

ELECTROMETALLURGY – NOW AND IN THE FUTURE

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Abstract

Electrolytic processing is used commercially to recover and/or refine metals such as aluminum, copper, magnesium, nickel, and zinc. There are also new and exciting opportunities to utilize electrometallurgy in the production of titanium, lead, and other metals. This paper reviews some of the main technologies that are used to produce and refine metals as well as some of the recent advances and future directions the electrometallurgy industry may implement to meet the challenges faced now as well as those that are likely to be faced in the future.

Introduction

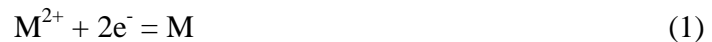
Electrolytic processing is used commercially to recover and/or refine metals that include large scale production for metals such as aluminum, copper, magnesium, nickel, and zinc as well as small scale production for metals such as gold and silver. There are also new and exciting opportunities to utilize electrometallurgy in the production of titanium, lead, and other metals. This paper will focus only on electrometallurgical processing of metals with relatively large production markets.

Electrolytic processing of metals involves common challenges. Energy is an important issue in electrometallurgy. Other important areas of interest are chemistry, productivity, and safety. In order to meet the present challenges in commercial electrometallurgy, a variety of technological advances have been made. Similar challenges will be faced in the future, requiring process improvements and innovations. This paper will review some of the main industry technologies

as well as some of the recent advances and potential future developments that enable the electrometallurgy industry to provide important metal products now and in the future.

Chemistry

Electrometallurgy is made possible by interaction of metals, electrons, and liquids. Metals dissolved as ions in liquid media can be reduced by the acquisition of electrons. The general reduction reaction can be written as:



The reduction of metal from solution is based on a combination of thermodynamics and kinetics. In most commercial electrometallurgy processes, electrodes (cathode and anode) and a power source are used. Metal reduction, which occurs at the cathode, is contingent on a supply of electrons that are provided by a counter reaction that occurs on the anode. The electrons are effectively forced from the anode to the cathode using a power supply. The medium in which the metal ions are reduced is known as the electrolyte. In aqueous media one common anode reaction is water electrolysis:



In molten salt electrometallurgy, the oxidation of carbon or chloride often provides the needed electrons for reduction. In electrolytic refining, the electrons are supplied from an impure anode. Each metal reduction reaction, and each counter reaction, requires a specific voltage or half-cell potential, to occur. Metals such as magnesium and aluminum have reduction potentials that are well below the reduction potential for water. Consequently, these metals are processed in molten salt electrolyte rather than water.

Metals with low potentials are easily contaminated by the presence of higher potential metals that preferentially accept electrons and deposit as impurities in the cathode. Thus, metals with low potentials such as zinc, aluminum, and magnesium require careful electrolyte purification in order to maintain cathode purity. Correspondingly, considerable efforts are made to ensure and improve electrolyte purity levels. This is a need that is present now that will extend into the future. This need will become more important as source materials have increasing levels of impurities that are difficult to remove, and as current densities rise and increase the tendency to deposit impurities from electrolytes.

The use of electrometallurgy to recover metals that are not traditionally processed by electrolytic processing, such as titanium and lead, is limited by the half-cell potentials and the electrolyte composition. In addition, the presence of impurities such as oxygen or water can play an important role in determining the viability of electrolytic reduction for the recovery of some metals. In the future, the use of alternative electrolytes and modified chemistries may play roles in determining what new metals are added to the list of those recovered electrometallurgically on a commercial scale.

Energy

The rate of the reaction is based on a combination of mass transport and overpotential, the potential above or below the half-cell potential (below for reduction, above for oxidation). The energy needed to force electrons from the anode to the cathode is based on the difference between the cathode and anode reactions plus the associated overpotentials and resistance-related potential loss. The overall voltage requirement for an electrochemical cell is often called the cell voltage. The cell voltage for metal reduction operations is commonly in the 2-4 Volt range for electrowinning and 0.2-0.4 Volts for electrorefining. The energy consumption in kilowatt hours per metric ton can be expressed as:

$$Energy(kWhr / tonne) = \frac{E_{cell}(n)26,800}{A_w \left(\frac{\beta(\%)}{100} \right)} \quad (3)$$

E_{cell} is the total cell voltage that includes overpotentials, resistance-related potential losses, and anode and cathode half-cell potential differences, n is the number of electrons per mole of metal, A_w is the atomic weight of the metal that is being reduced, and β is the current efficiency or the percentage of the total applied current that is used for the desired metal reduction reaction. The energy requirement for metal reduction is usually more than 1500 kWhr/tonne. Thus, electrometallurgy is a very energy intensive process. Correspondingly, there is a continual need to reduce energy consumption by increasing efficiency and reducing cell voltage.

Energy costs are based on a combination of electrochemistry requirements and energy purchase price. Many large scale electrometallurgy facilities are located near low cost energy markets. Because hydroelectric power is among the lowest cost power generation methods, many electrometallurgy facilities are located near hydroelectric power generation facilities, provided that the feed material transportation costs are low. Correspondingly, many electrowinning facilities are located in coastal areas with excellent water transportation and low cost hydroelectric power. Countries with relatively low cost power include Argentina, Australia, Canada, Finland, France, Indonesia, Norway, and the United States. The ongoing need to reduce energy and transportation costs will ensure that the trend to locate facilities in coastal, low power cost areas will continue.

Energy costs also result in a trend to utilize low energy consumption technologies in markets where power costs and transportation costs are high. Areas in the world with relatively high energy costs such as central Europe, and to a lesser extent, South America, have a strong interest in reducing energy consumption through energy reducing technologies such as alternative anodes that reduce cell voltages.

Productivity

Productivity is always a commercial manufacturing challenge. Commercial electrometallurgical processing continues to utilize productivity enhancement technologies. There has been and continues to be a trend toward more automation in electrode handling. Robotic technology has been an important part of increasing automation.

Another productivity trend is the move toward higher current densities. The move toward higher current densities generally has resulted in tighter spatial control and improved electrolyte mass transport and convection.

Safety

Safety is critical to electrometallurgical processing. Increases in productivity have often been made through automation. Automation is also beneficial to employee safety by providing fewer opportunities for exposure to chemicals and work hazards by employees. Automated systems are less likely to make errors that may lead to injury.

Gas handling is an area of concern to electrometallurgy. In many systems the anodic reaction involves gas evolution. In base metal electrowinning, gas evolution in electrowinning cells leads to acid misting. Gas evolution in light metals electrowinning such as magnesium production often lead to chlorine gas evolution. Zinc electrowinning leads to significant levels of hydrogen gas generation, which must be appropriately controlled for safe operation of the associated cells. Suppression, elimination, and ventilation are used to minimize the effects of gas evolution. The importance of appropriate handling of gas evolution and related effects such as acid misting will continue to be an important area for improvements in technology.

Refining

Refining is critical to high purity metal production. Most of the world's commercial copper is electrolytically refined after it is recovered by smelting. Many of the nonferrous metals are similarly refined to achieve high purity metals. Electrorefining utilizes a fraction of the energy needed for electrowinning. The reduced energy requirement is based on the elimination of the voltage between the anode and cathode reactions, which are the same in electrorefining. The energy requirement is further reduced by a lower anodic overvoltage. As a result, the overall energy consumption for electrorefining is often less than 20 % of the energy needed for electrowinning. Consequently, energy reduction is less critical in electrorefining than in electrowinning. However, other issues such as impurity control and productivity are of considerable importance to electrorefining and are likely to continue to be important.

Electrometallurgy for Selected Metals

Aluminum Electrowinning

The aluminum industry has evolved to its current position of approximately 41 million tonnes annual worldwide primary production produced in over 45 countries. This production is concentrated in around 20 major aluminum metal producing companies who account for up to 65% of this metal production. Most of these operations use alumina derived from bauxite. Both low and high silica bauxite are refined using the Bayer Process and the product is alumina powder which is then electrolytically reduced to aluminum metal by the Hall-Heroult process. There have been many advances made in the Hall-Heroult production process which have resulted in significant improvements in productivity, energy efficiency and its impact on the environment. However, the process used today that is based on a consuming carbon anode, a

cathode metal pool and fluoride based electrolyte is fundamentally the same as the process originally developed by Charles Hall and Paul Héroult 125 years ago.

There are two types of electrochemical cells or pots in use today. The Soderberg Cell (both the horizontal stud (HSS) and vertical stud (VSS) versions) is based on a continuous anode that is made from carbon paste that is fed to the cell and baked in-situ. This cell technology accounts for around 10% of the world Al production. The other type of cell technology, the Pre-bake (PB) Cell is based on multiple anodes that are made from coke and pitch which are formed and baked in furnaces outside of the cell accounts for the rest of the metal production. Schematic cross sections of both the Soderberg (HSS and VSS) and modern Pre-bake cells are shown in Figure 1.

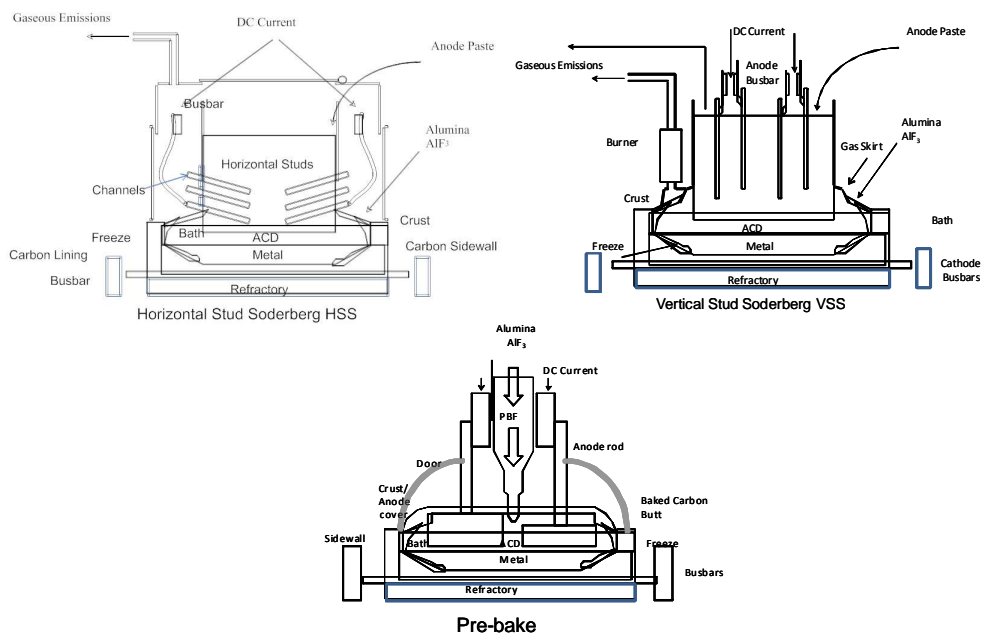


Figure 1: Schematics of the Soderberg (both HSS and VSS) and a PB Cell

Electrical power is used to both reduce alumina to aluminum and to keep the cell at its operating temperature of around 960°C. Since the first cells were developed, the major drivers in the technology for the industry have been to improve energy efficiency and to increase smelter production with the objective of reducing both the operating and capital costs. The environmental drivers have been to reduce fluoride emissions and specific to the Soderberg Cell technology, to reduce the formation of and release to the environment of polycyclic aromatic hydrocarbons (PAHs), some of which are carcinogenic.

One way to track electrolysis cell development is to look at the continuous increase in amperage capability that has been achieved by the introduction of new cell technologies, achieved by continuously increasing cell electrode areas. This trend in the industry in capability with time for each of the cell technologies is summarized in the historical plot of Figure 2.

Hall Heroult Cells 1889 to 2010 Amperage increase "State of the Art Cells"

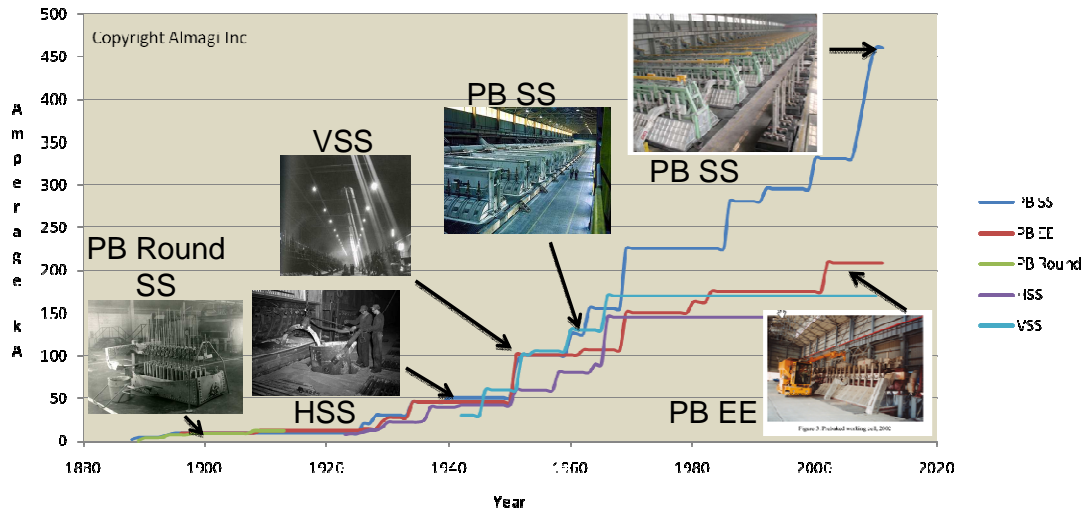


Figure 2: Change in amperage in the year of start-up achieved in commercial cell technologies (PB SS = Pre-bake, side-by-side; PB EE = Pre-bake, end-to-end; PB Round = Pre-bake, round anodes, HSS = Horizontal Stud Soderberg, VSS = Vertical Stud Soderberg). Photos from left to right: Shawinigan (Northern Aluminum Company (Rio Tinto Alcan), PB Round SS, 1901), Shawinigan (Aluminum Limited (Rio Tinto Alcan), HSS, 1942), Isle Maligne (Aluminum Company of Canada (Rio Tinto Alcan) VSS, 1952), Badin (Alcoa, PB SS, 1963), Gongyi City (Henan YulianZhongfu Industries, PB SS, 2008), Nag Hammadi (Aluminum Company of Egypt, PB EE, 2003)

The PB Round cell technology (Héroult) was first used in France with single and multiple carbon anodes in a cell (or pot). These small pots required hand feeding of the alumina and hand ladling of the molten aluminum metal that was produced.

The self-baking HS Soderberg anode (EE) technology was first commercialized in 1927 in Sabinanigo, Spain and was the basis for many cells constructed in the 30's through to the 50's. During this time period, many prebake cells of both EE and SS type were also built. The amperage of both cell technologies was limited to around 40 kA at this time. Soderberg patented a new VSS anode in 1938 which was first commercialized in 1949 at Valladolid, Spain. The VSS technology was widely implemented in the 50's through to the 70's because it offered the ability to increase amperage over the HSS technology. Smelter production increased by both increases in amperage and increases in the number of cells in a smelter that lead to a number of developments in material handling, mechanization and automation. During the 50's amperages were further increased up to 100 kA which appeared to be a limit because of severe magnetic problems which resulted in distortion of the metal pool (this was particularly severe with the EE technologies).

With two versions of Soderberg (HSS and VSS) and two versions of Pre-bake (PB SS and PB EE) technologies being built and operated in the early 60's it was not clear as to what cell

technology would eventually dominate the industry. This was shortly resolved when the 100 kA limit was exceeded with the introduction of the Alcoa P155 cell technology (PB SS) operating at 155 kA. This cell technology had a number of novel developments (point breaker feeders which resulted in improved bath chemistry control and reduced emissions from the cell, improved magnetics with anode side risers which helped to stabilize the metal pad at high amperage, a highly conductive graphite side wall to manage the cell internal heat at high amperage and a computer based resistance control system). This technology was first commercialized at Badin, NC in 1963 and Alcoa continued to introduce new PB SS cell systems into the 80's.

All technologies have since exceeded this 100kA limit but the PB SS technology has proven to be the one capable of reaching the highest operating amperages. Because of the high investment costs in technology, conversion within the industry is slow with all four technologies still in operation today. With continued improvements to the PB SS, e.g. SiC sidewalls replacing graphite, forced air convection on the shell and asymmetric current distributions helping to further stabilize the metal pad, cell technologies other than PB SS should be considered obsolete.

Aluminium Pechiney (Rio Tinto Alcan), as an example of a technology producer, developed, built and licensed a series of cell technologies since the 80's with continuously increased operating amperages; the AP 18 (180 kA), AP 22 (220 kA) and AP 3X (300 – 400 kA); technologies that have dominated the industry since the 80's. Continuing this trend of increasing amperage, Rio Tinto Alcan is piloting the AP 60 (600 kA) in Jonquiere, Canada with start-up scheduled for 2013. Another technology producer, the Northeastern University Institute of China, has recently developed the NEUI 400 HEEP, which is operating at 12.5 MWh/t energy efficiency at 430 - 460 kA at the Henan YulianZhongfu Industries smelter in Henan Gongyi City, China. Amperage increase has been achieved by increasing the anode area and decreasing the non-productive areas of the cell, however the productivity of the cell (normalized by the internal shell dimensions and the amperage at the date of cell's year of commercialization) remains relatively constant at around 16 tonnes Al/m²/year over this period of development. Allowing for capacity creep, the range in productivity in commercial cells is 16-18 tonnes/m²/year.

Future developments that are being actively worked on that when successful, would dramatically change the industry include such developments as the inert anode, dimensionally stable cathode and carbothermic reduction. These advancements are at various stages of development and are viewed more as long term initiatives rather than imminent commercialization opportunities.

The inert anode is the replacement of the carbon anode with a metal, cermet or oxide that is stable in the cryolite bath. The inert anode would eliminate the need for carbon anodes and the high maintenance that these anodes require. As well, the anode gas is oxygen rather than carbon dioxide, making a significant impact on the direct GHG's emitted from the cell. Development issues are focused on anode material development and cell design to accommodate the changes in heat balance and energy input that are associated with this change in technology.

The wettable cathode is the replacement of the current carbon cathode with a wettable material, most probably based on TiB₂. A wettable cathode has the potential to further improve the stability of the metal pad and potentially reduce the anode-cathode distance (further improving

the energy efficiency) and allow for non-horizontal electrode arrangements which could allow for an increase in pot productivity.

Carbothermic reduction would eliminate the electrolysis cell completely with a high temperature reactor for direct reduction of alumina by carbon. Carbothermic reduction could possibly reduce the overall intrinsic energy requirement for aluminum production and offer the potential for smaller scale smelters.

From the original work of Hall and Héroult, the aluminum industry has continued to evolve with significant improvements in energy efficiency, environmental controls, cell production and smelter size. Continued advancements in the cell performance are expected, achieved through better understanding of the process and improved control of the technology.

Copper Electrorefining and Electrowinning

Unlike zinc and nickel, copper recovery via electrolysis, either refining or electrowinning accounts for almost all refined production. This is because the main industrial use for copper is for electrical conductivity purposes and this requires very pure copper product that can only be produced on a large scale through electrolysis.

Historically large scale refined copper production occurred almost exclusively via electrorefining after the smelting of sulfide ores. Over the past four decades, there has been growth in the large scale hydrometallurgical recovery of copper by low cost heap leach, solvent extraction and electrowinning. Large refineries have remained in mature industrial regions and are growing in capacity in the new growth economies of China and India. Electrowon copper capacity growth has been in those regions where there is leachable copper at mine sites in the Southwest USA, Chile and central Africa. Electrorefining, now accounts for 70-80% of the worlds refined copper with electrowinning producing the rest.¹

Copper Electrorefining:Electrorefining (ER) as it is known has focused most technical development over the past years on productivity, automation and quality rather than energy reduction as electrical energy requirements are relatively low at ~340 kWh per tonne of copper.²Electricity had been discovered in the 1800's and the first refinery built in the USA was Balbach Smelting and Refining Company in Newark, New Jersey in 1883. The first in Europe was in Hamburg around the same time and within ten years, eleven more copper refineries were constructed in the USA, particularly in the New York/ New Jersey area, including Laurel Hill (Phelps Dodge), Raritan (Anaconda), Perth Amboy (ASARCO) and Carteret (AMAX), producing a quarter of the world's refined copper. This technology laid the foundation for the large scale electrorefining plants that would be operating twenty years later.

ER technology used starter sheet plating for many years and this remained the industry standard until the late 1970's when the first permanent cathode technology (called the ISA Process) was developed in Townsville, North Queensland, Australia at Copper Refineries Pty Ltd. (CRL). This technology was based on Zinc EW technology (Mitsui Hikoshima) concepts and automated the ER tankhouse (as like Zn) with copper being plated directly onto stainless steel cathode plates and stripped in automated stripping machines and removed the need for a starter sheet section.

The advantages of permanent stainless steel technology have been well documented. Permanent cathodes hang more vertically and so can be spaced closer together in the cells. Their use eliminates the need to manufacture copper starting sheets while increasing tankhouse productivity. Cathode verticality allows for operation at higher current densities while obtaining higher purity cathodes, fewer short circuits and higher current efficiencies.

Derivatives of this technology arose at Kidd Creek, Canada in the late 1980's and with Outotec in late 1990's. New developments in this field include automated crane and robotic electrode handling machines that are being installed in new Chinese refineries and are much faster than earlier models. Lower maintenance and simpler polymer concrete cells have replaced paraliner or lead lined concrete cells.

Recently further productivity gains are being achieved with higher current densities of over 400 A m⁻² with the Mettop BRX technology. The first demonstration cell was installed at Brixlegg, Austria in 2005 and is presently in full-scale operation, which produces high quality cathode. The technology uses a parallel flow device (PFD) installed in each cell and produces high electrolyte flow for a homogenous distribution of dissolved copper and heated electrolyte to the cathode face while not causing additional slime contamination. This enables current density to increase to 420 A m⁻², the highest current density in industry. METTOP BRX technology has been installed and operating in 720 cells in a new tankhouse at Xiangguang Copper at a starting current density of 385 Am⁻², with design at 410 Am⁻².

Focus on ER cathode quality has led to cathode smoothing reagent measurement technology. Reatrol technology was developed in USA in the 1970's and focused on thiourea control and measurement. Aurubis's Hamburg refinery in Germany developed the Collamat system that focused on glue measurement and addition. The Collamat system is more widely used as it is much more automated. Both thiourea and glue are widely used throughout the industry. Some refineries prefer more glue and some more thiourea.

There has been some energy savings development on contact systems and cathode design. Double contact technology is now being installed that uses equalizer bars to smooth the current distribution in a cell and improves current efficiency and cell voltage at high current densities. Cathode plate technology, such as Xstrata's low resistance design, has more electroplated copper on the cathode hanger bar and over the stainless steel substrate above the air/electrolyte line; which saves energy due to lower electrical resistance in the tankhouse.

Cell monitoring for voltage and temperature using wireless technology has been developed and installed at some locations. This information can be used to assist in locating short circuits or low flow cells.

Copper Electrowinning: Copper electrowinning (EW) has focused more on energy reduction technology than ER because EW consumes considerably more electrical energy (~2160 kWh per tonne of copper).³ Quality, productivity and acid mist reduction technology developments have also been very important.

In the years leading up to the First World War, two ventures in northern Chile (Chuquicamata) and Arizona (Ajo) began to plan, pilot and test for direct electrowinning of copper from copper leach solutions. These first large EW tankhouse designs were based on ER starter sheet technology. Based on these designs, direct EW plants would be built in Mexico, central Africa and USA.

One of the major issues that had existed with the older EW tankhouses was the purity of the electrolyte feed and its effect on operations and cathode purity. The application of solvent extraction (SX) technology to produce concentrated and purified electrolyte was critical to the growth of EW. Following their success in uranium and vanadium processing, General Mills Chemicals began developing organic extractants for hydrometallurgical copper production in the early 1960's. The target product from the SX process was a concentrated and purified copper electrolyte product that could be electrowon to make pure copper cathodes equivalent to refined copper cathodes. Pilot plants were set up first at Bagdad, AZ in 1965 (now Freeport-McMoRan Bagdad), Duval (at Esperanza) and then at Ranchers Bluebird near Miami, AZ which became the first commercial plant, and all of these plants produced saleable copper cathode. Copper SX production has now become the standard in the hydrometallurgical copper industry. In recent times more selective SX reagents have been developed for specific operating regimes.

Even though SX-EW technology was proven in the late 1960's, the world's energy crises in the 1970's and recession in the early 1980's delayed the expansion of SX-EW production. Sustained high copper prices in the mid 1990's coupled with an attractive investment climate and large copper deposits amenable to leach SX-EW copper production in Chile led to a boom in copper SX-EW production around this time

Productivity gains in EW design over the past 40 years have historically followed those in ER with the application of permanent cathode technology with Isa and Kidd Processes (now both Xstrata Technology) prevalent in USA and South American SX-EW projects. However recently in South America there are two productivity related technologies that are being installed that are unique to EW. Air sparging under the cathode in an EW cell allows for the production of high quality copper cathode at high current densities (400 A m^{-2}). In new plants, this results in a smaller tankhouse footprint. Several South American EW plants including Gaby, RadimiroTomic, Escondida, Spence and Cerro Verde use air sparging. At Anglo Los Bronces (north of Santiago, Chile) fiber reinforced plastic electrode frames manufactured by SELE have been installed into EW cells. The frames perfectly align electrodes for high current density, high quality copper production, and also remove the need for cathode edge strips. Some copper EW tankhouses are designed with relatively large electrodes (1.3m long and similar to Zn EW) such as at Safford, Arizona to minimize capital cost.

With higher current densities, air sparging and larger EW tankhouses, come the need to advance acid mist abatement technologies. Most of this development has occurred in Chile with cross flow ventilation systems, cell hood technology developed by SAME or Outotec and now a 'lateral flow' acid mist abatement technology that is being demonstrated in Chile at Cerro Miranda, west of Antofagasta.

Recently worldwide focus on energy reduction in metallurgical processes has led to energy reduction technology applications. These developments centered on the EW anode. In 2010, researchers from Freeport-McMoRan described work involving alternative anode reaction technology or AART.⁴ Whereas typical EW produces acid and oxygen at the anode, AART oxidizes ferrous ion to ferric ion at the anode and reduces cell voltage by approximately 50%. No acid mist is produced. Although promising, the technology has yet to be commercialized.

Another energy saving innovation, a PGM coated titanium mesh anode, was commercialized in 2007 with the first application at Chino, New Mexico.⁵ Similar anodes have been installed at other EW facilities in North and South America. The mesh anode has produced a 15% reduction in cell voltage and eliminated lead completely from the EW operations.

Copper Summary: All refined copper is produced by electrometallurgy. Electrorefining is the older and still dominate method to produce copper cathode. Technology development in ER has focused on productivity, automation and quality. Electrowinning due to its inherent higher electrical energy consumption has focused on electrical energy reduction as well as improvements in productivity, automation and quality. Often improvements can be utilized for both ER and EW operations.

Primary Lead Electrowinning

While lead electrorefining has been practiced from many years (the Betts Process), the primary recovery of lead from concentrate has not been practiced. This appears likely to change by 2013. Doe Run and Engitec have demonstrated Engitec's Flubor® Process on a pilot scale on and off since 2007. The pilot plant in Missouri was designed to process 8 tons of concentrate (80 percent Pb) per day, which equates to approximately 6.4 tons/day of lead. Doe Run has announced that it has plans to construct a commercial plant at an estimated cost of \$150 million by 2013.

The process involves ferric leaching of galena concentrate in a fluoboric based solution, electrowinning, and treating of residues for possible by-product recovery. The electrowinning portion of the process uses divided cells. Lead is deposited on permanent stainless steel cathodes. The electrolyte passes through a porous diaphragm to the anode where ferric ion is regenerated for return to leaching. The anode is reported to be graphite. Many operational details of the plant have not been released.

Magnesium Electrometallurgy

Unlike most metals, magnesium has two major raw materials – dolomite from the lithosphere, and contained magnesium in saline waters of the hydrosphere. Each raw material has its own electrometallurgical processes.

The lithospheric dolomite is calcined to calcium-magnesium oxide, and reduced with ferrosilicon at above 1250°C. One of the methods of the reduction is by an electro-thermal approach developed during the 1960's in France, which is called the Magnetherm Process. Here an electro-slag melting approach is used where a pool of partly molten slag containing 50% Ca₂SiO₄, 18%

Al_2O_3 , 14% MgO , and 18% CaO is formed from the continuous feed of calcined dolomite and low grade ferrosilicon. Magnesium vapor product is released from this process under a vacuum of 0.40-0.67 kPa. The power (4500 kW) is applied through a water-cooled copper electrode (a) from the top through the slag (g), to the bottom graphite lining (b) of the reactor, which acts as a power outlet through charge holes in the water-cooled furnace roof. Magnesium vapor condenses in a separate condenser system and the condensed metal is remelted into ingots.⁶ This process was used on a large scale at Addy, Washington (Northwest Alloy Plant) by Alcoa during 1975-2001.⁷ Another electro thermal process is called the Bolzano process developed in Italy during the 1980's. The Bolzano Process is practiced today by Rima Metallurgical Corporation (RMC), Brazil by a modified version developed by RMC. Here the high temperature is reached by resistance heating, where the resistor bed is the raw material calcium-magnesium oxide with ferrosilicon reductant along with iron [which is one of the products as well], magnesium vapor formed in the process condenses on the top section sides of the furnace.⁸

The previously described electro-thermal approaches most often are not covered by the subject 'Electrometallurgy', even though the basic laws of electricity are used in achieving the metallurgical. Electro metallurgy by electrolysis utilizes other fundamental electrochemical laws as well.

The Electro-winning process is used to extract magnesium from the hydrosphere raw material magnesium chloride in the saline waters of lakes or oceans, as well as marine evaporites found in the lithosphere such as carnalite [$\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$], or kainite [$\text{MgSO}_4\cdot\text{KCl}\cdot 3\text{H}_2\text{O}$]. It should be noted that the earliest known isolation of magnesium was done by Humphrey Davy in 1808; incidentally Davy used an electrolytic approach to isolate most of the metals from their compounds.

In 1808, Humphry Davy took moistened magnesium sulfate and electrolyzed it onto a mercury cathode. He also produced magnesium from red hot magnesium oxide with potassium vapors collecting the magnesium into mercury. Both of Davy's processes produced magnesium amalgam, from which he distilled out the mercury to produce metallic magnesium. In 1833, Faraday electrolyzed impure magnesium chloride in a molten state to obtain magnesium metal; two decades later Robert Bunsen made a commercial quantity of magnesium in a small laboratory electrolytic cell using molten anhydrous magnesium chloride. In 1886 by the Aluminium und Magnesium Fabrik, Germany, converted molten dehydrated carnallite [$\text{KCl}\cdot\text{MgCl}_2$] to magnesium metal by electrolysis. Chemische Fabrik Griesheim – Elektron further developed this starting in 1896 – the company later became I.G. Farbenindustrie in the twentieth century. Molten carnallite electrolysis still continues in the twenty-first century with various improvements made in the twentieth century.

Herbert H. Dow initiated extracting magnesium metal from brine well magnesium chloride in Michigan in the early twentieth century. Dow Chemical operated their magnesium production process from about 1915 through 1997 when they closed their magnesium plant in Freeport, Texas. The Dow plant in Texas used sea water magnesium and magnesium from calcined dolomite used in precipitating magnesium hydroxide, which was later converted to magnesium chloride. The magnesium chloride was then purified, dehydrated to $\text{MgCl}_2\cdot 1.5\text{H}_2\text{O}$ [with minimal formation of undesirable hydroxychlorides in electrolysis], and fed to cells operating

with steel cathodes and carbon/ graphite anodes which were slowly consumed by the partly hydrated feed. This cell produced magnesium metal at the cathode and a combination of chlorine and hydrogen chloride anode gas.

With the exception of the Dow Magnesium plant, most other magnesium electrowinning facilities operate using either anhydrous magnesium chloride or anhydrous carnalite as cell feed. 'Electrolytic Production of Magnesium', by Strelets is a book on electrolytic magnesium technology developed by the Germans, later improved by the Soviet Union by VAMI (the Soviet Aluminum and Magnesium Institute). Soviet magnesium plants in Solikamsk, Russia, Zaporozhye, Ukraine, and Kazakhstan operated until 1970.⁹ (These German and Soviet processes with further improvements have been practiced through the present time, at Solikamsk, Russia and the Dead Sea Magnesium Plant, Israel since 1995. These plants have used carnalite [KCl.MgCl₂.6H₂O] as the starting material, obtained from solution mined evaporite minerals in Russia or from the solar evaporated Dead Sea carnalite.

Evans, has provided a summary of the evolution of commercial processes in the light metals aluminum, magnesium and lithium industries over the last five decades.¹⁰ A summary of the 415 Kamp magnesium electrolytic cells operated by Norsk Hydro Canada – from 1991 through early 2007, are described in the articles by Wallevik, et al (2000)¹¹ and by Hans Eklund, et al (2002)¹². In these processes magnesium carbonate is converted to magnesium chloride on site. However the Norsk Hydro Canada plant operated only from 1991 to 2006 due to economic reasons. Improvements in the Electrolytic Process for Magnesium Production at U.S. Magnesium are noted in a Journal of Metals article.¹³ The raw material for the U.S. Magnesium Process, is the magnesium ions in the Great Salt Lake brine. U.S. Magnesium is in the process of expanding its production. The following Tables 1 and 2 are excerpted from the reference 13 showing comparisons of operating parameters of industrial cells.

Table 1. Electrolyzer Comparison

<u>Item</u>	<u>Diaphragm Cell</u>	<u>Diaphragmless Cell</u>	<u>USM cell</u>
Operating Temperature	704–760°C	704–760°C	676–704°C
Chlorine Strength	70%	80%	>96%
Chlorine Recovery	85%	98%	99.9%
Power, kwh/kg	18.8 to 19.9	16.6 to 18.8	12.1 to 14.3
Voltage	6.5 to 7.0	6.0 to 6.3	4.5 to 5.0
Production (Max)-T/day	0.8 – 1.0	1.2 – 1.6	2.8 -3.0
Melt Capacity – tons	20	42	90
Cell life, days	180 – 240	300 -600	1000 – 1500

Uday Pal developed a technique of using a yttria stabilized zirconia oxygen ion conducting membrane to electrolyze magnesium oxide in a magnesium fluoride containing melt, where the magnesium is produced at the cathode and oxygen evolved at the anode.¹⁴ Adam Powell, of Metal Oxygen Separation Technology – MOST, presented a paper on small-scale (40 gm per day) magnesium production using a solid oxide membrane cell using a molten silver anode. The magnesium vapors at the cathode are collected in a condenser located at the bottom of the cell.¹⁵ MOST is pursuing piloting this technology further towards low cost, larger-scale magnesium production.

Table 2. Comparison of Industrial DC Cells

<u>Company</u>	<u>Cell</u>	<u>Cell Type</u>	<u>Voltage, V</u>	<u>Power kwh/kg</u>	<u>tons Mg/day</u>
Norsk-Hydro	DLE	Monopolar	5.3 V	13.0	>4.0 t/d
Alcan Int.	MP3	Multipolar	NA	10	NA
MagCorp	M-Cell	Monopolar	5.0 V	12	2.8 t/d
AVISMA	Bottom entry	Monopolar	4.7 V	13.5	0.7 t/d
UKTMP (Kaz)	Top entry -anode	Monopolar	4.8 V	13.2	1.8 t/d

It should be noted that the electrolytic magnesium process used to be the dominant magnesium process prior to the year 2000 with the western world producing most of the metal. The first decade of the twenty first century saw the process dominance reversed to thermal reduction of calcined dolomite with ferrosilicon in retorts developed in the 1940's for the Pidgeon process. Today, China produces over 600,000 tons per year, which is over 80 per cent of world magnesium production, using the thermal process.

High Purity Nickel Production by Electrometallurgy

High purity nickel is produced from primary ore stocks using many routes. Several of these routes are electrometallurgical in nature. These include electrowinning from chloride electrolyte, electrowinning from sulfate electrolyte, electrorefining of cast impure nickel anodes and electrorefining of cast matte anodes.¹⁶ Significant tonnages of high purity nickel are produced by all of these routes. However, the electrorefining processes utilize older technology and newer plants utilize electrowinning. In this section, the electrowinning processes will be briefly reviewed and recent developments discussed. A description of the electrorefining processes can be found in the literature.¹⁶⁻¹⁷

Electrowinning from Chloride Electrolyte: The electrowinning of nickel from chloride electrolyte is used in a process to treat ground matte. Chlorine gas is generated at the anode and is used in matte leaching. Plants that perform electrowinning from chloride electrolyte are located in France, Japan and Norway.

Nickel electrowinning from chloride electrolytes use divided cells with the anode typically placed in a frame wrapped in a polyester diaphragm. The frame and diaphragm allows for chlorine capture. Nickel is commonly plated on starter sheets which had been grown previously on titanium blanks for 1 to 2 days. Nickel can also be plated on masked titanium cathodes to produce nickel crowns. Chlorine evolves from coated titanium mesh anodes. Typically, cells operate at current densities around 230-280 A m⁻² with a cell voltage of 3 V and current efficiency ~99%.

Electrowinning from Sulfate Electrolyte: Nickel electrowinning from sulfate electrolyte is used in a process to treat ground matte and has been demonstrated for laterite processing. The acid generated during oxygen evolution at the anode is used during atmospheric and pressure leaching. Plants that use this technology are located in Canada, Finland and South Africa.

Nickel electrowinning from sulfate electrolytes uses divided cells with either the anode or cathode placed in a frame wrapped in a polyester diaphragm. Placing the cathode in a bag is more common practice. The diaphragm minimizes the diffusion of acid generated at the anode to the cathode. The catholytic pH needs to remain around 3.5 to avoid excessive hydrogen gas evolution on the nickel. Most operations add boric acid to help buffer the pH and/or sodium lauryl sulfate to help hydrogen gas bubble release. All except one plant use nickel starter sheets. Typically, cells with sulfate electrolyte operate at current densities around 200-250 A m⁻² with a cell voltage of 3.6-3.9 V and current efficiency of ~95%.

Recent Developments: Recent developments in the electrometallurgical production of primary high purity nickel has been driven by the re-design of one operation and the design of another. Anglo American Platinum commissioned a new nickel tankhouse at Rustenburg, South Africa in 2011. Vale has designed a new nickel tankhouse for construction at Long Harbor, Newfoundland, Canada which should be commissioned in 2013.

The Rustenburg tankhouse has implemented several new technologies. These include permanent titanium cathodes, mechanical stripping, anode skirts and cell hoods. The titanium cathodes contain three 3-mm holes which are filled during deposition and hold the deposits onto the cathode. The use of permanent cathodes have allowed the use of mechanical stripping. Finally, significant efforts were made to reduce worker exposure to aerosol and mist exposure. Thus, cell hoods and anode skirts have been employed.

The Long Harbor tankhouse will be novel in that it is designed to use a mixed sulfate/chloride electrolyte. As such, the tankhouse will use coated titanium anodes. As some chlorine gas will be evolved and used during concentrate leaching, the anodes will be bagged. As design details become available, it is likely that other innovations at Long Harbor will be revealed.

Titanium electrometallurgy

In order to assess the present state of the art of titanium electrometallurgy, it can be useful to recall the history of its technical developments. Details can be found in the literature¹⁸. Wilhelm Kroll, in his 1940 thermochemical process patent, was aware of the intrinsic technical limitation of his process producing solid metal, and in his 1959 review article¹⁹, predicted that electrolytic titanium process will be competitively operated within 5 to 10 years. However in his 1960 review article²⁰, he warned that there were fundamental problems to be solved.

Why electrolytic titanium? Because Ti is one of the few metals that is currently commercially produced in solid form by chemical reactions. Most commercial metals, and the greatest tonnages, are produced as liquids, or by electrolysis: Fe, Al, Cu, Zn, Pb, Sn, etc. In industrial operations, producing solid metals is inherently much more expensive than producing metals in the liquid state.

Then why is Ti not produced commercially by electrowinning? It was thought that the history of Ti production would follow that of aluminum – beginning with a primitive thermochemical process with expensive limited production for a few decades, and then evolving to a large-scale industrial modern electrowinning process. Instead, after over 70 years a Ti electrowinning

process-plant is not operative because of the following types of difficulties which have heavily retarded its development:

- 1) Titanium electrochemistry is not completely understood yet, because of insufficient fundamental understanding.
- 2) Titanium physical-chemical characteristics are challenging for current engineering materials of equipment construction.
- 3) Incredible conceptual confusion between electrolytic titanium extraction from Ti compounds dissolved in the electrolyte, and titanium metal cathodic reduction of surface oxides.

For titanium electrochemical systems, a specific electrolyte has not been found that is equivalent to cryolite for aluminum. The incomplete understanding of the functioning of the aluminum production cell provides inadequate aid to the understanding of titanium electrolysis. In fact the knowledge of the electrolytic process for producing aluminum is incomplete, and its theoretical foundation is not commonly accepted.

During the past century researchers did experimental work on the electrochemistry of titanium, without having the proper tools for understanding what they were doing. There are no textbooks which give a good treatment of electrode kinetics (dynamic electrochemistry).

Studying the published scientific literature it can be observed that most electrochemists still fear entering deep into titanium electrometallurgy. Available research tends to be performed under conditions that are commercially uninteresting²¹.

Considerable work was done in the past to determine values of physicochemical parameters in the absence of live electrochemical processes. Those data are often of little use for designing industrial electrowinning plants. An additional complication is the lack of reliable reference electrodes for electrochemical measurements in medium –high temperature molten salts.

The third difficulty in developing Ti electrowinning technology is related to conceptual confusion. Some historical perspective helps to understand the origin of this challenge.

Prof. Albert Schlechten, Kroll's principal coworker in Ti and Zirconium metallurgy, became head of the Metallurgy Dept. of the Colorado School of Mines in 1965. The author of this section of the article went to study at the CSM, where he worked on the electrolysis of Ti and learned about Ti metallurgy. In his M.Sc. thesis, he experimented with the cathodic reduction of Ti oxides on the surface of Ti metal in aqueous solutions (the electrolytic deoxidation of Ti oxides)²².

In 1973 the author returned to Italy and with his company GTT, in order to understand the mechanism of massive deoxidation. The Pb/Ac system was used as a model. Specifically, the cathodic reduction of PbO₂ in H₂SO₄ aqueous solution was studied in an effort to understand processes relevant to Ti.

The model was transferred in molten salts to study the Ti oxides massive cathodic reduction, t. In 1983 a patent was obtained²³. However there was, among others, a fundamental problem: the current collector, the electron conducting connection which was physically present in the PbO₂ electrode and in the Ti oxide covered Ti metal was very difficult to obtain with TiO₂ because of the way it was formed. The effect, of great industrial significance, was the very low current

density at the production electrode, which resulted in a very slow process rate, with long residence times and thus no commercial interest. Then, the fundamental and operative differences between electrowinning Ti from its compounds dissolved in electrolytes, and the cathodic deoxidation of Ti oxides on a Ti metal surface, became very clear.

Additional research resulted in further progress in Ti electrowinning technology^{24,25}. Although progress has been made considerable challenges remain for both molten fluoride electrowinning and deoxidation approaches to titanium recovery.

Advantages of high temperature electrolysis are described in the literature²⁶. The value of making liquid cathodic product is evidenced by the fact that many industrial metals are produced as liquids. Furthermore, in the case of titanium the physical metallurgical operations of the ingots are expensive, thus the electrowinning process should give a product with dimensions close to the final semi-finished product. All the advantages of aluminum electrolysis can be implemented in a titanium cell, in addition to the specific beneficial characteristics of the titanium system. At above 1700°C titanium forms a liquid cathode with all the process advantages which are: complete physical separation between the metal produced and the electrolyte, with no entrapped electrolyte as with solid cathodes, thus there is no need for product separation steps such as vacuum distillation or leaching; constant electrode surface area that permits the maintaining of best steady-state values for the electrochemical process parameters; shorter interelectrode distance, thus lower operating voltages, since there is no need for allowing space for irregular crystal growth; easier coalescence of micro drops and metal fog, that are liquid, into the liquid cathode surface with horizontal geometry, as compared to chloride systems with suspended solid metal particles on solid cathodes with vertical geometry. Further, titanium electrowinning has the following specific advantages with respect to aluminum electrolysis: raw material feeding is easier with liquid TiCl₄, compared with solid alumina that needs special equipment because of slow dissolution and hard crust formation; titanium metal has a higher melting point than its electrolyte (which is opposite to that of aluminum), and a larger difference in density, at the operating temperatures, between the metal and the electrolyte. The processing rate of the Ti cell is inherently higher than that of the Al cell because, at the higher temperature of operation, all the electrochemical parameters are more favorable, and also because of the need to generate enough heat to maintain the electrolyte temperature.

Presently, the following areas of the high temperature fluoride electrowinning still need research:

- a. Find anode material that resists chlorine gas evolution at 1800°C.
- b. Understand passivation conditions of liquid Ti cathode surface.
- c. Find electrolyte composition for best TiCl₄ gas absorption reaction.

Clearly, more research is needed to bring Ti electrowinning to commercial scale success, although a significant amount of progress has been made²⁷.

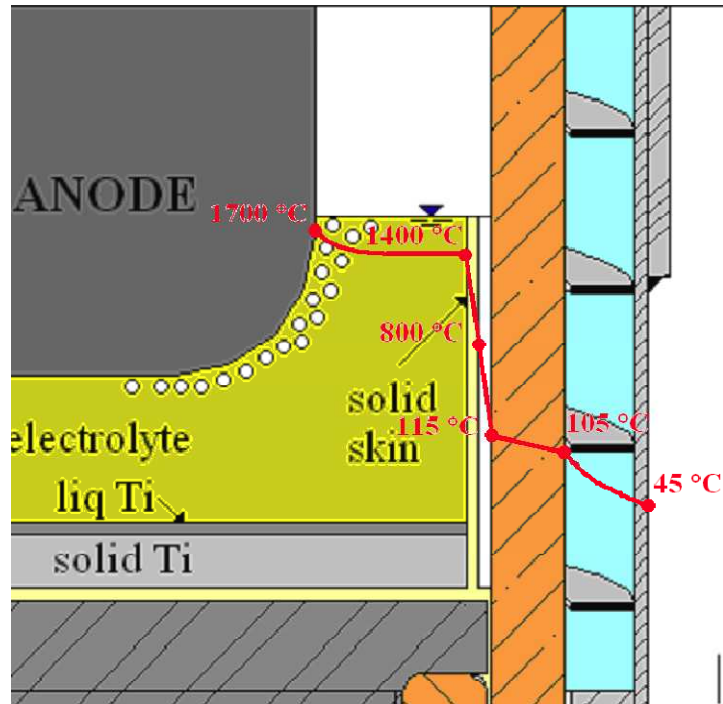


Figure3. Ti electrowinning cell in molten fluorides.

Zinc Electrowinning

Zinc electrolysis is an energy intensive process with specific electric energy consumption of about 3.5 KWh/Kg amounting to annual energy consumption of about 1GWh/y for a 275,000 t/y zinc plant. The high energy consumption is due to the relative high cell voltage during electrolysis mainly caused by the anodic reaction of oxygen evolution. As the zinc deposition process is carried out from acidic solutions, the process is sensitive to trace impurities necessitating an efficient purification process. The purification process is based on cementing the impurities onto zinc dust. As the kinetics of cementation were not favourable, high quantities of zinc dust were required to remove the impurities. In addition, the zinc electrolysis was initially labour intensive necessitating high labour for harvesting the zinc from the aluminum cathodes.

Efforts were therefore placed over the years in identifying means of decreasing the cell voltage such as using improved anodes and technologies rendering easier the harvesting of the cathodes of zinc. In addition, research activities were also focused in improving the purification process thus decreasing the zinc dust consumption. Continuous work is also conducted in the area of recycling of zinc from various industrial residues. This section of the article describes the various stages of technology improvements in the zinc electrowinning process with examples drawn mainly from the Canadian industry.

The most important development in the electrowinning of zinc was the mechanical stripping of the zinc cathodes that allowed for increased productivity and usage of larger cathodes. As a result of this technology, the zinc plants improved their productivity expressed in man-hour per tonne of zinc produced from 8.1 in 1993 to 5.1 in 2003.

The first technology for the automated stripping machines was developed in Europe (Italy and Belgium) and several variations and new designs were later on adapted and installed in the Canadian zinc plants. Optimization of the stripping machines to fit the needs of each zinc plant was conducted relating to the type of plastic edges as well as the insulators.

Canadian Electrolytic Zinc (CEZ) adopted the Vieille Montagne stripping machine in 1976. In 1991, a new Cellhouse No 3 was commissioned with a 230,000 t/y capacity. Cominco based on a pilot plant data initiated in 1977 and commissioned in 1983 an ultra-modern and highly automated cellhouse. Their operation is at low current density of 400-440 A/m² rendering the operation more energy efficient. Cominco also developed a new contact system to allow operation at low current densities

Various versions of electric contacts were also developed by CEZ and other zinc plants. The improvement in labour productivity in these new cellhouses has been dramatic resulting in a labour intensity reduction from 2-2.5 to about 0.6-0.8 manh/tonne.

At Kidd Creek, in the mechanical stripping, several options were evaluated (top down" knife entry at solution line, Flexing & Rapping and prepared edge of electro deposited Zinc through insulating disk cathode attachment) before a final design of the stripping machine was selected.

In February 1999, all of cell house was autostripped and final manpower reductions were realized. In November 1999 four Autostrippers were installed delivering 34 rows per day routinely.

Outotec has also provided various designs of zinc electrolysis processes and equipment for greenfield plants and modernizations, based on its own process knowledge, continuous R&D and technology. Outotec material management system, with key equipment such as automatic cathode stripping machines, anode washing/flattening machines and cellhouse cranes, provides safe material flow and the smooth harvesting of cathodes with the minimum labour force.

Fundamental work on electrolysis was conducted by the university of British Columbia and Teck as well as by Hudson Bay, Kidd and CEZ²⁸⁻³⁰. The effect of impurities on zinc electrolysis was investigated by Canmet³¹. The University of Laval in Quebec, Dr E. Ghali and his team was also active in the study of lead anodes by conducting work on the corrosion of various Pb- Ag anodes³².

Noranda technology Centre (Houlachi et al) developed an on line sensor for detecting the quality of the purified solution entering the cellhouse³³. This sensor was very useful during process upsets affecting the quality of the electrolyte.

Insoluble anodes for Zinc EW: Insoluble anodes are widely used in industrial hydrometallurgical processes. Anodes based on lead alloys have been used for over 100 years in the electrowinning

of zinc and copper. Good anode materials must be able to pass high current densities, survive in aggressive environments and possess very good corrosion and wear resistance.

Casting of lead alloy anodes used to be the standard method of producing anodes for the metal electrowinning industry. However, casting defects and holes contribute to penetrating corrosion and premature failure in the cast anodes, and cold or hot rolling technologies have replaced the casting method of making anodes³⁴.

The effect of surface finish has also been found to affect the corrosion of the anodes. The management of the protective PbO₂ layer is important to enhanced anode performance in its harsh working environment. A surface pre-treatment method for Pb anodes rapidly produces a thin adherent glass film of MnO₂ which facilitates adherent PbO₂. Another pre-treatment method was developed by CEZ using a KMnO₄ solution where the new anodes are immersed for a certain time to produce an MnO₂ film at the surface of the electrode. CEZ also use an alternative surface treatment consisting of peening the surface of the anode with various abrasive elements including sandblasting to enhance the corrosion resistance. The peening modifies the surface texture, enlarging the surface area and enhancing adhesion of active materials or coatings such as MnO₂ which further protects the anode during electrolysis.

Teck has preconditioned lead anodes by electrochemical treatment in fluoride containing solution to form an adherent PbO₂ layer, to which MnO₂ naturally adheres³⁴.

Integran Technologies in Toronto developed a method of improving anode performance by a process of selective and repetitive recrystallization, whereby cast or wrought starting stock of commercially pure lead, or of common electrowinning electrode material, is sequentially deformed (e.g., rolling, pressing, stamping, extruding, drawing, etc.) and heat treated to induce recrystallization³⁵ (Lehockey et al., 2000).

Alternative anodes for metal electrowinning: The main disadvantages of lead anodes are elevated power consumption, corrosion products fouling the cathode deposit, and generation of a hazardous by-product. If lead-alloy anodes are to be replaced, the alternative anodes must be economically justifiable. Currently, DSA (dimensionally stable anodes) are used in electrowinning in chloride-based solutions and recovery of metals from dilute solutions. Recently, implementation of the titanium coated anodes has been made in the copper electrowinning. The advantages of using DSA anodes in zinc electrowinning are: the ability to operate at higher current densities, the elimination of sludge, and the ability to operate at a reduced anode voltage (300 mV less than Pb-alloy anodes).

Over the past three decades, several attempts have been made to develop a DSA technology for sulfate-based electrowinning processes. The most significant technologies in terms of size of commercial testing have been standard DSAs and hybrid lead/coated titanium anodes. DSAs were investigated in the 1970s with several problems namely, high initial cost of the titanium structure, susceptibility to significant shorting damage, and relatively short lifetimes (about 1 year). These problems made the replacement of lead-alloy anodes uneconomical.

Improvements in DSA technology, such as reducing manganese deposition through amorphous coatings, combined with high energy costs may render their usage viable. In addition, environmental issues with the lead anodes could also assist in the implementation of alternative anodes³⁶.

Purification Process: At the University of British Columbia researchers have studied the electrochemical mechanisms by which cobalt is removed during cementation. Underpotential deposition of zinc is claimed to occur and hinder the removal of cobalt³⁷⁻³⁹. The formation of mixed Cu-Sb-Zn-Co phases has proven to be critical to the removal of cobalt. During cementation, basic zinc salts precipitate and passivate the zinc dust, hindering the zinc deposition reaction.

An important contribution in the understanding of cobalt cementation was conducted in 1990 at the Noranda Technology Centre by Houlachi et al on the effect of organics (flocculants and glue) on the kinetics of cobalt cementation⁴⁰. These reagents are used during settling of the solids in the leaching section of the plant. Accidental high residual concentration of these reagents could at times report to the purification section of the plant. It was found that the presence of these organics hinders the cementation of cobalt ions onto zinc dust. More research work was conducted in this area at a later stage by the University of British Columbia (Dreisinger and his team).

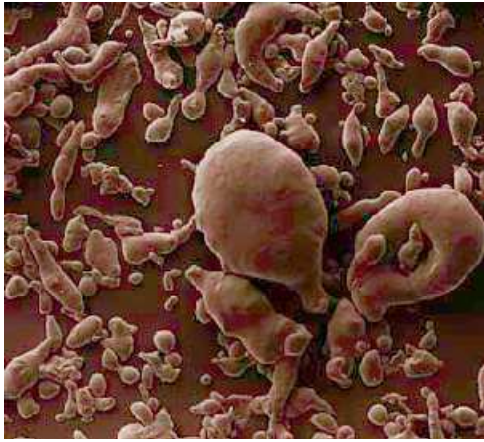
At Kidd Creek the use of a cementation reactor developed by Outotec was installed in 1989 in their purification process for cadmium removal. This is an innovative technology to improve the kinetics of cementation while producing a relative pure cadmium product. Kidd had made significant process improvements to adapt this technology to their process. The principle of this technology is based on the use of a high concentration zone of zinc particles fluidized by solution flow to suspend the particles in the various reactor compartments. Flocculants are added to the solution to prevent the agglomeration into excessively large zinc particles. The cadmium removal system is depicted in Figure 4.



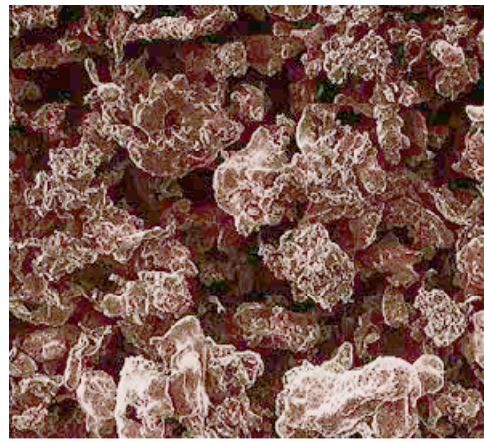
Figure 4. Fluidized bed reactor for cadmium removal

Another important technology developed by Canadian Electrolytic Zinc (CEZ) was the use of water atomized zinc dust for the purification process⁴¹. This technology is based on the formation of large surface area zinc dust particles. These particles provide larger cathodic sites for the cementation reactions (Figures 5a and 5b). As a result the zinc dust consumption during the purification process is significantly reduced. Other advantages include a reduction in energy consumption by the atomizer and a smaller footprint. The process has been licensed to Cominco.

a



b



Figures 5a and 5b.

Air atomised zinc dust 20µm view Water atomised zinc dust 20µm view

Zinc Recycling: Processing secondary zinc is less energy intensive than primary zinc. Galvanised steel manufacture is the segment exhibiting the most growth in zinc consumption, and makes up nearly half of total global zinc demand. Galvanized steel is used mainly for the construction and automotive industries. Today, over 30% of world zinc comes from secondary materials. Recycling of galvanised steel by electric arc furnaces (EAF) generates large tonnages of dust; more than 6 Mt/y of filter dust waste from EAFs all over the world. The Waelz process is the most common process to recover zinc from filter dusts from EAFs and represents 80% of the dust recycled. The second technology is based on rotary hearth furnaces and another new technology like Primus is being applied industrially. Primus has the advantage of producing a pig iron by-product instead of slag.

In Europe and North America, approximately 1.2-1.4 Mt/y of filter dust is produced. In 1997, in the European Union the Waelz process was used on 45% of the total amount of dust; ten years later, in 2007, the amount of dust processed through Waelz furnaces had risen to 80-90%, totaling around 250,000 t of zinc content. Currently, in the US, the recycling ratio of dusts accounts for 50-55% of total production. In spite of the good prospects, there are some factors that limit use of zinc recycling in primary zinc refineries: the complex composition of the dust leads to treatment difficulties. In addition to metallic impurities, the halogens (chloride and fluoride) cause problems since they concentrate in the electrolyte and thereby make it unsuitable for direct feed to zinc EW. Chloride attacks the anode, which is made of lead, and chlorine gases may be formed and thus be a hazard to worker's health.

Thus, the maximum chloride level might be in the range of 50-100 ppm for the production of high quality zinc. Typical zinc sulphide concentrates have a chloride content of 5-10 ppm while washed Waelz oxide contains above 1,000 ppm and unwashed Waelz oxides account for 5-8% chloride. As a consequence, only washed Waelz oxides can be fed to the roaster in a primary zinc refinery after blending with sulphide concentrates in a proportion not higher than 15-20% of its total capacity, in order to keep the heat balance and the impurities under control. That limitation disappears when the ZINCEX technology is used to process washed or unwashed zinc

oxides, in such a way that eventually a conventional zinc refinery can be fed with 100% recycled zinc.

The ZINCEX solvent extraction (SX) system is designed to be a “perfect barrier” for metallic impurities (Cd, Cu, Ni, Co, etc), halogens (Cl, F), alkaline metals (Na, K), and other components like Ca, Mg, Mn, etc. The SX process is much simpler and totally automated, requiring low labour and minimum reagent and energy consumption.

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