FINAL TECHNICAL REPORT

Project Title: AN INSOLUBLE TITANIUM-LEAD ANODE FOR SULFATE ELECTROLYTES

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Abstract

The project is devoted to the development of novel insoluble anodes for copper electrowinning and electrolytic manganese dioxide (EMD) production. The anodes are made of titanium-lead composite material produced by techniques of powder metallurgy – compaction of titanium powder, sintering and subsequent lead infiltration. The titanium-lead anode combines beneficial electrochemical behavior of a lead anode with high mechanical properties and corrosion resistance of a titanium anode. In the titanium-lead anode, the titanium stabilizes the lead, preventing it from spalling, and the lead sheathes the titanium, protecting it from passivation.

Interconnections between manufacturing process, structure, composition and properties of the titanium-lead composite material were investigated. The material containing 20-30 vol.% of lead had optimal combination of mechanical and electrochemical properties. Optimal process parameters to manufacture the anodes were identified. Prototypes having optimized composition and structure were produced for testing in operating conditions of copper electrowinning and EMD production. Bench-scale, mini-pilot scale and pilot scale tests were performed. The test anodes were of both a plate design and a flow-through cylindrical design. The cylindrical anodes were composed of cylinders containing titanium inner rods and fitting over titanium-lead bushings. The cylindrical design allows the electrolyte to flow through the anode, which enhances diffusion of the electrolyte reactants. The cylindrical anodes demonstrate higher mass transport capabilities and increased electrical efficiency compared to the plate anodes.

Copper electrowinning represents the primary target market for the titanium-lead anode. A full-size cylindrical anode performance in copper electrowinning conditions was monitored over a year. The test anode to cathode voltage was stable in the 1.8 to 2.0 volt range. Copper cathode morphology was very smooth and uniform. There was no measurable anode weight loss during this time period. Quantitative chemical analysis of the anode surface showed that the lead content after testing remained at its initial level. No lead dissolution or transfer from the anode to the product occurred.

A key benefit of the titanium-lead anode design is that cobalt additions to copper electrolyte should be eliminated. Cobalt is added to the electrolyte to help stabilize the lead oxide surface of conventional lead anodes. The presence of the titanium intimately mixed with the lead should eliminate the need for cobalt stabilization of the lead surface. The anode should last twice as long as the conventional lead anode. Energy savings should be achieved due to minimizing and stabilizing the anode-cathode distance in the electrowinning cells. The anode is easily substitutable into existing tankhouses without a rectifier change.

The copper electrowinning test data indicate that the titanium-lead anode is a good candidate for further testing as a possible replacement for a conventional lead anode. A key consideration is the cost. Titanium costs have increased. One of the ways to get the anode cost down is manufacturing the anodes with fewer cylinders. Additional prototypes having different number of cylinders were constructed for a long-term commercial testing in a circuit without cobalt. The objective of the testing is to evaluate the need for cobalt, investigate the effect of decreasing the number of cylinders on the anode performance, and to optimize further the anode design in order to meet the operating requirements, minimize the voltage, maximize the life of the anode, and to

balance this against a reasonable cost for the anode. It is anticipated that after testing of the additional prototypes, a whole cell commercial test will be conducted to complete evaluation of the titanium-lead anode costs/benefits.

Project Objective

The principal goal of this project was to optimize the titanium-lead anode composition, structure and fabrication technology, fabricate bench-scale, mini-pilot scale and pilot scale prototypes, and conduct performance testing of the prototypes in copper electrowinning conditions as a possible replacement for a conventional lead alloy anode, and in manganese dioxide production conditions as a possible replacement for a conventional titanium anode. Efforts were directed towards developing insoluble anodes of both a plate design and a flow-through cylindrical design with longer life, higher mechanical strength, dimensional stability and uniformity, improved operability and higher quality of the product for industrial electrowinning of copper and manganese dioxide production.

Background

The insoluble titanium-lead anodes are made of titanium-lead composite material produced by techniques of powder metallurgy – compaction of titanium powder, sintering and subsequent lead infiltration [1,2]. Titanium and lead are combined on a macroscopic scale. In the titanium-lead anode, titanium stabilizes lead, preventing it from spalling, and the lead sheathes the titanium, protecting it from passivation. Copper electrowinning and electrolytic manganese dioxide production represent the target market for the titanium-lead anodes. Electrowon copper and EMD are manufactured on a very large scale.

A growing percentage of the world's copper is produced hydrometallurgically, by the leach-solvent extraction-electrowinning route [3-5]. Copper electrowinning is a key component of the hydrometallurgical approach. In a conventional copper electrowinning cell, the cathodic reaction is the electrodeposition of copper from an aqueous solution of copper sulfate containing free sulfuric acid, and the anodic reaction is the dissociation of water into hydrogen ions and oxygen. The deposition of copper occurs on copper starter sheets, titanium blanks or stainless steel blanks. Anodes provide an adequate surface for oxygen evolution. The essential requirements for the anodes are electrochemical stability in sulfate electrolytes, resistance to the chemical effects of oxygen liberated on the anode surface, low oxygen overvoltage, mechanical stability and structural integrity under operating conditions, product quality and environmental safety.

Lead-based anodes are generally used in electrochemical processes where the electrolyte contains sulfuric acid. Lead alloy anodes (Pb-Ca-Sn alloys) are currently the most common anodes in the copper electrowinning. A major problem with the lead anodes is lead dissolution and transfer from the anode to the product. A lead oxide layer forms on the lead anodes in the electrowinning cell. This layer can spall off the anode surface, and flakes of lead oxide can attach to the growing copper deposit, leading to lead contamination in the final product. To stabilize this oxide layer and prevent spalling under controlled operating conditions, cobalt sulphate is added to the electrolyte circuit. At present, levels of 120 ppm cobalt are sufficient in stabilizing the lead oxide layer. The cost of the cobalt is a significant operating cost, which could be eliminated through the use of the titanium-lead anodes.

The hydrometallurgical production of copper is extremely energy intensive. Electricity accounts for a significant part of the cost of production. The energy consumption in the copper electrowinning step represents more than ¼ of the total energy requirement of copper production. The titanium-lead anodes could reduce the energy use as a result of increased cell energy efficiency, and could offer an opportunity to lower operating costs of the electrowinning.

EMD is widely used as a solid-state oxygen electrode in dry-cell batteries [6]. EMD is manufactured by electrolyzing acidified manganese sulfate solution and depositing the product on an insoluble anode. The requirements of the anode for the deposition of EMD are long-term resistance to warping from the stresses of EMD removal by hammering, tight adhesion of EMD to the anode, resistance to corrosion from sulfuric acid, low tendency to develop high electrical resistance at the anode/EMD interface from higher current density, lower temperature or higher acid-to-manganese ratio in the electrolyte, and long life. Commercially pure titanium is used as anode material. The titanium anodes are not energy efficient. They do not pass current satisfactorily because of the buildup of oxide coatings and passivation. The main advantage of the titanium-lead anodes over the pure titanium anodes for the EMD deposition would be greater avoidance of high electrical resistance and passivation at the anode surface under a wider range of electrodepositing parameters, which could yield significant power reduction and cost benefits.

Data and Discussion

Optimization of Technology

Titanium powder metallurgy related journals, commercial on-line databases, materials organizations publications and patents were reviewed to evaluate the current status and future direction of the titanium powder availability and powder metallurgy manufacturing processes for production of metal-metal composites, including infiltration of porous metal matrix with metal filling [7-18]. Based on the review and analysis, a series of experiments were conducted in order to investigate relationships between titanium powder morphology, purity, particle size distribution and processing conditions. The technological properties (particle size, apparent density and compressibility) of several titanium powder grades (sodium reduced, magnesium reduced, calcium reduced and HDH titanium), and consolidation conditions for titanium compacts having porosity about 20% to 60% were investigated.

Titanium porous plates about 10 inch long, 8 inch wide and 0.25 inch thick were produced using Mg reduced titanium powder (-630+180 micron) and Na reduced titanium powder (-149 microns). The production method consisted of pressing and sintering under vacuum at temperatures in the range of 1000- 1200 ^{o}C for about 2 - 4 hours. The sintered plates were rolled at room temperature for additional densification. Effects of titanium powder characteristics on sintering, rolling and metal-working parameters were studied. The Na reduced titanium powder has lower cost and better ability to be processed into porous compacts with a wide range of porosities compared to other evaluated titanium powder grades.

Based on analysis of chemical and mechanical nature of the interfaces between titanium and lead, the prevalent ways to carry out lead infiltration of the titanium matrix and to obtain a pore-free homogeneous titanium-lead structure were determined. Dependence of wetting and reaction conditions between titanium and lead upon temperature and time was evaluated. The contact angle formed between liquid lead and solid titanium was close to zero at 650-700 ^{o}C. When the contact angle was zero, the liquid lead spread across the solid surface of titanium. The aim of infiltration was to obtain a pore-free titanium-lead composite structure. It is detrimental to achieve a satisfactory bonding of titanium and lead particles during the infiltration and keep reaction between the metals to a minimum in order to prevent erosion of titanium matrix. The infiltration process was carried out by placing the appropriate amount of solid lead below the porous titanium compact and applying heat in a neutral atmosphere. Once the assembly was heated to the sufficient wetting temperature, the liquid lead was drawn into the titanium compact by capillary action. Along with this process, infiltration of the porous titanium compacts by immersion in a lead bath at a temperature of about 650-700 ^{o}C was used. Provided that the porosity in the titanium matrix is interconnected, the distance penetrated is a function of time. The infiltration rates were investigated to determine the adequate duration of the infiltration process. Since residual porosity degrades the properties of composite material, the infiltration process should be fully completed. Upon completion of infiltration, excessive infiltrating metal should be removed from the surface.

10” x 8” x 0.25” titanium-lead plates having about 20 to 60 vol. % of lead and residual porosity 0-3% were fabricated. The plates were further machined to produce samples for structural analysis, mechanical testing, fractographic analysis and electrochemical testing. The test work was conducted at Drexel University.

The results of X-Ray diffraction tests indicated that the titanium-lead composite materials contained Ti, Pb and a very small amount of PbO, and did not contain any intermetallic compounds. An MTS tensile testing machine was used to test ASTM standard flat tensile specimens. Values for stress, strain and elastic modulus were calculated. The stress at fracture values were in the range of 80-250 MPA, and elastic modulus values – in the range of 50-90 GPA [19]. All of the test samples broke in the elastic regime before any plastic deformation could take place. The stress at fracture values, as well as the elastic modulus values, increased fairly linearly with increasing Ti content and decreasing Pb content (Figure 1, 2). Since pure Ti has an ultimate tensile strength of about 220 MPa, while pure Pb - 18 MPa, these results were expected. The fractography analysis showed that the mode of fracture was brittle and intergranular. The fracture occurred at the interface between grains (Figure 3). The tensile test data showed that Ti-Pb composites containing up to 35% Pb have ultimate tensile strength of 160 – 250 MPA. This strength is sufficient to prevent warping and extend the lifetime of the anode.

For electrochemical testing in copper electrowinning conditions, short-term deposition tests were performed in the electrolyte composed of 40 g/l Cu^{2+}, 190 g/l H_2SO_4 and 1.5g/l Fe^{2+} in distilled water at temperature 49 ^{o}C. 3 cm square Ti-Pb plates were used in the analysis, with a 3 cm square stainless steel plate serving as the cathode. The anode samples had Pb content in the range of 20 to 50 vol.%. A stainless steel cathode and titanium-lead anode setup was placed in the electrolyte solution 2 cm apart. A constant current density of 30 A/ft^2 was passed through the setup for two hours. The cell voltage and electrolyte temperature were measured in half hour intervals. After two hours, the current was interrupted, the anode and cathode were rinsed in

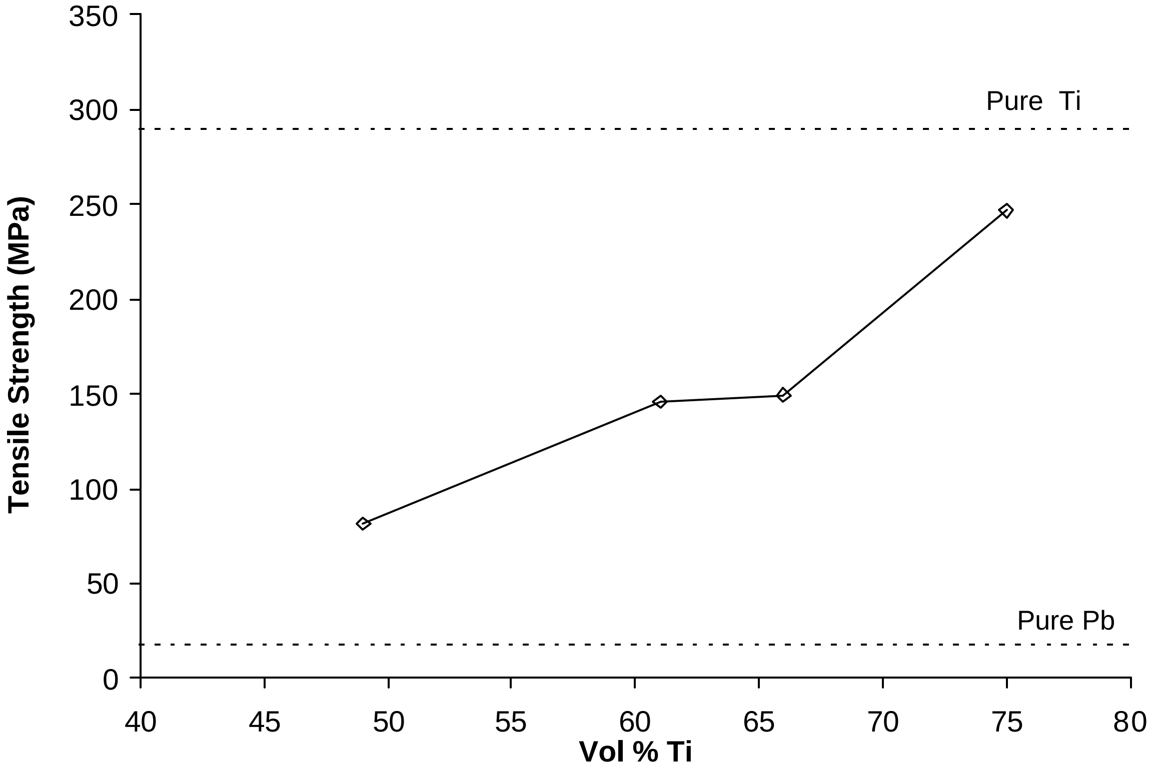

Figure 1 : Measured variation of the tensile strength of the Ti-Pb composite with varying Ti concentration.

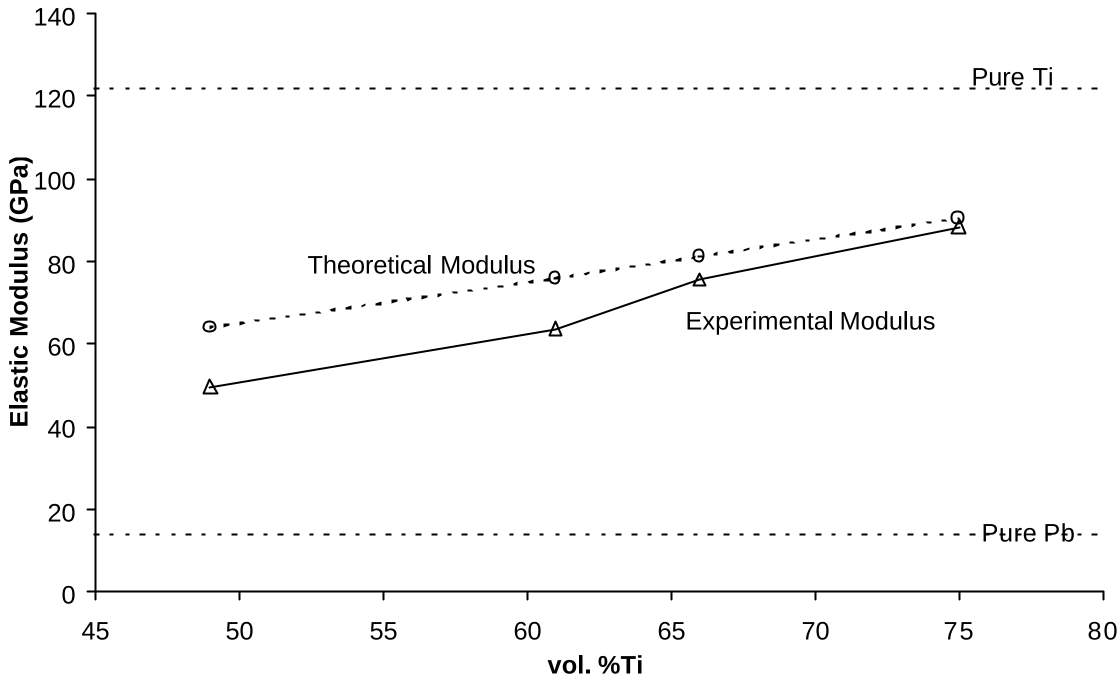

Figure 2 : Variation of the elastic modulus of the Ti-Pb composite with varying Ti concentration.

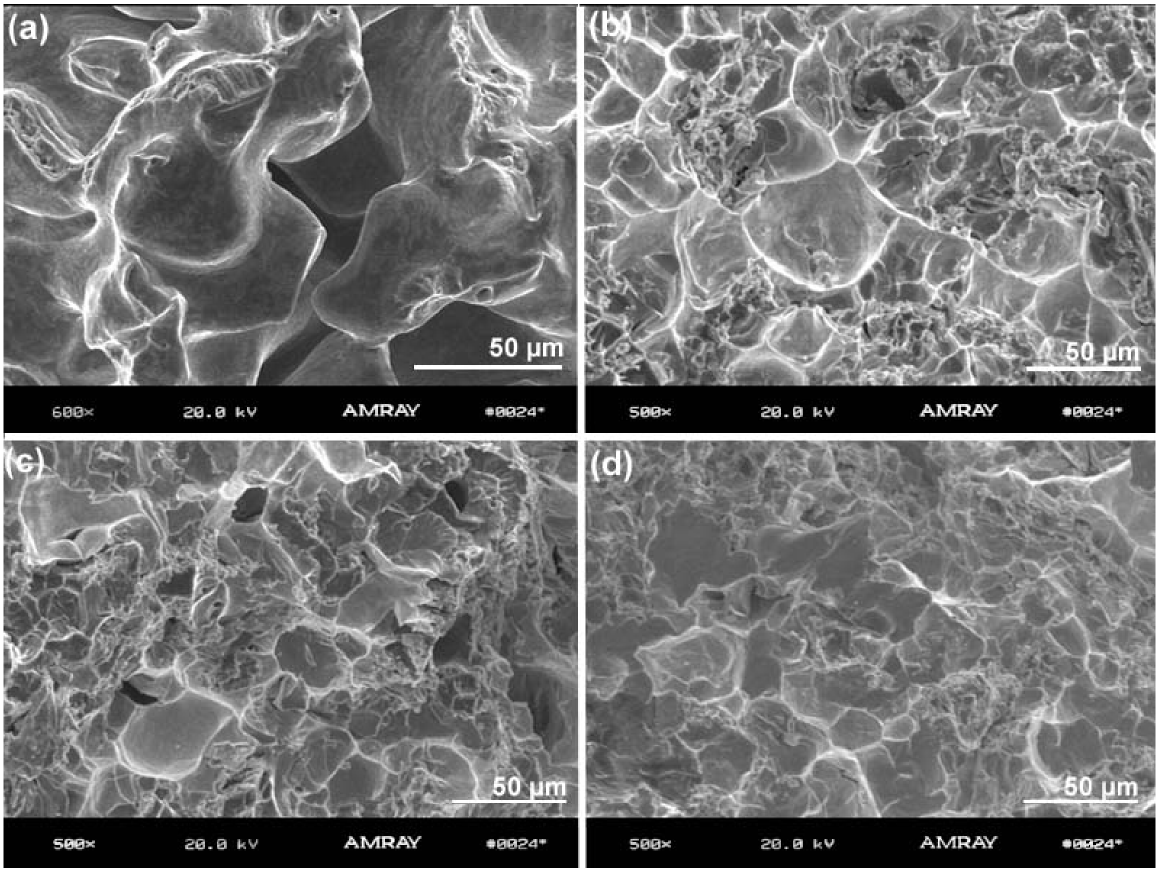

Figure 3: SEM images of Ti-Pb composite material fracture surface. Image (a) is 20% porous Ti; (b) 24 vol.% Pb, 75 vol. % Ti, 1% pores; (c) 51 vol.% Pb, 49 vol.% Ti, 0% pores; (d) 37 vol.% Pb, 61 vol.% Ti, 2% pores.

distilled water, dried and weighed, and the electrolyte was replenished. A lead alloy anode served as reference. The two-hour cycles were repeated up until 14 hours for each composition. All of the copper deposits were smooth, compact and uniform across the cathode surface. The lead content in the copper deposits was in the 2-3 ppm range. The voltage was 1.91-1.93 V. The current efficiency was about 90-95%. The voltage and current efficiency were fairly constant with all of the anodes. There was no measurable change in the anode weight or dimensions.

Significant amounts of cobalt are being added to rich in manganese sulfate electrolytes to retard oxidation of the Mn^{+2} to Mn^{+4} and prevent passivation of lead alloy anodes. To investigate the effect of manganese on the titanium-lead anode performance, the anodes were tested in the copper electrowinning acid electrolyte containing manganese: 44 g/l Cu, 180 g/l H_2SO_4, 1.5 g/l Fe and 13.4 g/l Mn, at 22.5 amps/ft^2 and 40 ^oC. The Ti-Pb anodes showed no sign of passivation with no cobalt added.

Based on the test results, the Ti-Pb anode materials retain essential electrochemical properties of the lead alloy anodes, while having significantly higher mechanical characteristics. The Ti-Pb material containing 20-30 vol.% Pb had the optimal combination of mechanical and electrochemical properties in the copper electrowinning conditions.

Fabrication of Ti-Pb anode prototypes and testing in EMD production conditions

Titanium-lead plates were produced for testing upon industrial operating conditions of the EMD production in a lab scale cell at Delta EMD. The objective of the experiments was to compare the Ti-Pb anodes containing 20 vol.% Pb and 35 vol.% Pb to a pure titanium anode and to a dimensionally stable anode DSA (composed of titanium with a thin coating of RuO_2 and IrO_2) in terms of their polarization under anodic load in an acidified $MnSO_4$ solution. Sandblasted commercially pure grade 2 Ti anodes are currently used for the deposition of EMD at Delta E.M.D. The DSA have limited commercial use in EMD production due to high cost and coating failure. Polarization of anodes as a function of current density during electroplating of manganese dioxide on the anodes was studied. The experimental setup was as follows: anodes had a geometrical surface area of average 18,5 cm^2; electrochemical cell volume was 300 cm^3; temperature = 87 ^oC; the solution consisted of acidified $MnSO_4$. The excitation signal was a simply linear current scan between the working electrode (anode) and the counter electrode. The scan was done from 100 A/m^2 to 170 A/m^2 at a rate of 10 A/m^2/s using a galvanostat, and the absolute current was calculated from each sample's geometrical surface area. The response signal that was measured was merely the polarization of the working electrode against an Ag/AgCl reference electrode that was in a liquid junction at 18 ^oC. As illustrated by the graph (Figure 4), no passivation of the Ti-Pb anodes was observed under a wide range of current densities, while the pure Ti anodes developed high electrical resistance and voltage. The anodes performed well in terms of polarization potential, specifically at current densities exceeding 150 A/m^2. It is anticipated that the Ti-Pb anodes would be capable of operating under a much wider range of EMD deposition parameters, such as current density, electrolyte temperature and sulfuric acid concentration, and would have a substantially lower tendency toward anodic passivation than that observed for conventional commercially pure titanium anodes. The titanium-lead anodes could provide technological and financial benefits for the deposition of EMD.

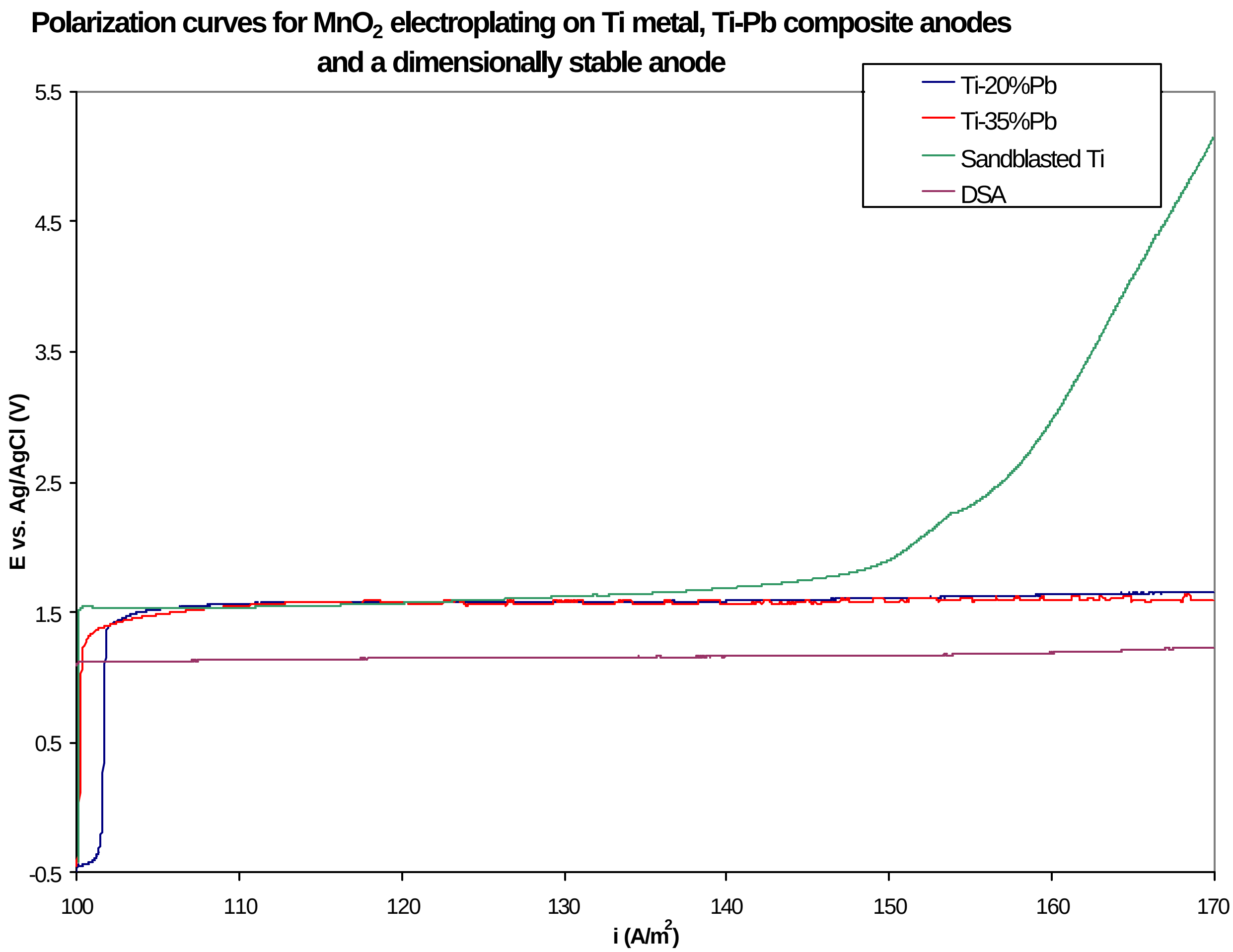

Figure 4: Polarization of anodes as a function of current density during electroplating of manganese dioxide.

Kerr-McGee Chemical LLC, a global inorganic chemical company, was contacted regarding further testing of the anodes in EMD deposition conditions. The company is currently using corrugated commercially pure titanium anode for the electrolytic removal of manganese dioxide from a solution of manganese sulphate [20]. The problem with the conventional titanium anode is its high tendency to develop high electrical resistance (passivate) at the anode/EMD interface. The company's requirement was that the test anode could be corrugated into triangular shape. The attempts to corrugate the titanium-lead plates into triangular shape were unsuccessful, and no additional information on the titanium-lead anode performance in the EMD deposition conditions was generated.

Further efforts were concentrated primarily on fabricating the anode prototypes for testing in copper electrowinning conditions.

<u>Fabrication of Ti-Pb anode prototypes and testing in copper electrowinning conditions</u>

Bench-scale and mini-pilot scale testing

Titanium-lead anode prototypes having from 20 to 35 vol. % Pb were manufactured for bench-scale testing in copper electrowinning conditions at Phelps Dodge Process Technology Center. The bench-scale anodes measured about 5 inches long by 3 inches wide. The cathode in each test was stainless steel. The tests were conducted by operating a small copper electrowinning cell continuously over 5-day periods at a current density of 30 amps/square foot of cathode surface. This corresponded to a current of 2.6 amps. Cell voltages in the testing measured 1.92 to 1.93 volts. The anodes appeared stable. The results of the bench-top testing were evaluated as favorable. Based on those tests, it was recommended that mini-pilot cell anode samples were fabricated for further testing on a mini-pilot scale.

Mini-pilot cell Ti-Pb anodes of a flat design were fabricated for testing in industrial conditions of copper electrowinning. The mini-pilot scale anodes measured approximately 43 inches long by 9 inches wide and were about ¼ inch thick. First, titanium porous plates were produced by cold rolling and subsequent sintering in dry argon atmosphere of 1100^{o}C for 2 hours. Then the porous plates were lead infiltrated at 650^{o}C for 20 minutes. The infiltrated plates had 30-35 vol.% Pb. Copper hanger bars were attached to the infiltrated plates by riveted joint and brazing. The upper zone (4 cm wide) of the plates was covered with a copper layer about 30 micron thick to provide a high quality electrical contact.

Along with the flat design, Ti-Pb mini-pilot cell anodes of an alternative flow-through cylindrical design were developed and manufactured for testing. The cylindrical anodes were composed of cylinders containing titanium or titanium-clad copper inner rods and fitting over titanium-lead bushings. Several variations of the mini-pilot cell cylindrical anodes, having diameter of cylinders in the range of $1^{1}/_{8}$ -inches to $^{9}/_{16}$ -inches were fabricated. The mini-pilot cell anode with dia. $1^{1}/_{8}$ -inches cylinders was produced using the following manufacturing process. First, titanium bushings $1^{1}/_{8}$" OD x $^{25}/_{32}$" ID x $1^{9}/_{16}$" L with porosity 20-25% were made from titanium powder by closed die compaction, using organic lubricants, and subsequent vacuum sintering of the compacts at 1200 ^{o}C for two hours. Then the porous bushings were put over titanium rods having dia. $^{25}/_{32}$ -inches and length 43 inches. The obtained cylinders were lead infiltrated by immersion into a lead bath of 650 ^{o}C for 15 min. During the lead infiltration process, along with filling the pores of the bushings, the lead also filled the spaces between the bushings and the titanium rods, and a metallurgical bond between the bushings and the rods was formed. The lead infiltrated cylinders were mechanically cleaned from the excessive lead. Six cylinders, each composed of the titanium rod with fitting over twenty five Ti-Pb bushings (75-80% Ti and 20-25% Pb), were joined by attachment (arc welding) to a connecting bar and a hanger bar, both made of titanium. A part of the hanger bar at the connection to the rods was covered with copper to improve the electrical contact. The cylindrical mini-pilot cell anode having dia. $^{9}/_{16}$ -inches cylinders was similarly fabricated by using $^{9}/_{16}$ " OD x $^{13}/_{32}$" ID x $^{9}/_{16}$" L bushings and dia. $^{13}/_{32}$ -inches titanium rods. Twelve cylinders, each composed of the titanium rod with fitting over sixty titanium-lead bushings, were joined into the cylindrical anode. The third anode with nine dia. $^{25}/_{32}$ -inches cylinders had $^{25}/_{32}$ "OD x $^{1}/_{2}$" ID x $^{25}/_{32}$" L bushings and dia. $^{1}/_{2}$ - inches titanium clad copper inner rods instead of pure titanium rods.

The flat and cylindrical anodes were tested in a copper electrowinning mini-pilot test cell at the Phelps Dodge Process Technology Center test facility. The tests were conducted in a 5-day continuous run at a current density of 30 amps/square foot of cathode surface (the current was 141 amps). The anodes were found to give satisfactory voltage and cathode deposit. Cell voltages (anode hanger bar to cathode hanger bar) typically measured 1,92 to 1.96 volts. The mini-pilot anode that had the titanium clad copper inner rods showed a small voltage reduction (of 30 mV) compared to the anodes having pure titanium inner rods. The Ti-Pb anodes operate approximately at the same voltage as the conventional lead alloy anodes. Figure 5 and Figure 6 illustrate the titanium-lead mini-pilot cell anodes after the tests.

The results obtained for the titanium-lead anodes were compared to the data for the conventional lead alloy anodes. The copper electrowinning process presently employs a lead-calcium-tin anode. The lead alloy anodes flake over time, depositing lead sludge in the bottoms of the electrowinning cells, which must be periodically cleaned. Lead particles are entrained in the copper deposit, thus contaminating the deposit with lead. Typically over 100 ppm of cobalt is added to the copper electrolyte to help stabilize the lead surface. Because electrolyte must be bled out of the system to control impurities, the cobalt is lost and must be replenished, which is an expense. In the Ti-Pb anode, the lead is intimately mixed with the titanium. The titanium helps to stabilize the lead, and therefore a significant operating cost of the cobalt could be eliminated. There are several other potential advantages of the titanium-lead anodes over the lead alloy anodes:

- A lifetime of about 10 years versus 5 years for the conventional lead alloy anodes.
- The chance of contaminating the copper cathodes with lead would be reduced. The active layer of the anode contains approximately 20-25 vol.% of lead. The lead is trapped and cannot dissolve.
- No spalling, no need for periodic cell cleaning. This would save on labor and lead disposal/recycling costs.

Figure 5: Picture of mini-pilot titanium-lead anode of plate design after testing.

Figure 6: Picture of mini-pilot titanium-lead anode of cylindrical design after testing.

- Higher strength and dimensional stability. No warping. Potential for energy savings due to minimizing and stabilizing the anode-cathode distance.
- Smoother and more uniform copper deposits.

The cylindrical anode design has the advantage of flexibility versus the solid slab design. The titanium-lead composite material is used on the surface of the cylindrical anode as a primary anode material. As to the supporting inner rods, along with titanium, it is possible to use other materials, such as titanium clad copper or titanium clad lead, having better electrical conductivity. The cylindrical design allows the electrolyte to flow through the anode, which enhances diffusion of the electrolyte reactants. The cylindrical anodes demonstrate higher mass transport capabilities and increased electrical efficiency compared to the solid slab anodes. Dimensional stability of the cylindrical anodes would enable better control of the anode-cathode distance. The processing of the cylindrical anodes is well suited to automatic mass production. Further efforts were devoted to fabrication and testing of the full-size cylindrical titanium-lead anode prototypes.

Pilot testing

Based on the mini-pilot cell test results, it was recommended to move to the next testing stage and conduct a pilot test of the full-size cylindrical titanium-lead anodes in one of the copper production tankhouses. Commercial size anodes having different number and sizes of cylinders have been designed. The anodes were engineered to be retrofittable to the current electrowinning cells (without a rectifier change). A full-size cylindrical titanium-lead anode (Figure 7) was fabricated and placed for phase one long-term testing in a commercial copper electrowinning cell at Phelps Dodge Morenci Stargo electrowinning plant.

The full-size test anode had thirty seven 0.781” dia. cylinders, about 3450 inch^2 active surface area (120% active surface area of a flat sheet with the same width and height) and about 167 pounds overall weight. The Ti/Pb ratio in the titanium-lead bushings was about 75-80%Ti to 20-25% Pb by volume. The cylinders were attached to a steer-horn hanger bar made of copper with a thin lead coating (to protect the copper from corrosion). Co-extruded titanium clad copper rods were used to connect the titanium inner rods to the hanger bar. The titanium clad copper rods are high conductive and can be easily attached to the copper hanger bar by welding. The titanium cladding thickness in the rods was about 0.050”.

The test plan included measuring:

- Cathode amperages.
- Anode to cathode voltages and anode contact resistance readings.
- Rectifier setting.
- Solution temperature.

Once a month the anode was lifted from the cell, and the following data were collected:

- Measurements of the diameter from five cylinders top, middle and bottom.
- Anode weight.
- Cathode weight in random places in the cell and the two on each side of the anode.
- Overall visual inspection and pictures.

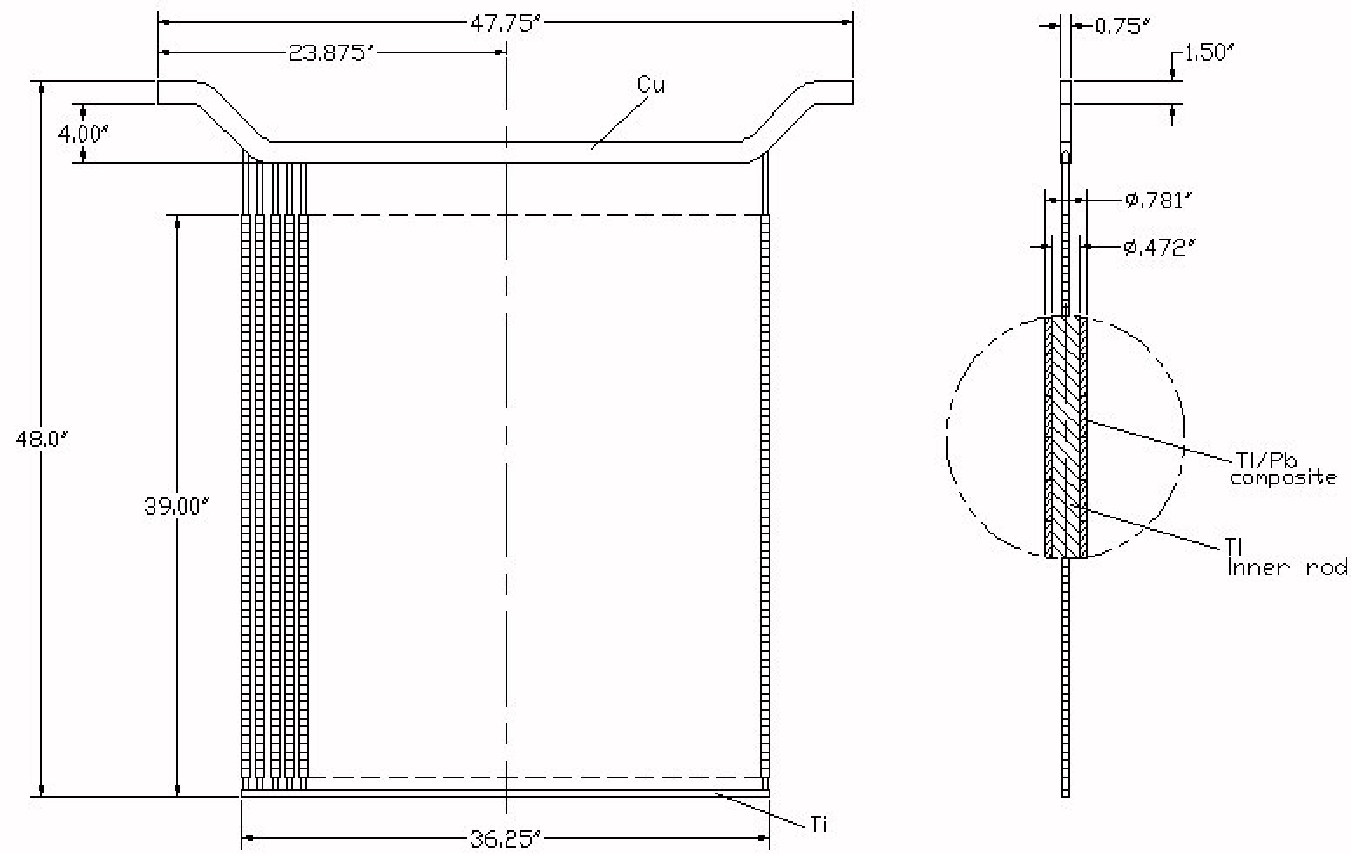

Figure 7: Drawing of a full-size Ti-Pb cylindrical anode for copper electrowinning.

All other anodes in the cell were the lead alloy anodes.

The anode performance in Stargo electrowinning conditions was monitored over a period of nearly 1 year. Picture of the titanium-lead anode after one-year testing at Stargo tankhouse is shown in Figure 8.

The test anode to cathode voltage was stable in the 1.8 to 2.0 volt range. There was a slight voltage reduction compared to a conventional lead alloy anode. The anode contact resistance was generally in the 0 to 60 mV range, which is similar to a conventional lead anode. The copper cathodes, which the anode was servicing, were very smooth, uniform, compact, and covering the whole surface (Figure 9). There was no measurable anode weight loss during this time period. The sizes of the cylinders have not changed. The full-size anode test results were found to be promising. The test data indicate that the titanium-lead anode is a good candidate for further testing as a possible replacement for a conventional lead anode.

Metallographic analysis of the post-test anodes

Optical, electron microscopy and spectroscopy study of the anode surface after the pilot testing was conducted at Drexel University. Prior to the testing, the Ti-Pb bushings contained about 20% Pb by volume, which corresponds to 38% Pb by weight. The main purpose of the anode analysis was to determine whether the lead content on the service of the anode decreased. Figures 10-12 show ESEM images of material at different magnifications. The light/bright areas are lead and lead oxide, while the dark areas are titanium. The chemical EDS analysis of the anode surface was done on the surface overall along with several points through the image shown in Figure 12. The results of chemical analysis are presented in table 1. Figure 13 shows chemical spectrum of the anode surface (overall image and various locations). The lead amount on the anode surface remained unchanged. This correlates with no measurable anode weight loss during the pilot test and ensures that the high quality of the product will be maintained. It is anticipated that by taking samples as a function of time and examining the lead content on the anode surface, it will be possible to extrapolate the anode life under copper electrowinning conditions.

Based on the collected long-term test data and the metallographic study of the anodes used in the cells, recommendations on further changes/modifications to the anode structure and process were made.

A key benefit of the titanium-lead anode design is that cobalt additions to copper electrolyte should be eliminated. Cobalt is added to the electrolyte to help stabilize the lead oxide surface of conventional lead anodes. The full-size titanium-lead anodes still have to be evaluated in the absence of cobalt additions to verify that the presence of the titanium intimately mixed with lead eliminates the need for cobalt stabilization of the lead surface. This has to be demonstrated in a circuit without cobalt. The anodes should last longer than a conventional lead anode, perhaps twice as long. The anode lifetime check under copper electrowinning conditions is still outstanding. Energy savings could be achieved due to minimizing and stabilizing the anode-cathode distance in cells. The anodes are easily substitutable into existing tankhouses.

A key consideration is the anode cost. Titanium rods are used in the anode structure. Titanium costs have increased recently. One of the ways to get the anode cost down is manufacturing the anodes with fewer cylinders.

Additional commercial size Ti-Pb anodes (Table 2, Figures 14, 15), in which the cylinders are reduced in progression from 30 cylinders down to 20 cylinders were designed and manufactured for the next phase of long-term testing. A full-size anode has a cumulative width of 36 inches and a cumulative height of 39 inches. The anodes with 30, 25 and 20 Ti-Pb cylinders dia. 27/32-inches have about 110%, 90 and 75% of the surface area of a flat sheet of corresponding cumulative dimensions. Different hanger bar materials (copper, Ti-clad copper) and more efficient ways of the hanger bar attachment (welding, press-fit) were used. The goal is to minimize the voltage and maximize the life of the anode, and also try to balance this against a reasonable cost for the anode.

Figure 8: Picture of titanium-lead anode after one-year testing at Stargo tankhouse

Figure 9: Picture of copper deposit produced using Ti-Pb test anode.

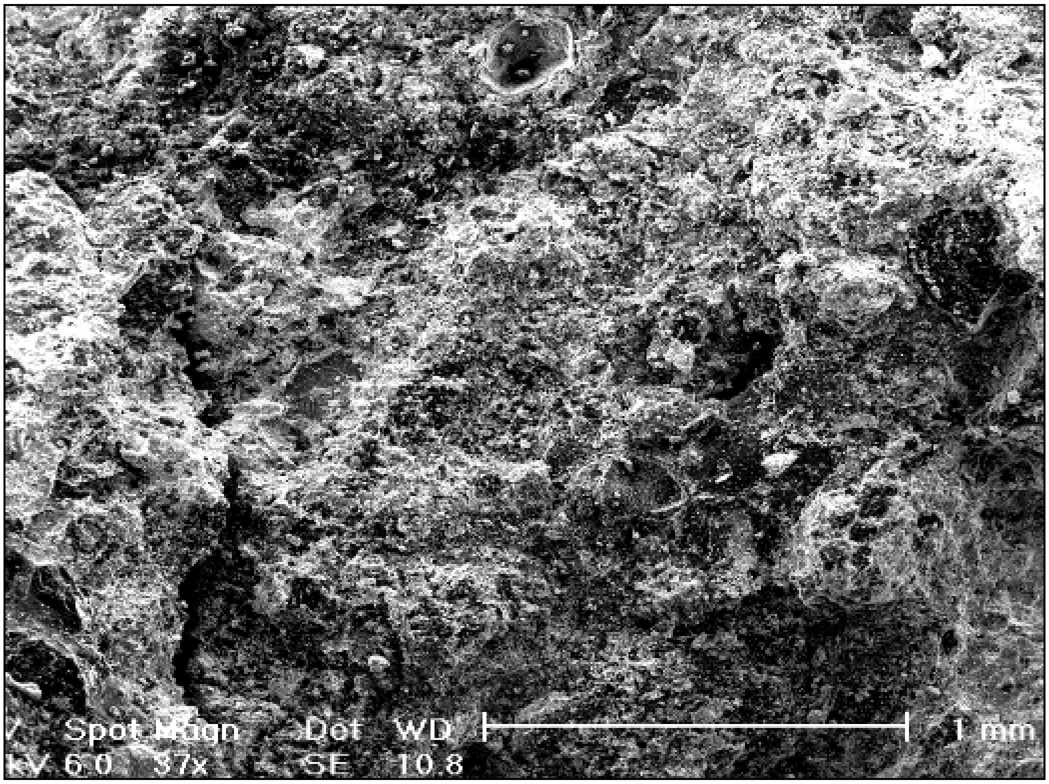

Figure 10: ESEM image of Ti-Pb anode surface, magnification 40x.

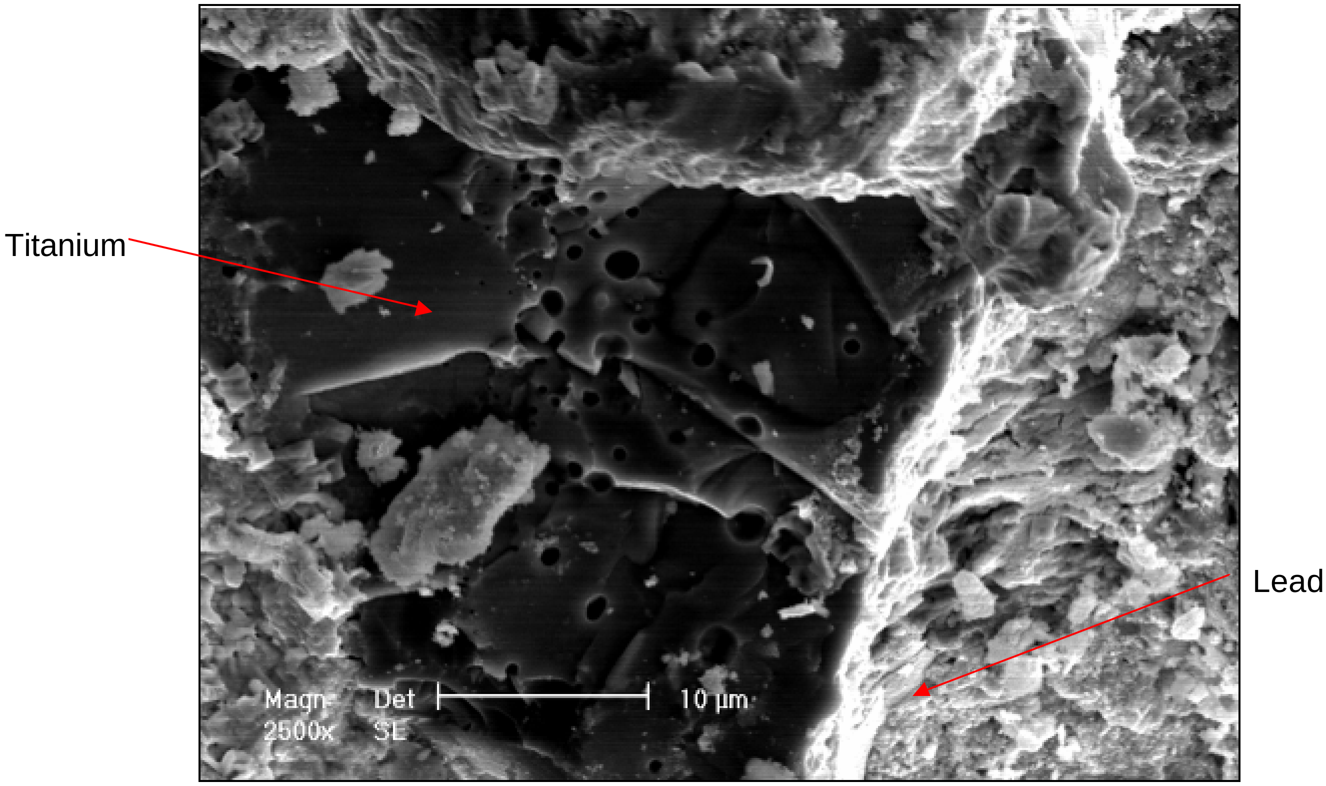

Figure 11: ESEM image of Ti–Pb anode surface, magnification 2500x.

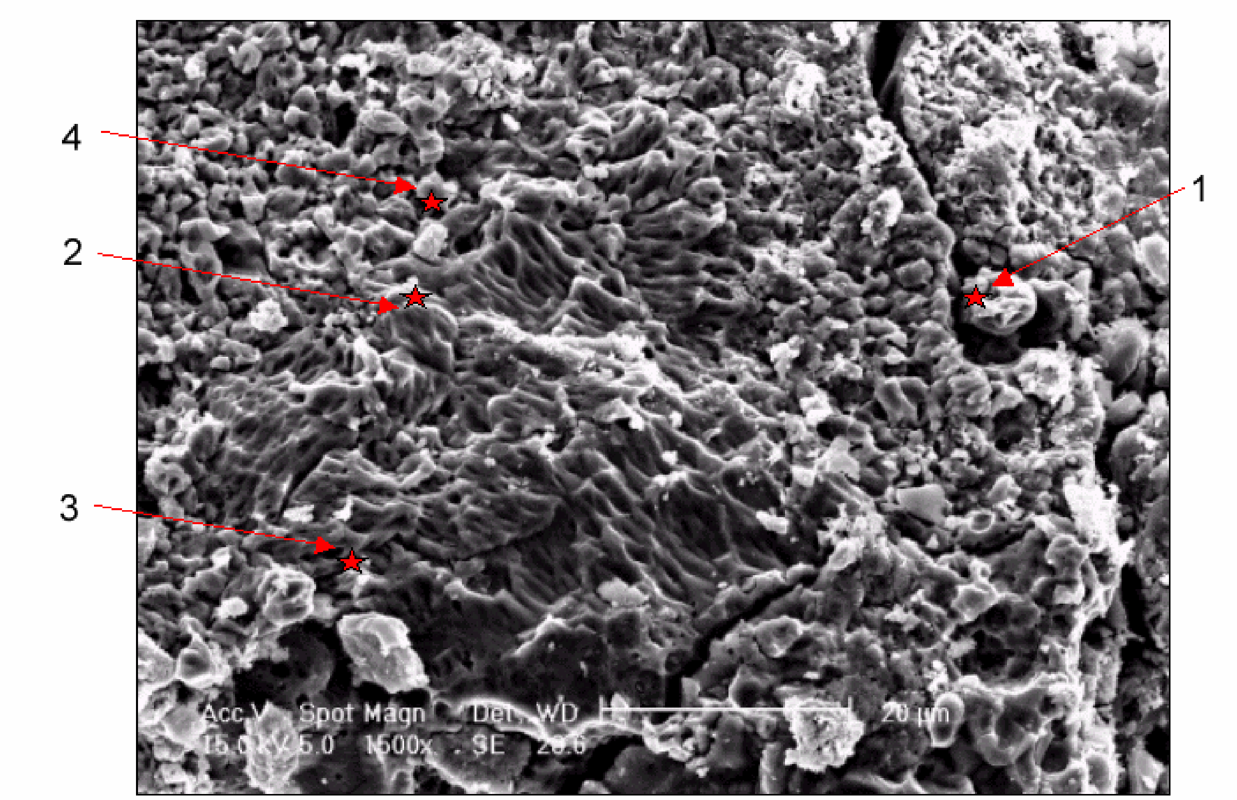

Figure 12: Surface image used for EDS analysis, magnification 1500x.

Table 1: Chemical analysis of Ti-Pb anode surface.

Element	*Wt%*	*At%*
Surface Image : Overall Analysis		
O K	12.68	39.35
TiK	49.85	51.67
PbL	37.47	8.98
Surface Image : Point #1		
O K	18.98	71.58
TiK	4.98	6.27
PbL	76.04	22.15
Surface Image : Point #2		
O K	7.97	41.34
TiK	16.34	28.33
PbL	75.69	30.33
Surface Image : Point #3		
O K	15.94	37.35
TiK	78.87	61.71
PbL	5.18	0.94
Surface Image : Point #4		
O K	11.33	27.67
TiK	88.67	72.33
PbL	0.00	0.00

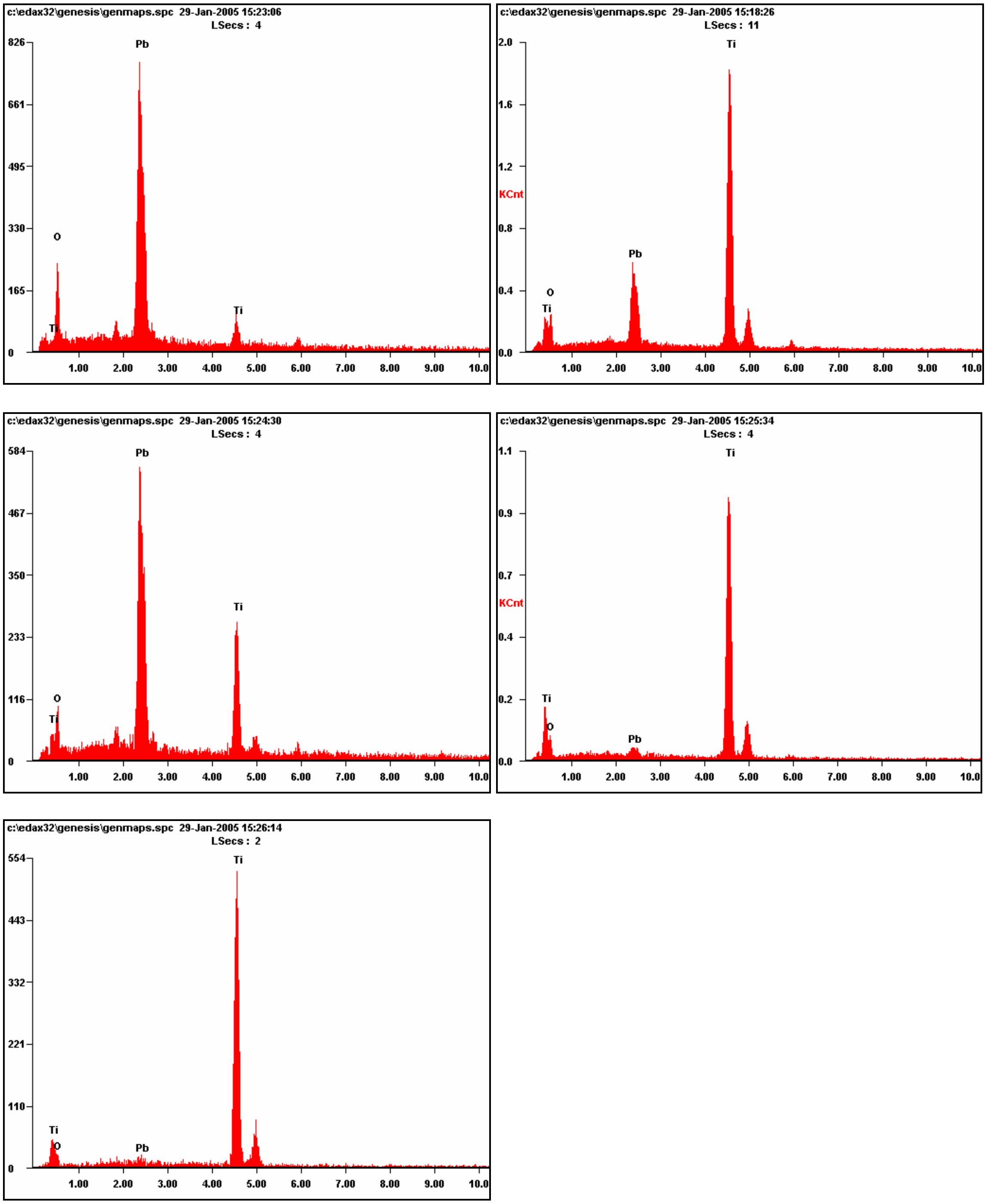

Figure 13: Chemical spectrum of Ti-Pb anode surface in various locations.

Table 2: Parameters of commercial size Ti-Pb test anodes.

NO	Diameter of Ti-Pb cylinders, inch	Number of cylinders	Hanger bar		Anode active surface, $inch^2$	Anode weight, pound
			Material	Method of attachment		
1	0.844	30	Ti clad Cu	Welding	3111	154
2	0.844	25	Ti clad Cu	Welding	2545	132
3	0.844	20	Ti clad Cu	Welding	2121	110
4	0.844	20	Cu	Press-fit	2121	115
Conventional lead alloy anode					2828	160

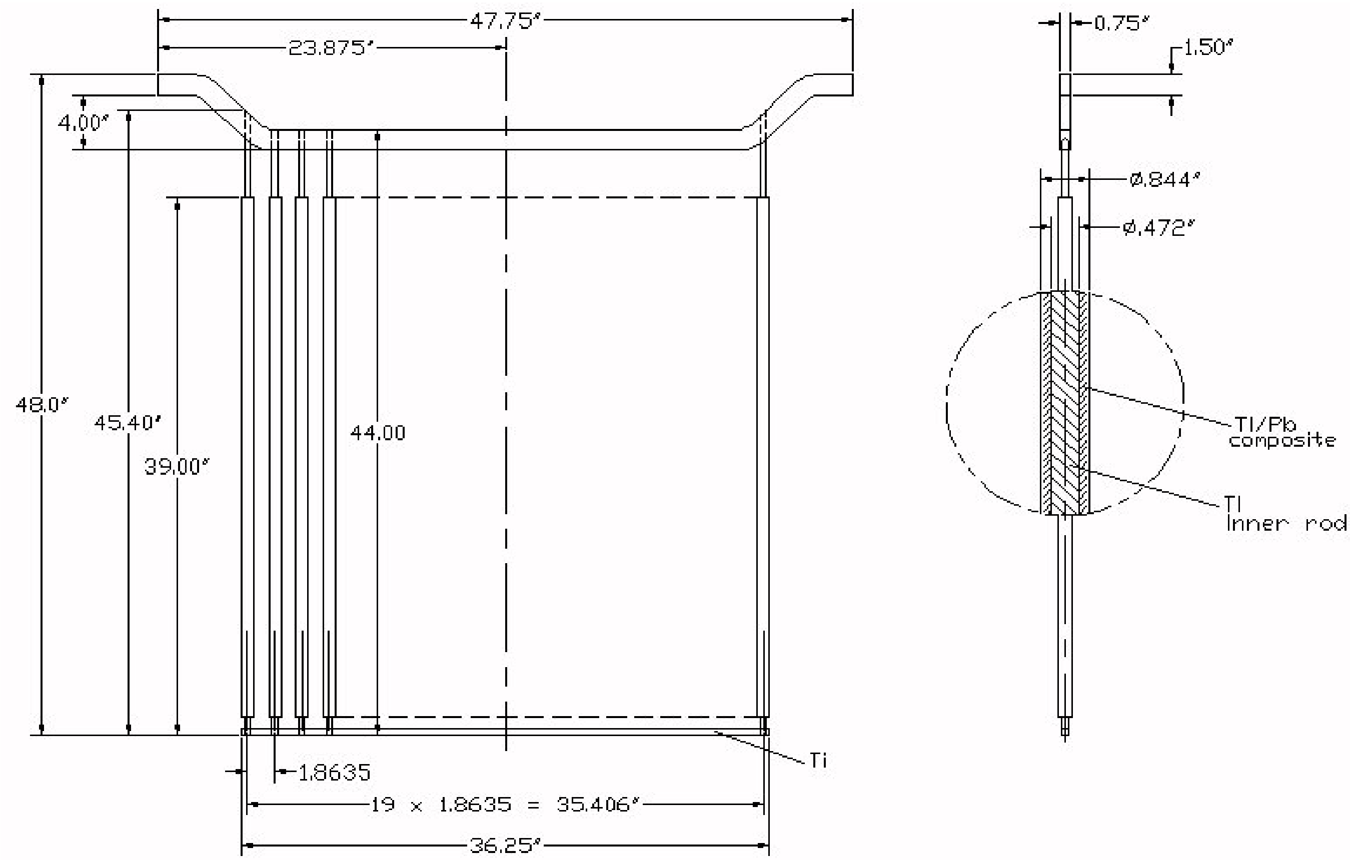

Figure 14: Drawing of a full-size Ti-Pb cylindrical anode with 20 cylinders.

Figure 15: Picture of a full-size Ti-Pb cylindrical test anode with 20 cylinders.

Market Analysis and Business Planning

Market Analysis

Research on competitors revealed that rolled lead alloy anodes predominate in the copper electrowinning. The main problem associated with standard lead anode operation is that the anodes are consumed during electrolysis, and their energy use is high. Numerous theoretical and experimental studies have been carried out on the alternative anodes. Various dimensionally stable lead-base and titanium-base anode concepts have been attempted over recent years: Eltech System Corporation developed a hybrid anode Mesh on Lead (MOL), which consists of titanium mesh, coated with an electrocatalyst, attached to a standard lead anode [21]; the Merrlin Composite anode is a conventional lead anode coated with a mixture of lead and manganese oxides [22]; Metakem GmBH developed MMO-coated anodes with titanium substrate and a mixed metal oxide coating, which includes precious group metal oxides [23]; Optima and Daiso anodes – iridium oxide coated titanium [24]; Showa Entetsu is a manufacturer of lead clad titanium anodes [25], etc. These anodes are not widely used. Along with studies on the alternative anodes, alternative anode reactions for copper electrowinning and alternative electrowinning cells are also being developed. In the conventional copper electrowinning process, the anode reaction is the decomposition of water to form hydrogen ions and gaseous oxygen, which bubbles off of the anode. In the newly proposed FFS process, ferrous oxidation replaces the water oxidation [26]. It is anticipated that this new process will enhance the copper electrowinning by reducing the energy consumption and lowering the operation costs. Electrometals Technologies Limited has developed a new EMEW cell, which is constructed as a closed cylinder with the cathode forming the outside wall of the chamber and centrally placed rod-like anode [27]. The solution containing the target metal is pumped through the cylinder, and metal ions attracted to the cathode through the application of electrical current between the two electrodes. The cells can be combined in series to form production plants. The most recent survey, conducted by CTI ANCOR & University of Arizona, shows that 86% of the surveyed EW plants use rolled lead-calcium-tin anode, and the remaining 14% utilize lead cast anodes. The average reported anode life in the electrowinning tankhouse is 5-6 years. None of the surveyed plants are using alternative anodes.

Initial market assessment for the titanium-lead anodes was performed by an independent party-Materials Extreme Company (Appendix 1). Preliminary market size and preliminary market price equivalent for a commercial titanium-lead anode was estimated. The potential for the U.S. copper industry is a market of 120,000 anodes.

Several cost evaluations of the anodes have been carried out. An expected cost of a commercial size copper electrowinning titanium-lead anode was estimated based on a high scale of production - 20,000 anodes. The cost of the anode was determined by averaging the total material, labor and overhead costs. Based on the preliminary estimates, the expected cost of one cylindrical titanium-lead anode with 25 cylinders would be in the range of $ 750-800. One of the ways to get the anode cost down is manufacturing the anodes with fewer cylinders.

The lead alloy anodes for copper electrowinning are being manufactured on a very large scale. To succeed in commercialization, it should be shown that the cost of the titanium-lead anode with the associated benefits would compete with the conventional lead alloy anode on a value basis. The conventional anode cost is about $200. Cobalt is added to copper plating baths to stabilize the lead anodes. The cobalt helps to maintain a lead oxide surface on the lead anodes and prevent flaking. At present, levels of 120 ppm cobalt are sufficient to ensure that the high quality product is maintained. The amount of the cobalt consumed by a typical copper electrowinning tankhouse during one year is about 1,350,000 lbs. The average price of the cobalt used in the electrowinning tanks is about $20/lb. It is anticipated that the titanium-lead anodes would function without the cobalt. If the cobalt addition to the electrolyte could be significantly reduced or eliminated, this would be a major advantage of the titanium-lead anodes over the currently used lead alloy anodes. It would take a whole cell long-term commercial test in order to complete evaluation of the titanium-lead anode benefits, such as elimination or reduction of cobalt additions to the electrolyte, decreased lead contamination of the cathode, decreased cell cleaning, and longer life.

Future plans

Additional full-size cylindrical anodes have been manufactured for the phase two testing. The objective of the testing is to evaluate the need for cobalt, investigate the effect of decreasing the number of Ti-Pb cylinders on anode performance, measure the difference in voltage and find the minimum operating requirements. The anodes will be tested in the absence of cobalt additions to verify that the presence of the titanium eliminates the need for cobalt stabilization of the lead surface. It is anticipated that if the testing of the additional anodes proves technical feasibility and cost efficiency, a full-cell test of the Ti-Pb anodes will be conducted. 70 prototypes will be constructed for a whole cell long-term commercial test in order to complete evaluation of the anode costs/benefits. Conclusions and recommendations regarding this technology's commercial potential will be made. Several manufacturers with production equipment in place will be contacted to determine where the commercial Ti-Pb anodes can be manufactured least expensively.

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Conclusions

Copper electrowinning represents the primary target market for the titanium-lead anode. All the data obtained from pilot testing over period of one year in the Phelps Dodge-Stargo copper electrowinning tankhouse indicates that the titanium-lead anode is a good candidate for further testing as a replacement for a conventional lead anode.

The cylindrical design allows the electrolyte to flow through the anode, which enhances diffusion of the electrolyte reactants. The cylindrical anodes demonstrate higher mass transport capabilities and increased electrical efficiency compared to the plate anodes.

In the new titanium-lead design, the lead is intimately mixed with the titanium. The titanium is helping to stabilize the lead, preventing it from spalling. A key benefit of the titanium-lead anode design is that cobalt additions to copper electrolyte, which are required to stabilize the conventional lead-calcium-tin anode surface against oxidation and flaking, should be eliminated. The titanium-lead anode is expected to last twice longer than the conventional anode. The anode is easily substitutable into existing tankhouses without a rectifier change. Significant savings in the operating costs may be achieved through the use of the titanium-lead anodes.

Energy savings should be realized due to minimizing and stabilizing the anode-cathode distance in the electrowinning cell. Improving cell energy efficiency would lower overall energy requirements for copper electrowinning. It would take a whole cell long-term commercial test in order to estimate the value of the energy savings.

A key consideration is the anode cost. Titanium costs have increased. Efforts are being continued to improve the anode design, minimize the cost and bring this anode technology to the market.

Patents: No patents have been applied for or resulting from this award.

Publications: Chmiola, J., Gogotsi, Y., and Ferdman, A. Mechanically Stable Insoluble Titanium-Lead Anodes for Sulfate Electrolytes. *Science of Sintering*, 2003, 35, 75-83.

Acknowledgements

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Appendix 1

Preliminary Market Assessment for DOE Project: "An Insoluble Titanium-Lead Anode for Sulfate Electrolytes"

Project: DE-FG36-01GO11061 to Electrodes International, Inc.

Author: Scott R. Boyd

Date: March 21, 2003

Contents

Overview

As global environmental pressures have increased on producers of primary metals to adhere to ever more demanding requirements for limits on air pollution, alternatives to the traditional methods of refining have been adopted. In place of the traditionally employed "concentration-smelting-electrolytic refining process" many metals producers have increasingly turned to the "leaching-solvent extraction-electrowinning process" (SX/EW) as a cost effective, environmentally acceptable alternative. This method of metal refining is the target of this study due to the insoluble anodes employed in the process.

The Copper Industry serves as a case in point for the conversion of traditional metal refining methods to the SX/EW process. The proportion of Global production accounted for by this method has increased rapidly throughout the past decade to the present level of 17.7 percent of total primary refined production in the year 2000 (figure 3.)

Market forces apply significant pressures on the producers for lower cost, higher quality metals and non-metallurgical compounds that can be refined from less pure inputs by using electrometallurgical processes. In the case of the global copper markets, refined copper (metal containing 99.85% by weight of copper or 97.5% by weight of copper with limits on certain other elements) is required for the manufacture of wire and cable to be consumed by the major market sectors of building construction, appliances, electronics, automobiles and power transmission. Refined copper is also consumed in substantial quantities by brass mills, foundries and various chemical plants. The U.S. consumption of refined copper, measured as mill and foundry product shipments including imports of mill products, continues to trend higher. Despite recent setbacks due to a general economic slump, U.S. consumption rose to 3.9 million metric tons in 2000, up 43 percent from 1990 levels. Imports have become increasingly important as a source of refined copper to satisfy the growing U.S. demand, accounting for 37 percent of apparent consumption in 2000.

In the case of manganese dioxide, an electrochemical process employing insoluble anodes is used to produce a high purity synthetic product. This method and the resulting product is referred to as electrochemical manganese dioxide or simply EMD. While the global annual production of EMD is still very small in relation to the total of processed manganese metal (.245 Mt and 8 Mt respectively) this high purity synthetic material is growing increasingly important as a component in high performance dry cell batteries for portable electronic devices.

The copper industry, and specifically those producers who have committed to the SX/EW process, represents the primary target market for insoluble anodes. This industry is of sufficient scale to justify development and would stand to benefit significantly from the efficiencies promised by the insoluble titanium-lead composite anodes. Of somewhat lower potential is the industry producing EMD, which while small in comparison to the refined copper industry, is attractive due to its growth potential and a demand for higher purity yields. Other electrowinning metal operations that hold potential for the insoluble titanium-lead anode are the zinc, nickel and cobalt refining industries. In all cases, the potential for the insoluble titanium-lead anode is dependent upon several factors including: scale of the industry; prevalence of electrochemical methods employed by the industry; stage of process development of the individual producer; type of anode presently utilized; purity demanded of the final electrowon product and the economic benefit of local operational efficiencies to the producer.

Manganese Metal and Manganese Dioxide (MnO_2)

Manganese, in its elemental form, is the fourth most used metal as measured by tonnage. Trailing only iron (~780 million tons), aluminum (~17 million tons) and copper (~10 million tons), approximately 8 million tons of manganese metal is extracted from ores each year [2]. The overwhelming majority of this manganese metal is consumed as an alloying element in the manufacture of steel. In the United States, the consumption of manganese in steel-making, as ferroalloys and metal, has held steady over the past five years at about 6 kg/metric-ton of raw steel produced. Significant quantities are also used as alloying elements in the manufacture of aluminum.

Manganese also has other non-metallurgical applications, the most important of which is in the form of manganese dioxide where it acts as a depolarizer in dry-cell batteries. In this application, manganese dioxide acts as a deoxidizing agent to form water of product hydrogen as it is produced at an electrode. Standard dry cell batteries can utilize naturally occurring manganese dioxides (NMD) but higher performance batteries require synthetically produced manganese dioxide. Few ores around the world have the inherent properties from which to produce high quality NMD and producers are generally confined to the countries of Gabon, Brazil, China, Mexico and India. The market for NMD is estimated to be between 0.180 and 0.200 million tons.

As demand for higher performance dry cell batteries is driven by ever more powerful portable electronic devices the demand for synthetic manganese dioxide has increased significantly, at a rate approaching 6 % per year during the 1995-2000 period. In North America, alkaline dry cell batteries that use synthetic MnO_2, have secured a 91 percent share of the manganese containing battery market as of the year 2000. Still, synthetic manganese dioxide is a relatively small market for manganese when compared to the total global market for manganese metal. The limited market for this derivative, synthetic manganese dioxide, is supplied by a global production capacity estimated at approximately 0.250 million metric tons per year (figure 1). Synthetic manganese dioxide is produced by either electrochemical processes (EMD) or by a purely chemical process (CMD). The EMD process is of primary interest in this analysis as it represents a potential market for insoluble titanium-lead anodes.

EMD

World production of EMD is confined to a relatively few countries. The short list of seven countries holding the vast majority (> 99% percent) of global capacity, estimated at 245,000 metric tons, include: Japan (29 % share), China (23 %), United States (19 %), Australia (10 %), Ireland (8%), Greece (6%) and South Africa (4%). Tosoh of Japan, with EMD operations there and in Greece (Tosoh Hellas), stands as the company with the largest global market share at 18 percent. Australian capacity is set to expand significantly when HiTec Energy NL opens a 40,000 metric ton per year facility. South African producer Delta EMD is also in the process of doubling the capacity of their facility to 22,000 tons per year.

While in the United States manganese is no longer mined due to the low quality of the mine reserves, processing of imported Mn ore via electrochemical means to produce EMD is carried out by three companies, Kerr-McGee Chemical Corporation, Erachem Comilog and Energizer Holdings, Inc (formed in a spin off of Eveready Battery by Ralston Purina in April, 2000). In addition to these domestic sources of EMD, dry cell battery manufacturers in the U.S. rely upon increasing quantities of imported material from Australia, Ireland and South Africa (figure 2).

The potential market for insoluble titanium-lead anodes in the EMD industry will be dependent upon the stage of process development of the individual producer. Some producers have already abandoned the "industry standard" all-lead anode in favor of the environmentally benign all-titanium anode. EMD producers who have made this change away from lead may be reluctant to reintroduce any lead component into their process having previously made the commitment to eliminate it. Significant advantages in operational efficiency will be required of the insoluble titanium-lead anode over the present design to warrant a change by the producer. Additionally, EMD anodes are commonly specified in a corrugated form (as opposed to a flat plate) and are generally about twice the surface area of a standard anode used in electrowon copper production; requirements that will complicate the anode manufacturing process. These challenges will need to be addressed in order to take advantage of the growing market for insoluble anodes as global EMD capacity expands to meet the demands of higher power, dry cell batteries.

Country	Company	EMD Capacity	Planned Additions
		(metric tons)	(metric tons)
Japan			
	Tosoh Hyuga	29,000	
	Mitsui Mining & Smelting	24,000	
	JMC	18,000	
China			
	Xiagtan Electrochemical	10,000	
	Other State Owned Enterprises	47,000	
United States			
	Kerr McGee Chemical (NV facility)	23,000	
	Erachem Comilog (TN facility)	15,000	
	Energizer Holdings, Inc.	9,000	
Australia			
	Delta EMD Ltd.	25,000	
	HiTec Energy NL		40,000
Ireland			
	Mitsui Denman	19,000	
Greece			
	Tosoh Hellas	15,000	
South Africa			
	Delta EMD Ltd.	11,000	11,000
India			
	MOIL	600	0
Total		245,600	51,000

Figure 1. EMD Production Capacity by Country and Company[1,2]

Country	1999		2000	
	Gross weight (metric tons)	Customs Value (thousands)	Gross weight (metric tons)	Customs Value (thousands)
Australia	21,400	$30,200	25,400	$36,500
Belgium	591	$913	769	$1,260
China	24	$31	1,060	$1,320
Greece	16	$22	1,580	$2,060
Ireland	8,380	$11,700	9,510	$13,100
South Aftrica	10,400	$14,700	12,200	$17,200
Other	154	$628	633	$1,300
Total	**40,965**	**$58,194**	**51,152**	**$72,740**

Figure 2. United States EMD imports[2]

EMD Industry Contacts

Kerr McGee:
Kerr McGee is currently using some pure titanium anodes and some coated (with graphite) titanium anodes. Their EMD facility is using some flat plate anodes and some corrugated. They reportedly abandon lead anodes several years ago due to environmental and safety concerns.

- Mr. James Worthington, Vice President of Operations (including EMD). Office in Oklahoma City, OK. PH: 405-270-2925 Fax: 405-270-3285
- Mr. Rick Howard, Engineer, Kerr McGee Technical Center
  PH: 800-654-3911

Erachem Comilog:

- Contact Erachem Comilog (formerly Chemetals) New Johnsonville, TN facility which is dedicated solely to the production of EMD.

Electrowon Copper

Production of refined copper by electrowinning (SX/EW), as a proportion of all primary refinery output, has increased significantly in the United States as well as globally in the past decade. Electrowon copper as a proportion of total refinery output in the year 2000 in the U.S. was nearly 36 percent (up from 31 percent in 1999) and in the world over 17.7 percent which is up significantly over the past 5 years despite a drop from a record high of 18.4 % in 1999 (figure 3). A combination of market forces, environmental considerations and economics are driving the move toward the leaching-electrowinning process and away from the traditional process of concentration-smelting-electrolytic refining in many leading companies.

Country	1995	1996	1997	1998	1999	2000
Australia	36	44	51	55	83	78
Burma	-	-	-	7	27	27
Canada	3	2	3	2	-	-
Chile	372	636	881	1,108	1,361	1,373
Congo (Kinshasa)	23	40	38	38	31	21
Cyprus	-	2	4	5	5	5
Iran	-	2	10	14	14	14
Mexico	39	45	48	49	51	48
Mongolia	-	-	3	2	2	1
Peru	33	88	98	102	115	127
United States	539	574	586	609	586	557
Zambia	62	58	64	81	57	55
Zimbabwe	-	3	3	2	1	-
Total Electrowon	1,107	1,494	1,789	2,074	2,333	2,306
SX/EW as % of primary refined	11.3%	14.0%	15.7%	17.0%	18.4%	17.7%
SX/EW as % of refined (primary + secondary)	9.3%	11.8%	13.3%	14.6%	16.0%	15.4%

Figure 3. World Refinery Production of Electrowon Copper[3]
(thousands of metric tons except where noted)

Demand for high purity metals by wire & cable producers, the primary consuming market (figure 4), and the electronics industry is pulling copper producers toward reliable and controllable processes like electrowinning. Pressure from governmental and private environmental forces likewise favor electrowinning as it eliminates the need for the air polluting smelting stage of refining. A solution extraction-electrowinning operation can also allow a producer to utilize low-grade ores and discards to economically produce high quality copper cathode. Industry experts predict a continuation of this trend toward SX/EW at the expense of more traditional processes. The magnitude and speed of the shift will be largely dependent upon global market demand for copper which is greatly affected by the general health of the global economy; this is an uncertain prognosis at the present time.

Year	Wire rod mills	Brass mills	Other plants	Total
1998	2,170	659	57	2,890
1999	2,230	691	64	2,990
2000	2,240	723	57	3,020
2001	1,930	623	63	2,610
2002 Jan-May	737	256	26	1,020

Figure 4. U.S. Consumption of Refined Copper (thousands of metric tons) [3]

Chile is by far the country with the largest impact upon this shift in refining preferences. Chile's output of electrowon copper accounted for over 59 percent of the global production by this method in the year 2000. The country has seen a dramatic increase in electrowon copper production in the last half of the 1990's from 372,000 metric tons in 1995 to 1,373,000 metric tons in 2000. Electrowon as a proportion of total refined copper production in Chile rose from 25 to over 51 percent during the same period. State owned Corporacion Nacional del Cobre de Chile (CODELCO), the world's largest copper producer has invested heavily in SX/EW production. U.S. based Phelps Dodge Corp., BHP Billiton of Australia and a collective of consortia members (Falconbridge Ltd, Minorco S.A. and a group of Japanese companies) also have significant SX/EW operations in Chile.

The United States followed Chile in global SX/EW output having produced 557,000 metric tons in 2000. Peru (127,000 metric tons), Australia (78,000), Zambia (55,000) and Mexico (48,000) round out the list that when combined with Chile and the U.S. accounted for 97 percent of the world's output of electrowon copper in 2000. A number of expansion projects currently underway or recently completed and new projects under consideration will continue to drive SX/EW growth in the coming years.

Electrowon Copper in the US

Environmental and economic factors continue to drive up the share of copper in the US provided by the electrowinning process to represent 38 percent of estimated primary refined production in the year 2001 (figure 6). This trend of steadily increasing share of electrowon continues even in years where the total mine production volumes decline as in 2000.

The U.S. Copper producers have not been immune from industry restructuring and consolidation during the past decade. The primary consolidator has been Phelps Dodge Corporation whose recent acquisition of Cyprus Amax in late 1999 left it as the undisputed market leader in U.S. mine production with a 56 percent share of capacity, as well as the leading U.S. electrowon cathode producer holding a commanding 85 percent share (figure 5). The other two significant mine operators in U.S. are Kennecott Utah Copper Corporation (17 % share of capacity), a unit of Rio Tinto plc of the U.K. and ASARCO Inc. (16 % share), part of Grupo Mexico, S.A. de C.V. since late 1999. Of these two only ASARCO maintains SX/EW facilities holding a 10 percent share of U.S. electrowon cathode production.

The list of U.S. electrowon producers is completed with a minor participation by BHP Copper (a unit of BHP Billiton) which has shuttered all mining operations in the U.S. but maintains two small SX/EW facilities that together hold a 4 percent share of U.S. production. The only other significant mine operator, Montana Resources Inc. (49.9 % owned by ASARCO), operates only the Continental mine at Silver Bow, MT and holds a 3 percent share of U.S. mine capacity. Montana Resources does no refining of its ores.

Phelps Dodge Corporation, with its overall presence in U.S. copper and its commitment to SX/EW represents the primary target company for development and commercialization of the insoluble titanium-lead anode. Phelps Dodge's Morenci operation in Greenlee County, Arizona, is the largest copper producing operation in North America. The site includes an open-pit mine, a concentrator and two SX/EW facilities. Phelps Dodge has recently converted all refinery production at this site to SX/EW. The Morenci operation is supported by a Process Technology Center which is to be fully equipped with an SX/EW pilot plant to augment the existing bench-top and mini-cell testing facilities.

ASARCO also represents a development and commercialization opportunity for the insoluble titanium lead anode as this company appears to be committed to SX/EW as an important refining technology.

Mine	County, State	Operator	Total Capacity	EW Cathode Production
Morenci*	Greenlee, AZ	Phelps Dodge	490,000	258,621
Bingham Canyon	Salt Lake, UT	Kennecott Utah	310,000	0
Ray	Pinal, AZ	ASARCO	150,000	38,800
Chino	Grant, NM	Phelps Dodge	125,000	44,465
Bagdad	Yavapai, AZ	Phelps Dodge	115,000	10,889
Sierrita	Pima, AZ	Phelps Dodge	120,000	23,593
Mission Complex	Pima, AZ	ASARCO	110,000	0
Tyrone	Grant, NM	Phelps Dodge	75,000	71,688
Miami (Inspiration)	Gila, AZ	Phelps Dodge	75,000	53,539
San Manuel@	Pinal, AZ	BHP Copper Co.	85,000	10,000
Continental	Silver Bow, MT	Montana Resources#	50,000	0
Robinson^	White Pine, NV	BHP Copper Co.	35,000	0
Silver Bell	Pima, AZ	ASARCO	21,000	18,300
Miami^	Gila, AZ	BHP Copper Co.	12,000	0
Pinto Valley	Gila, AZ	BHP Copper Co.	10,000	14,000
Total			**1,783,000**	**543,895**

Figure 5. Leading Copper Producing Mines in the U.S. in 2000 [3]
(data in metric tons)

Notes on Table:
Table represents ~99 percent of the SX/EW mine capacity in the U.S.
*Sumitomo Metal Mining Co. and Sumitomo Corp. hold a 15% interest in Morenci
@San Manuel mine production ceased in 1999 but SX/EW production remains
#Montana Resources is 49.9% owned by ASARCO
^Robinson and Miami mine production was discontinued in 1999 by BHP

Production Type	1998	1999	2000	2001*
Primary:				
Mine, recoverable	1,860	1,600	1,440	1,340
Refinery:				
Electrolytic:				
Domestic ores	1,290	1,110	865	823
Foreign materials	238	196	163	185
Electrowon:	609	587	566	628
Total	2,140	1,890	1,590	1,640
Electrowon as % of all refined	28%	31%	36%	38%
Secondary recoverable				
Refineries			208	154
Ingot makers			129	121
Brass and wire-rod mills			844	727
Foundries, etc.			63	67
Smelter, total	1,720	1,290	1,000	947
Consumption:				
Apparent	3,020	3,130	3,130	2,500
Refined (reported)	2,890	2,990	3,020	2,610
Purchased Cu-base scrap			1,600	1,380
Stocks at end of period:				
Total refined	532	564	334	953
Blister, etc.	160	138	122	98
Prices:				
U.S. producer cathode				
(cents per pound)	79	76	88	77
Imports:				
Ores and concentrates	1,190	1,280		122
Refined	683	837	1,060	991
Exports:				
Ores and concentrates	412	395	175	45
Refined	86	25	94	22

*estimate

Figure 6. United States Copper Industry Statistics [3]
(thousands of metric tons except where noted)

Copper Industry (SX / EW) Contacts

Phelps Dodge Corporation, Morenci SX/EW Complex, Morenci, AZ: Phelps Dodge has recently expanded the SX/EW operation at Morenci to a size capable of producing 736 million pounds of copper (2001). The Morenci complex utilizes 63,000 anode/cathode pairs and operates with approximately 10 million liters of electrolyte in the tankhouse. The Pilot Plant technology center has bench tested a prototype titanium-lead anode and is now moving to a mini-cell test of the same.
Contacts include:

- Mr. Ruben D. Griffith, General Manager, Processing Organization, North America Mining (928-865-4521)
- Mr. Charles Maxwell, Director Process Technology Center (928-865-6450)
- Mr. Scot Sandoval, Supervisor Pilot Plant Test Facility (928-865-6404)
- Mr. Chris Morales, Assistant Supervisor Pilot Plant (928-865-6818)
- Mr. Jackson Jenkins, Hydrometallurgy Manager (928-865-6450)

Asarco Inc., (a wholly owned subsidiary of Grupo Mexico, S.A. de C.V.) Ray Complex, Hayden, AZ: The Asarco Ray Complex is a fully integrated business unit that includes operations in both the Hayden and Ray units. The SX/EW operation of the Complex is located at the Ray unit and has an annual capacity of approximately 90 million pounds of copper. Cathode copper produced in the SX/EW operation is shipped to Asarco's Amarillo Refinery or to outside customers.
Contacts include:

- Mr. Steven McGhee, Concentrator and SX/EW Manager, Ray unit (520-356-7811 ext. 2444)
- Mr. Neil Nebeker, Metallurgist, Ray Operation (520-356-7811 ext. 2359)

Preliminary Market Price Equivalent Estimate

- Present Anode employed in a typical U.S. based SX / EW operation is a Lead anode alloyed with Calcium and Tin. The header bar is of copper, welded to the anode plate.
    1. Anode dimensions are ~ 36 inches x 44.5 in x 0.250 in
    2. Average anode life is from 5 to 7 years (avg. 6 yrs) when it is replaced due to warpage
    3. Anode-Cathode spacing in a cell is from 1.75-2.00 inches on centers
    4. Cell voltage should be 2 volts or less for efficient power consumption
    5. Present anode (Pb alloy) costs ~ $ 180 each
    6. The EW electrolyte is doped with 120-130 ppm (avg. of 0.125 g/L) of Cobalt to suppress lead contamination of the cathode

- Proposed Insoluble Titanium-Lead anode will be comprised of a base structure of porous titanium (~ 60-80 percent dense) that has been infiltrated with lead.
    1. Average life expectancy is from 10 – 15 years (avg. of 12.5)
    2. Power consumption should be equivalent to or better than with present process
    3. Cobalt doping of the electrolyte will not be required

- Operating assumptions:
    - Each cell cycles approximately 40 times per year
    - Approximately 25 percent of the added cobalt is lost during electrolyte recovery
    - Cobalt value is $ 10.50/lb (average 2001 price)
    - The Titanium-Lead anode will experience double the life of the present Lead anode

- Operating Costs (based on a 'typical' large EW facility):
    - Cobalt cost is: (.125 g/L)(10 x 10^6 L)(1/454 g)($10.50/lb) = $28,910
    - Annual Cobalt cost: (.25)($28,910)(40 cycles/yr) = $289,100
    - Cobalt cost per anode: ($289,100/yr)(12.5 yrs)/63,000 anodes = $57
    - Equivalent anode cost with 12.5 yr life: ($180)(12.5 yrs/6 yrs) = $375
    - Net anode cost (12.5 yr life with no cobalt) = $57 + $375 = $432

- Estimated Market Price Equivalent for Titanium-Lead anode based on above:

Assuming all other operating characteristics are equivalent to or an improvement on the present Lead alloy anode the estimated Market Price Equivalent for the Titanium-Lead anode is $432.

Preliminary Market Size Estimate-Copper

U.S. Market:

- SX/EW production in the U.S. (2001 est.) is 1,384 million pounds
- A large SX/EW facility operating at capacity and producing 736 million pounds with 63,000 anodes yields an average output of: 736 million pounds/63,000 anodes or an average of 11,682 lbs/anode-yr.

The potential for the U.S. copper industry is a market of 118,500 anodes at an approximate market value of $432/anode or ➔ $51,000,000 (assuming all existing anodes are eventually replaced with the titanium-lead anode)

Global Market (excluding the U.S.):

- SX/EW production in the World (excluding the U.S.) in 2000 is estimated at 3,855 million pounds
- Assuming an average yield per anode of 9,000 lbs/anode-yr (lower than the 11,682 lbs/anode-yr of the large scale, newly constructed facility referenced above)

The potential for the Global copper industry (excluding the U.S.) is a market of approximately 428,000 anodes at an approximate market value of $432/anode or ➔ $185,000,000 (assuming all existing anodes are eventually replaced with the titanium-lead anode)

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