The demand for continuous improvement in the industrial world is an ongoing process. Some sectors, where the competitive forces are well established, have led the development of new and reliable technological innovations. Although the metallurgical industry can rightfully be proud of its process improvements, there is still work to be done in materials and in material handling. In some cases, the improvements will be as simple as adopting technologies that have been perfected in other processing or manufacturing industries.

This paper discusses the next design generation for copper tankhouses which will yield:

- Improved copper quality
- Improved equipment availability
- Lower life cycle costs
- Safer operations.

These benefits will be realized through new developments and design improvements in:

- Permanent cathodes
- Cathode washing
- Cathode stripping machines
- Anode preparation machines
- Improved lead anode design
- Recycling of lead anodes and refurbishment of cathodes.

The demand for base metals, and in particular copper, has led to more research into improving efficiencies in electrowinning and refinery plants around the world.

One of the areas previously taken as a matter of course was the production of lead anodes and stainless steel cathodes. In South America alone there are over 600 000 cathodes and anodes in circulation—a very significant figure.

**Lead anodes**

Much has changed in the manufacture of lead anodes over the past 50 years.

**Alloys**

Similar to the automotive battery, antimony was the first metal to be used as an additive to
improve the grain structure and give the anode more mechanical strength. The additional strength was mainly required to give the anode blade more rigidity and reduce shorting caused by the anode buckling due to deformation occurring during normal handling in the cleaning or stripping process. Six% to 8% antimony was added to the refined lead. Antimonial lead was used in the recovery of copper, cobalt and nickel. One% silver alloy was used for the recovery of zinc and manganese. The automotive battery manufactures had in the interim reduced the antimony content in their alloys with the addition of arsenic and selenium, and subsequently introduced calcium as an alloy, particularly in relation to the maintenance free battery.

Calcium, for the same reason, was first introduced worldwide as an additive to a silver lead alloy in a patent developed by Michael Thom in South Africa in 1982. The addition of calcium enabled the end user to reduce the silver content first from 1% to 0.75% and then eventually to 0.5%. Prior to this the silver lead alloy anode was easily bent, causing shorting on contact with the cathode. The addition of the calcium gave the blade more rigidity and increased the life of the anode by more than double.

Calcium, with tin and aluminium, was then introduced into anodes for the recovery of copper, nickel and cobalt. Whereas lead antimonial and silver lead alloys cast relatively easily, problems were encountered in casting calcium lead alloys, which necessitated a change in manufacturing techniques.

Method of manufacture

Casting

Initially the anodes were cast in book-type moulds. Casting was from the top with the copper hanger bar in position. To get sufficient flow and give sufficient strength the anode, blade was cast up to 16 mm thick. Casting from the top resulted in air entrapment, dross inclusion and hot spots in the centre of the anode. The latter items all increased corrosion of the anode, reduced the life of the anode, and in some cases increased the migration of lead into the electrolyte.

Another South African first was the introduction of a semi-pressure die casting method by casting the anode through a valve and runner at the bottom of the mould. The runner (later cut off from the blade bottom) absorbed the heat and eliminated the hot spot. The lead pushed the air upwards and escaped through air vents above the copper hanger bar. The moulds are hydraulically operated and water cooled. It must be emphasized that temperature control is critical in the process.

Rolled anode

At the time South Africa was a leader in the improvement of casting lead anodes. The same success was not achieved elsewhere, particularly with calcium lead alloys, and in some cases this accelerated the introduction of the anode with a rolled blade. The automotive battery manufactures had moved to a process involving a continuous cast rolling mill producing thin lead plates.

The electrical flux density (the capacity of a conductor to convey electrical current) is directly proportional to the grain size and grain structure in the metal conveyer. The smaller the grain size, the better the electrical current properties. It was found by rolling the blades, particularly in the case of calcium lead, the size of grain structures decreased. Lead, similar to copper, also work hardens. The rolling also increased the mechanical strength of the blade. The anode manufacturers cast the header bar section (encapsulating the copper in position) and rolled lead plates on a conventional rolling mill. The lead blade was then lead burnt (welded) to the header bar section.
In the case of calcium lead, it is extremely difficult and in fact not practical to weld calcium lead sheet to calcium lead sheet. The calcium lead oxidizes immediately on the introduction of the welding heat. It is virtually impossible to weld once it is oxidized. As a result it was found that the hanger bar had to be cast in antimonial lead (normally 6% antimony) and then welded to the calcium rolled plate using a flux and antimonial rod. It is a well-known fact that even in steel the weld is more susceptible to corrosion than the rest of the plate. Lead and the other base metals are not the exception.

Another method of overcoming the above welding problem was slotting the lead blade into the pre-lead plated copper hanger bar and soldering the blade in place.

In 2005 John Turner and Thomas Meyer developed a patent for the manufacture of a rolled anode with no weld or joint between the lead and copper hanger bar. This was a seamless rolled anode and was described by a leading international consultant as the first meaningful innovation in lead anodes in 20 years. In principle, the patent is held on the process whereby a complete anode with its busbar cast in position and the blade portion of the anode then put through a rolling mill and the blade thickness reduced with resulting benefits including the reduction of grain size, added mechanical strength and weight reduction. The seamless rolled anode is manufactured as follows:

**Plant and equipment**

- A casting facility incorporating water cooled hydraulically operated mould.
- A patented rolling mill, which enables the cast anode to be rolled with the copper busbar in position with a minimum of 5 mm lead encapsulated around the copper and eliminating all soldered or welded joints.

**Method of manufacture**

After casting the anode is rolled with the copper busbar section in position and reduced by 30% to 40%. This work hardens the metal hence giving the anode more rigidity, and the lead has a finer grain structure, giving the anode a longer life than a cast anode.

Conventional rolled anodes as described are being supplied to base metal electrowinning plants around the world. While these conventional rolled anodes are an improvement on a cast anode, the conventional rolling method has the following disadvantages when compared to the patented anode.

- The conventional rolled anode has a welded or soldered joint. The weld is dependent on manual welding (lead burning) which is subject to human error. The same applies to a soldered joint, which could be prone to corrosion from mechanical damage to the plated lead layer. The corrosion attack on the weld is at times greater than that on the rest of the anode and as a result the solution level in the cell may have to be kept lower than the level of the weld of the anode. The weld leads to the common corrosion found in the liquid gas phase corrosion area, which is often the most severely attacked area in a reaction vessel. The soldered joint is also subject to splashing and any mechanical damage to the plated copper busbar will expose the copper to a corrosion attack. The lead covering on the cast header bar is at least 5mm thick, which will protect the copper busbar.
- The conventional rolled calcium anode has a calcium lead blade but the lead used covering the header bar is often antimonial lead (As mentioned, the antimonial lead facilitates the welding of the joint.) When recycling, the two different alloys (antimonial and calcium) are often not separated before the time, and the alloys are then mixed. Costly alloy adjustments have to be done to adjust the alloys to the original compositions. The seamless rolled anode has calcium lead throughout with the distinct advantage that on recycling, the calcium lead alloy is not contaminated by the antimonial lead.
• The method of manufacture of the new anode eliminates the weld and this makes the anode more competitively priced in comparison to the conventional rolled anode. It must be emphasized that the anode in question is not a new anode but an improved anode.
• Anodes from this method of manufacture have performed to expectation in the DRC (Democratic Republic of Congo) for over two years. Resultant samples from these anodes passed on to Mintek (Mineral technology of South Africa) showed no visible corrosion. It has been estimated that a service life of at least five years can be achieved, provided the electrolyte remains constant. In particular chlorides must be kept to a minimum. Replacement of the anodes will mostly be due to mechanical damage and not due to catastrophic failure of the anode.

Cathodes

This section describes the cathode blanks available from the vendors, outlines the relative advantages and disadvantages of these cathodes and provides a ‘qualitative level’ valuation of several common parameters of the cathodes.

Cathode design alternatives

Outotec cathode

This cathode blank is manufactured by welding the stainless steel sheet to a stainless steel hanger bar, which has an internal solid copper core.

We have limited knowledge of the service experience of this Outotec cathode. To the best of our knowledge the Outotec cathode is in at least five plants that are in commercial operation or in construction. The plants include Las Cruces SX-EW in Spain, the Milpilas SX-EW plant in Mexico, the Frambros refinery in China, a small SX-EW plant in Laos, and a refinery in Finland.

Cobra unsheathed cathode

This cathode blank is manufactured by welding the stainless steel sheet to a copper hanger bar, using a dissimilar metal weld.

This cathode is based on cathode designs that have been used for over 30 years. The number in service exceeds five hundred thousand (500 000) cathodes.

EPCM sheathed cathode

This cathode blank is similar in design to the Cobra unsheathed cathode described above, except that it has a stainless steel sheath covering the hanger bar above the sheet. The sheath provides protection for the copper and the Cu/SS weld against corrosion attack by acid mist. The ends of the cathode sheath can be sealed to the hanger bar using either a seal weld or by installation of a copper sleeve, with a chemical resistant sealant.

Xstrata ISA cathode

This cathode blank is manufactured by welding a stainless steel hanger bar to the stainless steel sheet. To provide electrical conductivity, a 2.5 mm copper layer is plated over the hanger bar and 15 mm down the sheet.

This cathode is based on cathode designs that have been used for over 30 years. The number in service exceeds one million five hundred thousand (1 500 000) cathodes.
Xstrata Kidd cathode

This cathode blank is similar in construction to the EPCM sheathed cathode described above, except that the cavity between the sheath and the hanger bar is filled with a chemical resistant filler to isolate weld from contact with electrolyte.

It is important to note that all of the available cathodes are now supplied with a 90 degree V-groove along the bottom edge of the sheet. The V-groove aids in separation of the copper deposit from the cathode blank.

Electrical resistance

The electrical resistance is an important parameter of the cathodes as it affects the cell voltage drop and the overall power consumption of the tankhouse. For the purpose of this paper, the resistance is calculated by adding the theoretical resistance in the hanger bar copper from one end of the bar to the centre, and the calculated resistance in the stainless steel sheet from the hanger bar attachment point to the electrolyte level. This is an approximation only as several factors will affect the resistance of the cathode in service. However, it provides a close approximation to the relative resistance between the different cathode types and is appropriate for this paper.

The estimate of the cathode resistance also determines the estimated annual power cost per cathode, for this cathode resistance, based on the nominal current density and operating time of the refinery.

Another important aspect to the electrical resistance is the increase in resistance over time. As discussed any exposed copper on the hanger bar is subject to dissolution over time due to contact with sulphuric acid in the atmosphere above the cells. While dissolution rates as high as 1 mm per year have been reported in some SX-EW plants, the slow dissolution of the copper can significantly affect the electrical resistance over time.

Corrosion resistance

Generally, three types of corrosion occur with stainless steel cathodes, as follows:

- *Chloride pitting of stainless steel*—corrosion of the stainless steel sheet can occur, generally in the form of pitting near the solution line. The cause of this corrosion is normally high chloride levels in the electrolyte and it generally occurs in SX-EW plants, and is a rare occurrence in refineries. All of the cathodes being considered would be similarly affected by chloride pitting, as they all use the specified 316L stainless steel for the sheets. New materials are being substituted for 316L stainless steel and this will be discussed further in this paper.

- *Dissolution of copper on hanger bars*—due to the solubility of copper in sulphuric acid and the presence of acid mist in the air above the cells, some dissolution of any exposed copper on the hanger bar will occur. This is very prevalent in some SX-EW plants due to the high levels of acid mist but is generally less prevalent in refineries. Nevertheless, some copper dissolution will occur and cathodes with exposed areas of copper will require repair or refurbishment at some point.

- *Galvanic corrosion*—any area where dissimilar metals are in contact in the hanger bar or at the hanger bar/sheet connection will be subject to galvanic corrosion. Again this is most prevalent in SX-EW plants as condition is aggravated by acid mist, but it does occur in refineries. Experience has shown that some refineries have inherently more corrosive environments than others and there is no obvious technical reason for this.

Durability

The durability of a cathode blank relates to how it will withstand the normal operations of a copper refinery, excluding corrosion that is discussed earlier. Generally, cathodes face possible damage due to the following:
• **Overloading of hanger bar**—cathode hanger bars can sometimes be overloaded by over-plating on the cathode, impact loading on the cathode during handling, or excessive force being applied in the CSM, normally during copper stripping. Over-plating is not normally an issue as the weight of the copper is well within the load carrying capacity of the hanger bar. However, impact loading during handling and excessive forces in the CSM can sometimes lead to large forces being applied to the hanger bars.

• **Abrasion of the hanger bar**—abrasion of the hanger bar occurs during handling of the cathode, mainly by the CSM. During processing through the CSM the cathode is necessarily supported by the hanger bar on transfer cars, conveyors and in flexing/stripping stations. Additionally, abrasive media brushing normally cleans the end of the hanger bar where it contacts the busbar.

• **Bending of sheet**—bending of the sheet may occur due to overflexing of the sheet or otherwise overstressing the sheet with a compressive force, most frequently in the CSM. Generally, this affects the verticality of the cathode so that it is not acceptable for use in the process, but does not lead to structural damage to the cathode.

**Maintainability**

Maintainability refers to the ease at which minor and major repairs can be performed on a cathode. Minor repairs include:

- Replace edgestrips
- Repair minor scratches on sheet
- Straighten slightly bent sheet
- Straighten slightly bent hanger bar
- Repair cathode verticality
- Clean sheet.

Major repairs are normally required only as a result of gross damage to the cathodes from handling or CSM mishaps and include the items listed below. Major repairs include:

- Replace entire hanger bar
- Replace entire sheet
- Recuperation of damaged sheet
- Replate stainless steel header bar.

**Alternative materials of construction**

The sharp increase in nickel and molybdenum during the period of 2004 through 2008, led both permanent cathode suppliers and customers to look for alternative and substitutes for the traditional 316L stainless steel cathode sheet.

The substitutes currently being offered are lean duplex stainless steels. Duplex stainless steels contain approximately 50% ferrite and 50% austenite, which result in a material that has properties representative of both classes of stainless steels.

Like nickel free ferrite grades, duplex grads are magnetic and more resistant to chloride stress corrosion cracking than austenitic series grades.

Duplex alloys have a good ductility and toughness, approaching that of the austenitic grades. Also duplex alloys are stronger than comparable austenitic and ferritic stainless steels.

Lean duplex stainless steels have been designed to have the properties of a duplex material, but contain less nickel and molybdenum than standard duplex grades such as 2005, which results in a cost savings.
Tom Marsden
Marketing Manager, Thutuka Group Limited, South Africa

Tom Marsden joined the family business in 1961 to eventually become sole owner and Managing Director in 1969. Introduced Lead anodes as a product line in the latter part of the nineteen sixties and has been involved in the manufacture of anode plant and manufacture ever since. With Michale Thom patent. Introduced calcium as a beneficial addition to the silver lead alloy. This was a worldwide first for lead anodes as used in the zinc industry. Introduced new casting techniques for the casting of all lead alloys and in particular calcium and strontium lead alloys. Since involved in various methods of rolled anodes including plant and equipment for the manufacture of seamless rolled anodes. Besides the anode industry, has been involved in development of continuous cast lead sheet programs in Australia, the UK and the USA and lead radiation shielding with various international companies.

John Jickling
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John Jickling studied Mechanical Engineering at Queen’s University in Canada. After completion of his Bachelor’s Degree, he joined EPCM Services Ltd. A consulting and technology company located in Ontario Canada. After working for two (2) years at EPCM, he was prompted to start-up Technologies Cobra S.A., an EPCM Technology Group Company located in Antofagasta, Chile. While at Tecnologias Cobra, EPCM developed our services to provide after market support to the Permanent cathode Technology users in the Copper Refining Industry. John has been active in Permanent Cathode Product development, Manufacturing processes and the development of Permanent Cathode Refurbishment Technologies.