The design of all ISA PROCESSTM cathode stripping machines ensures that there is no damage to the ISA cathode plate and associated edge strips whilst maintaining design throughput.

CONCLUSION

Cathode plates are a capital item and should not be considered as a consumable. Careful management of the electrowinning (and electrorefining) operation will ensure the longevity of the stainless steel cathode plate and enable the production of commercially saleable cathode copper. Management practices from mining through to the electrowinning plant all play an important role in the maintenance and preservation of the permanent cathode plate.

The ISA PROCESSTM is an integrated system that combines a robust cathode plate with a safe and high performance stripping machine design. When combined with good process management the long-term effectiveness of licensed facilities is ensured.

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