Mixed Metal Oxide "MMO" Insoluble Anode System for Enhanced Operational Acid Copper Plating of Printed Wire Boards "PWB"

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Abstract

Advances in the printed wire board industry toward miniaturization, finer traces and HDI technology, smaller through-holes and microvias have placed higher demands on board design, manufacturability and quality. One primary aspect in the overall board function is the acid copper plating process. The present process utilizes titanium anode baskets with soluble copper-phosphorus balls or anode slabs. Limitations associated with this standard anode technology is seen in low current density plating requirements, over-plating of copper to meet minimum plated board specifications and nodule defects plated into the boards due to copper-phosphorus impurities entering the bath, to name a few. Today there is an alternative, the mixed metal oxide (MMO) insoluble anodes, that is provided to the PWB industry. The company which produces custom fabricated Dimensionally Stable MMO anodes, provided a PWB manufacturer an insoluble anode package including a fully automated feedback controlled copper oxide feeder unit. The all-titanium mesh anodes are designed to provide long-life, superior plating uniformity across all board surfaces and with improved MMO anode throwing power producing a near 1:1 through-hole to surface plating ratio. The MMO anodes are supplied with a patented coating formulation addressing specific requirements of PWB acid copper bath chemistries. The company anodes are qualified in all commercial acid copper plating bath chemistries, demonstrating superior organic additives stability, with equal or better than copper-phosphorus soluble anode balls or slabs organic consumption requirements. The value added commercial PWB manufacturer, with the incorporation of the company's MMO plating system demonstrated beneficial enhancements to their quality and technology driven, engineered commercial board packages. Dimensionally stable all-titanium MMO anodes create a safer, reliable, reproducible and higher producing plating operation for the PWB manufacturer. MMO anodes allow for the elimination of required maintenance for copper-phosphorus replenishment and copper generated sludge/passivation, providing greater operator safety. Immediate improvements in total rack and individual PWB copper uniformity and throwing power are observed on every engineered product, most importantly high technology designs (near 1:1 ratios hole to surface), especially fine traces and through-holes. Compared to soluble anodes, the company MMO plating system offers fewer impurities resulting in the elimination of nodules and provides better tensile/elongation (IPC Class 3A) and copper purity performance. The fully automatic controlled copper oxide replenishment system allows the PWB manufacturer to achieve 100% copper addition utilization and provides tighter control of copper plating bath concentration, resulting in the elimination of dummy plating and greater process control. The PWB manufacturers' use of the company insoluble anode plating system yields a quality driven and world class manufacturing solution to meet the advancing technology demands for present and future PWB development and fabrication. Overall Copper plating distributions with the installed insoluble anode system were reduced by more than 50%.

Introduction

Acid Copper Plating

Acid copper plating with industrial organic brightener packages is the preferred method of electrodeposition of copper onto printed circuit board substrates. The electrodeposition of copper, or plating of copper, is a critical step in the development of a circuit board. It is here, where the traces and electrical connections are formed or enhanced by plating the through-holes or vias.

As these traces are moving toward miniaturization, the quality and uniformity of the copper deposit determines the ability to manufacture continually shrinking trace and space widths with advancing technology demands. Uniform copper deposit allows for tighter impedance tolerances to be met and smaller trace and space size to be achieved due to the tendency of small features to over-plate and become statistically difficult to process downstream. The ability to produce next-generation technology board designs relies on the capability of the PCB manufacturer to plate copper that is smooth, repeatable and with uniform physical attributes. The principals of acid copper plating rely on creating an electrolyte with copper metal dissolved in solution that a current can be passed through from an anode to a cathode (the circuit board), where copper is then reduced to copper-zero, a solid plated form on the substrate. In its simplest form, an electroplating cell can be described by Figure 1.

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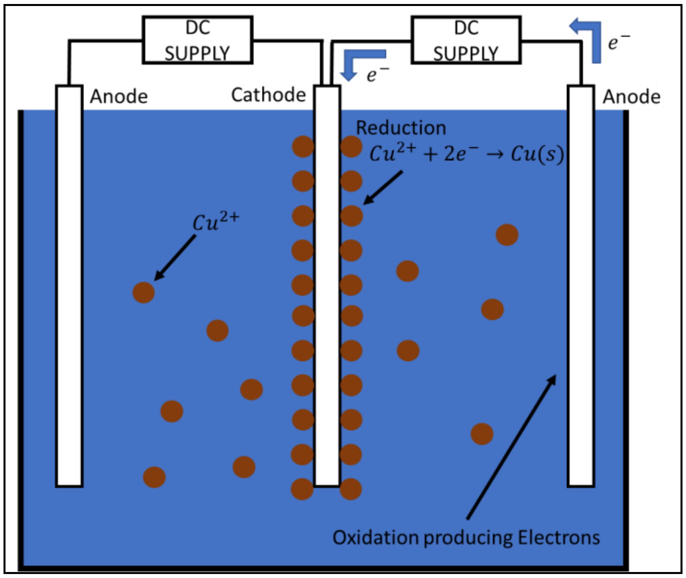

Figure 1: Diagram of Simple Copper Electroplating Cell.

This copper electrolyte consists of several components, both organic and inorganic, that aid in the function of the bath. The inorganic components are:

- Copper - Copper ion is the main ingredient as it is the source of plated copper. Controlling the concentration of the ion is important to making an even and consistent deposit. [1]
- Sulfuric acid - This creates conductivity in the solution, as well as forming an electrolyte with the copper ion in the form of copper sulfate. [1]
- Chlorides - Used in small amount as chloride ions aid in the absorption adsorption and suppression of the carrier molecule (described below), and assists in leveling the deposition of copper. Additionally, the chloride ion facilitates the controlled dissolution of the copper-phosphorus (copper-phos) soluble anodes. [2]

The organic components of the electrolyte are important in creating a copper deposit that is fine grained and produces a dense copper structure, that is also flexible. It is important to deposit copper in a fashion that creates an even and uniform grain of deposited molecules. These organic components are:

- Carrier- Also known as the "wetter" compound, this molecule tends to be a large polyoxy-alkyl like compound. The carrier acts as a current suppressor and is absorbed adsorbed onto the surface of the cathode to increase the diffusion layer thickness which suppresses mass transfer. This effect creates an improved grain structure and uniformity of the copper deposit. [3]
- Brightener - Also known as accelerators, the compounds are small organic molecules containing a sulfur functional group. The brightener adsorbs at low agitation areas, such as the middle of a via, to promote plating in areas that suffer from poor copper diffusion. This additive directly impacts the tensile strength and elongation properties of the copper deposit. [3]
- Leveler - This molecule is a cyclic aromatic compound that is attracted to higher current density areas, like the knee of a hole, or protrusions on the surface. It is also absorbed adsorbed on areas exposed to high electrolyte agitation, like the surface of the panel. This is necessary to keep high current density areas from plating too rapidly and creating an overplate condition. [3]

The combination of these components forms a robust electrolyte. The components work in unison to achieve a desirable copper deposit that plates evenly on the surface of the substrate as well as in the holes drilled onto the substrate or "through-hole". This ratio of plated copper on the surface versus plated copper in the through-hole is known as "throwing power" and is the most desirable attribute alongside even distribution across the surface of the board substrate. Having high throwing power in high-aspect ratio holes is important as it allows the amount of plating (and thus the plating time) to be reduced to produce conforming through-hole plating depositions. High aspect ratio through-holes would be considered holes that have a diameter at least 10 times smaller than the length of the projected barrel.

The principles of plating a targeted amount of copper on a circuit board are grounded in Faraday's Law, which characterizes the relationship between current supplied, time and the weight of the copper plated [2]. The relationship between electrons transferred and the weight of copper can be directly related by this law[1]. Board plating requirements are often denoted in copper weight applied over a known plated surface area. Faraday's law can then be expressed by the Equation 1 below in a useful form for the plating of circuit boards with various plated surface areas. This form of Faraday's Law relies on current density (current per area). The current supplied can then be easily calculated by multiplying the current density by the plated area.

$$Weight\ of\ metal\ plated\ (grams) = \frac{current\left(\frac{amps}{ft^2}\right) * 60\ \frac{seconds}{min} * MW\ of\ metal\left(\frac{grams}{mol}\right) * plating\ time\ (\mathrm{min})}{96500\,\frac{Amps * seconds}{mol} * \frac{moles\ of\ electrons}{moles\ of\ metal}}$$

Equation 1: Faraday's Law for Acid Copper Plating

The electrons are transferred by supplying DC power to the anodes, and the amount of plated copper is directly related to the number of electrons transferred, thus a well-regulated power supply to control current/electrons to the circuit board is critical yet, often overlooked, the anodes themselves are also fundamental to the plating process. Recent advances in anode technology and characteristics for acid-copper electroplating have facilitated higher technological capabilities for circuit board manufacturers.

Soluble Anodes

In an acid-copper plating system, the circuit board is the cathode, where deposition of copper occurs. Traditionally, the anode consists of soluble copper balls nestled in a titanium basket to transfer electrons. The copper balls are alloyed with a small amount of phosphorus to aid in uniform dissolution of copper and to control the galvanic copper corrosion resulting in an increase in copper concentration within the bath due to small differences in the electro-potential of the anode and cathode reaction [2]. As current is passed between the anode and the cathode the following reactions (Equation 2) occur.

$$Reaction\ at\ the\ anode: Cu(s) \rightarrow Cu^{2+} + 2e^-$$

$$Reaction\ at\ cathode: Cu^{2+} + 2e^- \rightarrow Cu(s)$$

Equation 2: Anode and Cathode Reactions in Soluble Plating System

There are several advantages of this system: it is simple and efficient, relative low cost, widely available and provides uniformity of copper-phos alloy consistency. Moreover, since the anodes themselves are the source of copper, there is no need for secondary processes to be used to regulate copper concentrations.

However, the use of soluble anodes presents several drawbacks to production and advancing technology of board configurations. Due to the mechanism of copper transfer, the anodes are constantly changing in geometry, resulting in an unpredictable anodic electric field and results in greater variation in copper distribution. Additionally, as the copper dissolves both copper needles and an anode sludge are formed, which requires bagging and periodic removal. This sludge creates impurities that must be plated out of solution before production can be run to avoid the formation of nodules being plated onto the surface of the circuit boards. As the anodes dissolves, they must also be physically replenished and tamped further down into their baskets to maintain electrical current path. All of this results in a significant amount of operator maintenance that must be performed, reducing overall production capacity and impacting plated board quality/reworks.

Insoluble Anodes

[1] Weight of copper is then correlated to plating thickness, as 1oz. of plated copper over 1 ft^2 plates 1.4 mils (0.0014 in.) of copper on the surface. Often in industry plating is denoted by "ounces" of copper plated (i.e. 1oz. plating)

[2] Typical purity of the soluble balls is stated to be 99.93% copper and phosphorus alloyed to ~0.05%, impurities can include iron, sulfur, lead, nickel, tin, arsenic and zinc

An alternative approach to current transfer is the use of mixed-metal oxide (MMO) insoluble anodes. These all-titanium anodes are manufactured with an electrocatalytic coating specifically formulated for PWB plating that are not consumed by the overall reaction, and thus are dimensionally stable in plating service. With this system, dissolved copper oxide is the source of copper ions rather than the dissolution of the anode itself.

A cross-sectional diagram of the MMO titanium anode is provided in Figure 2. The base titanium mesh anode structure is surface-prepared to accept the intermediate valve-metal oxide barrier layers (VMO), followed by multiple applied catalytic coating layers of primary iridium oxide + tantalum pentoxide (PMO+VMO), completed with a novel engineered PWB coating technology. The applied enhanced coating is created to achieve a microporous outerlayer allowing for a free exchange of the bulk electrolyte and primary anode reaction of water splitting, while preventing the large molecular weight bath organics from contacting the iridium catalyst and becoming degraded by the oxidation reaction. The applied MMO coating formulation maintains bath organic composition stability and thus achieves full cathode plating characteristics.

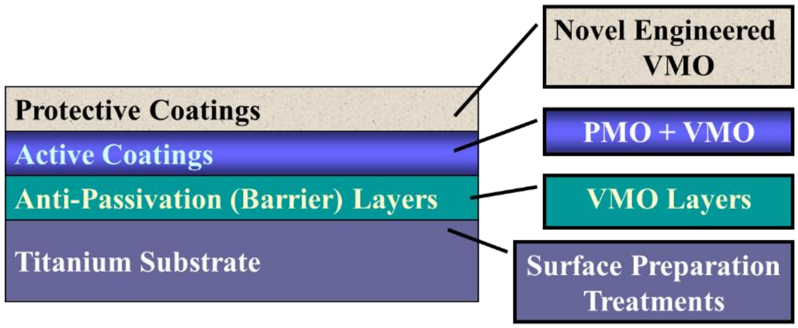

Figure 2: Cross-sectional Diagram of MMO All-Titanium Plating Anode.

Figure 3 demonstrates the ease of installation on operation of the MMO insoluble titanium anode. The anode is attached to the in-cell busbar via a stainless steel "U" bolt, with all other materials grade 1 chemically pure titanium. Once the anodes have been secured to the busbar and position/spacing evaluated for optimum plating distribution, the position will remain the same for the duration of the anode's service life. The base mesh anode structure is designed for ~15 years of active service life. While the catalytic coating will provide ~3 years of plating service life before required recoating application and return to customer plating service. Figure 3, provides a view of the all-titanium MMO anode installed onto the in-cell busbar as the anode in the first photo and in the second photo the anode with installed oxygen capture bag ready for board plating service. Based on the engineering design use of a stable titanium anode structure and select precious metal catalysts for the PWB acid copper anode plating environment, including the installed anode oxygen capture bags, the engineered package and the stability of the catalyst coating formulation provides for 24/7/365 steady-state quality board plating with no further operator maintenance or intervention required for the life of the anode.

A typical vertical mesh MMO anode depicted in Figure 3 incorporates a titanium busbar with a design current rating of 75 amperes to provide for uniform copper plating over the full range of current densities 7 to 36 ASF. Typically, soluble copper phosphorus alloyed anode balls are limited to a maximum ~25 ASF current density operation. Above this current density, increased surface copper oxides are formed driving the anodes to increased anode polarization resulting in anode passivation. An elevated current density operation increases copper anode passivation and operational issues. Local anode surface passivation results in diversion of current flow to non-passivated regions of the copper anodes driving up cell voltages and producing non-uniform cathode board plating characteristics. Additionally, copper anode passivation increases copper sludge captured within the anode bags, also adding to blinding of the available copper anode surface area and plating defects, such as nodulation inclusions.

The ability to operate the MMO anodes at higher current densities can improve through-put by reducing plating times and, with appropriate organic additives, provides enhanced control to achieve target thickness and distribution. Industrial electronic chemistry suppliers have adjusted their bath additive packages to allow for these improvements when using MMO anodes.

In other industrial acid copper plating applications, such as copper foil production, the MMO anodes are designed to operate in the 10 KA/M^2 (929 A/ft^2) current density range.

However, the anode and cathode structures, busbars for current feed are significantly more robust to accomplish the task. The applied catalyst loading will also be increased to maximize the operating lifetimes at these elevated current densities, but the catalytic coating formulation can remain the same.

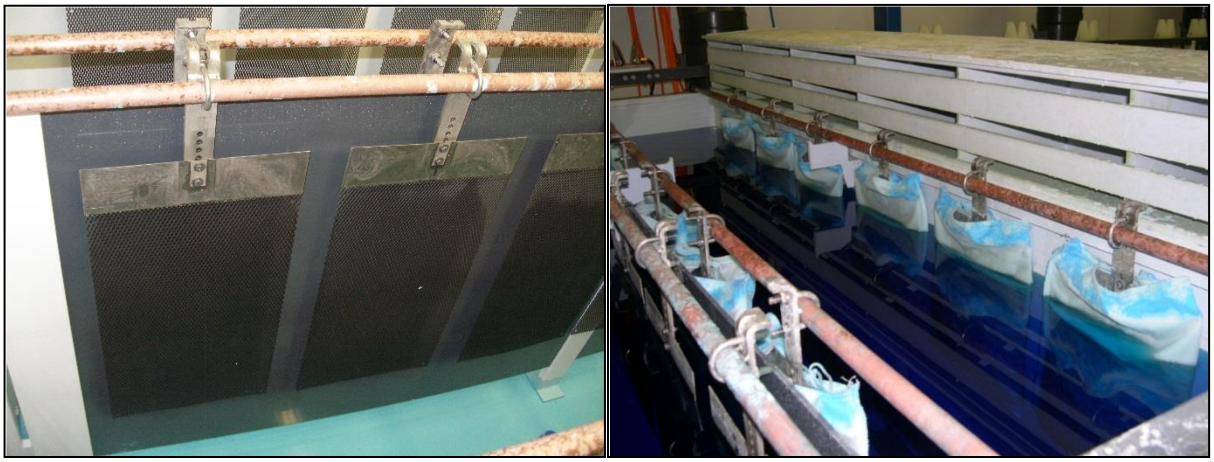

Figure 3: Installed MMO Anode in Plating Tank (Before and After Oxygen Capture Bag Installation).

In Equation 3, there are three equations presented showing a complete system of equations describing the MMO insoluble anode plus copper oxide feeder addition system contribution to the copper plating operation. The primary added material compared to soluble anode plating is the insertion of copper oxide powder to replenish the copper ion in the plating bath. The titanium anode structures with an applied iridium oxide + tantalum peroxide + DT electrocatalyst are not consumed in the reaction, but instead facilitate the flow of current and water splitting anode reaction (oxygen evolution).

$$Reaction\ at\ Anode: H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

$$Reaction\ at\ Cathode: Cu^{2+} + 2e^- \rightarrow Cu(s)$$

$$Reaction\ at\ Cu\ Dissolution\ Unit: CuO + H_2SO_4 \rightarrow Cu^{2+} + SO_4{}^{2-} + H_2O$$

Equation 3: Insoluble Copper Plating System Reactions.

The use of insoluble anodes presents several improvements over the soluble system. Due to a stable geometry, the distribution and reliability of the copper deposit become tighter and more predictable. Additionally, the routine maintenance needed with soluble anodes is reduced with insoluble anodes. Instead of stopping production to replenish the dissolved anodes, an operator simply must fill the feed hopper of the copper dissolution unit with more CuO, which does not disturb the normal operation of the machine.

Methods/Data

Plating Setup

The board plating line described in this paper is a fully automated, vertical racked, acid copper DC plating system. The system contains six 550-gallon plating cells that each hold up to six 18x24 inch panels or up to five 21x24 inch panels. The electrolyte system is managed by 3 filters and incorporates board side to side agitation along with vertical eductor solution flow. The filters feed a sump in which the solution is then filtered and replenished to the plating cells. Figure 4 depicts the general setup of the plating system, and Table 1 lists the key parameters of the plating setup.

Table 1: Plating Cell Configuration.

Plating Cell Volume	550 Gallon
Anode to Cathode Spacing	10.5 in.
Filter Replenishment Rate (per cell)	45 Gal/min
Bath solution turnover refresh rate	5/hour
Eductor Flow Rate (per cell)	35 gal/min

Because copper is not provided by the anode itself, a copper replenishment system is incorporated, described by Figure 5. Spent plating electrolyte enters the replenishment system and a portion of the electrolyte is diverted to a copper analyzer. The analyzer uses a colorimeter that determines the copper sulfate concentration in solution. The rest of the solution enters a secondary tank that has copper oxide fed into it. This copper oxide feed based on a smart relay, is controlled by the analyzer results. This system provides real-time continuous control of the bath copper concentration. The copper oxide rich solution is then sent through the rest of the baffled tank to ensure the powder is dissolved and the copper rich electrolyte overflows back into the main sump.

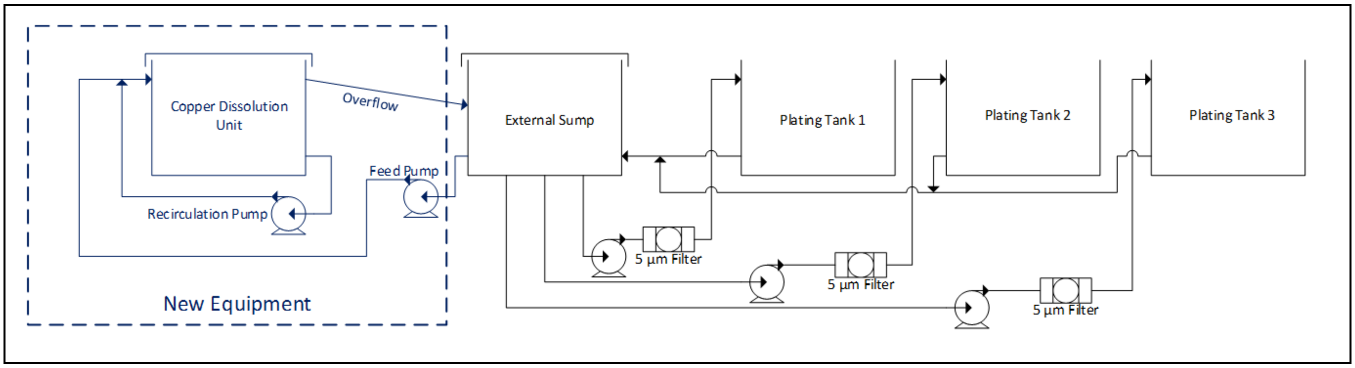

Figure 4: Simplified Diagram of Vertical Racked Plating Set-up.

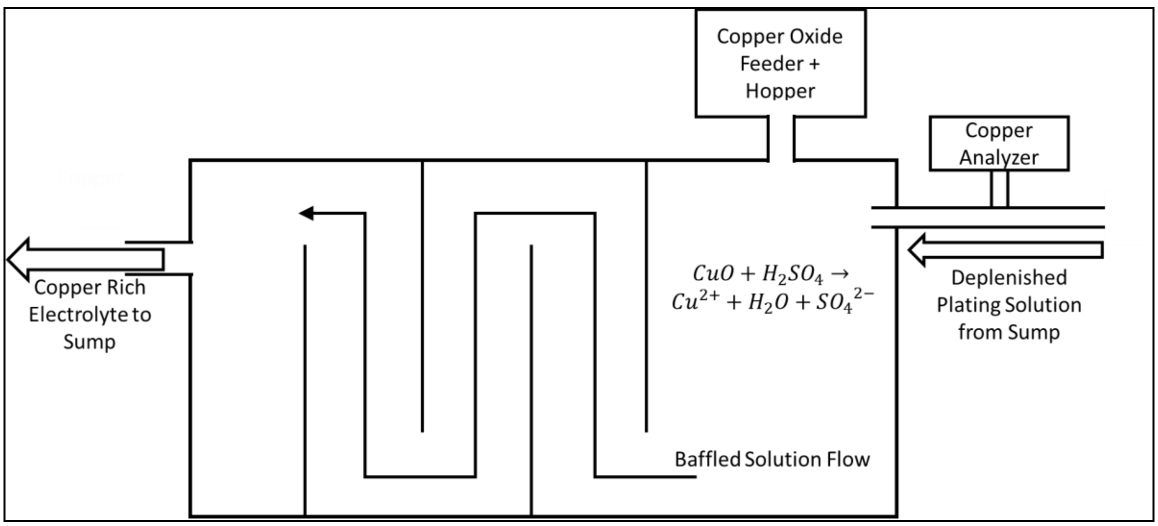

Figure 5: Diagram Depicting Action of Copper Dissolution Feeder Unit (Copper Replenishment System).

Installation of Anodes

The transition from soluble anodes to an insoluble system is a simple conversion process. The required changes to completely transition from the soluble setup to the present system does not require a change of the bath, chemistry or tank configuration and has minimal extensive periods of down time. For the plating setup described by this paper, it is best described as a drop-in replacement. The copper replenishment system is comprised of a stand-alone unit, and only requires an electrical supply hookup and plumbing to the sump (Figure 6). Once connected, and the system programmed, it can be turned on and calibrated for correct parameters and process control. This installation does not require the sump to be drained and can be installed before the installation of the anodes themselves. For anode installation, the soluble anode baskets are removed and the cell is drained to an offline storage tank. The new (recommended titanium clad copper for long-life) anode busbar is installed and the anodes affixed to the busbar. Once the anodes have been spaced, leveled and bagged, the tank is filled once again. This process is repeated for the remaining plating cells. Once the anodes have been installed, the plating solution is carbon treated to remove impurities introduced when the soluble anodes were removed. The anodes are then sent through a series of plating tests to determine distribution and adjustments are made if necessary. The highlight of this system is there are no changes required to perform to the existing system-in-place other than a swap of the anodes and minor cosmetic changes to the tanks/sumps.

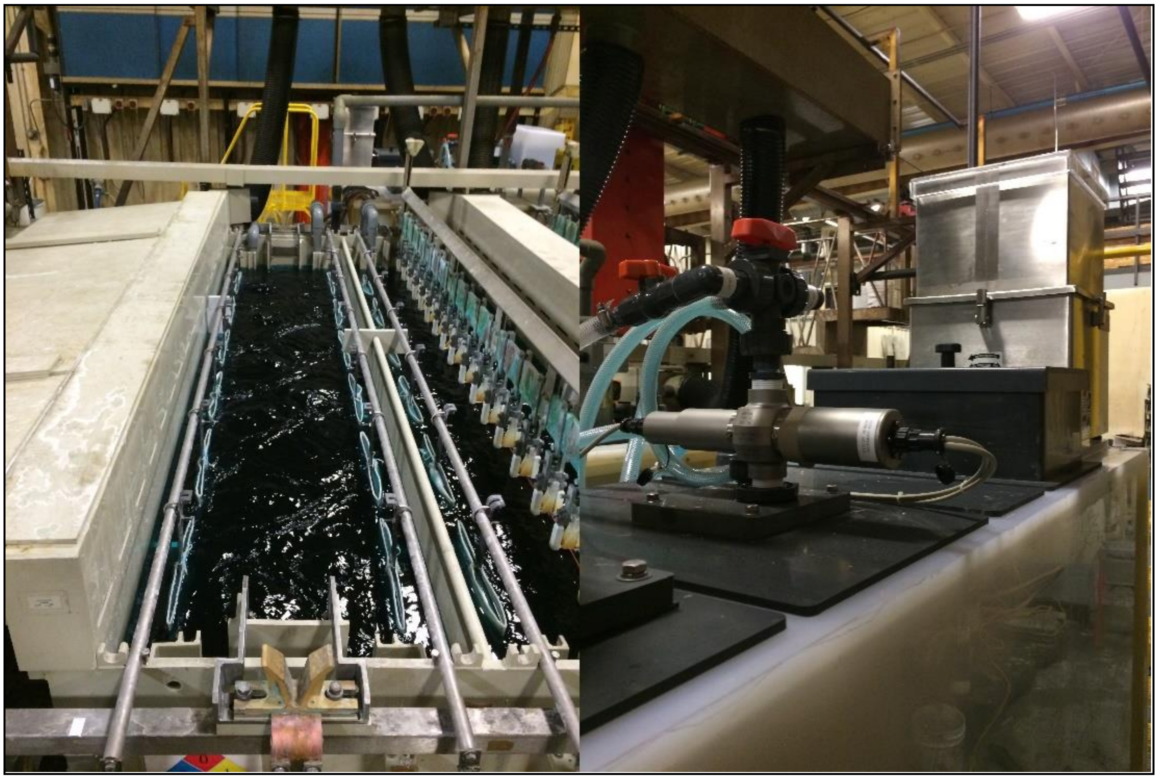

Figure 6: Anodes Installation (left) and Copper Replenishment System (right).

Results

Improved Distributions – Gateway to Advanced Technology Products

Along with increased production comes an ability to plate advanced technology and higher density boards. Due to dimensional stability, the electric field produced by insoluble anodes is more predictable and uniform. Traditional soluble anodes move and reposition themselves as they plate, creating an erratic electric field. Additionally, the electric field produced from a soluble anode basket tends to be non-uniform at the surface of the cathode as the curved basket is interfacing with a flat cathode (the circuit board). This creates areas of localized high current density. Flat insoluble anodes interfacing with the flat cathode lends itself to produce a uniform even electric field across a panel.

Copper distribution testing was carried out on both soluble and insoluble anodes. A test vehicle was used with surface pads plated on each side (Figure 7). Two separate test panels were created to account for the two main sizes of circuit board panels commonly used in the manufacturing, 21"x24" and 18"x24" panels. The 18" test vehicle consists of 12 pads in a 3x4 array, and the 21" test vehicle employs 20 pads in a 4x5 array. Figure 7 shows a 21" test vehicle after strip-etch-strip. The panels were processed using a LDI imaging unit with 2.5 mil (0.0025 in.) dry film resist. Test vehicle plating parameters are shown in Table 2. Plating thickness was measured using an Eddy current probe placed on the center of each test pad.

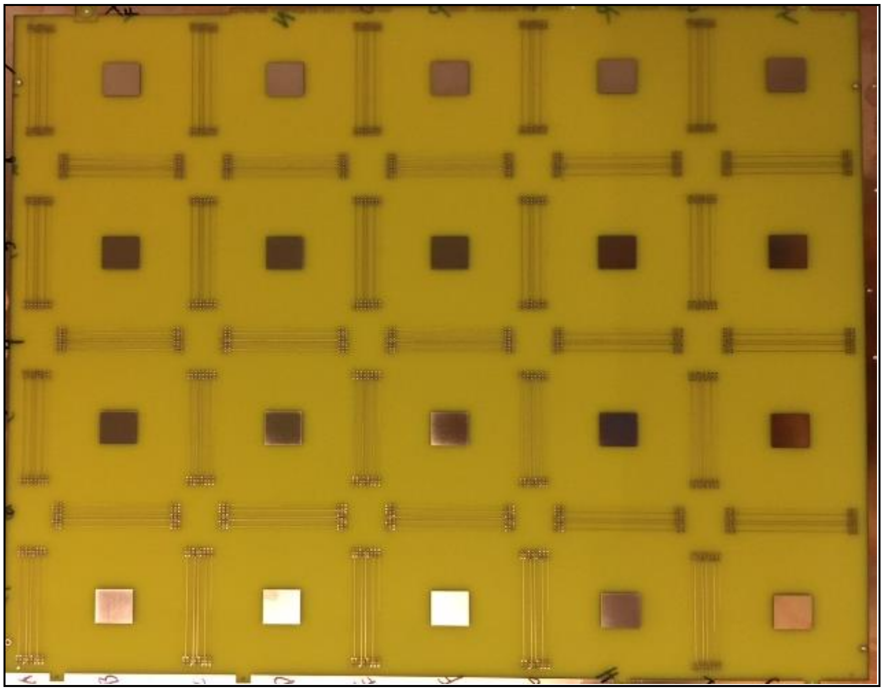

Figure 7: Test Vehicle for Plating Distribution Analysis.

Table 2: Test Vehicle Parameters for Distribution Analysis.

	18" Test Vehicle	**21" Test Vehicle**
Surface Area/Side	0.371 ft^2	0.495 ft^2
Total Surface Area	0.742 ft^2	0.99 ft^2
Current Density	14 amps/ft^2	14 amps/ft^2
Plating Time	90 minutes	90 minutes

Table 3 provides the overall decrease in distributions and deviations observed using insoluble anodes on distributions across panel and flight bar (5 and 6 panels across).

Table 3: Reductions in Range and Standard Deviation of Plating Thickness.

	All Data Points	**Averaged by Position**
Range	55% Reduction	38% reduction
Standard Deviation	50% reduction	42% reduction

To visualize the improvements in distributions, a surface plot was created using the 21"x24" panels. Each panel on the flight bar was tested at 20 different points on each side, resulting in 100 data points across the flight bar. Figures 8 and 9 show results of best-case and worst-case results[3] for flight bars using soluble anodes. Figures 10 and 11 depict the results of the insoluble anodes. These results show that using dimensionally stable and optimized anodes improve the distributions of copper plated on the surface. Note that the results of the best-case flight bar using soluble anodes are still more varied than the results of the worst-case flight bar using insoluble anodes. The high spots seen in Figure 11 (best-case) are the measured pads in the center portions of the panels. This is most likely a phenomenon witnessed as a result of the board design. Higher current densities are witnessed in the center pads, as they do not have solid strips of copper (seen on the border of the panel) to thieve current, which results in higher values in the center of the panel. These profiles will not change over time, 1.5 years in present service.

[3] "Worst-case" and "best-case" are defined as the flight bars that had the most and least overall variation (range) across the flight bar. The flight bar with the largest range of measurements is considered the "worst-case" and the flight bar with the smallest overall range was considered the "best-case"

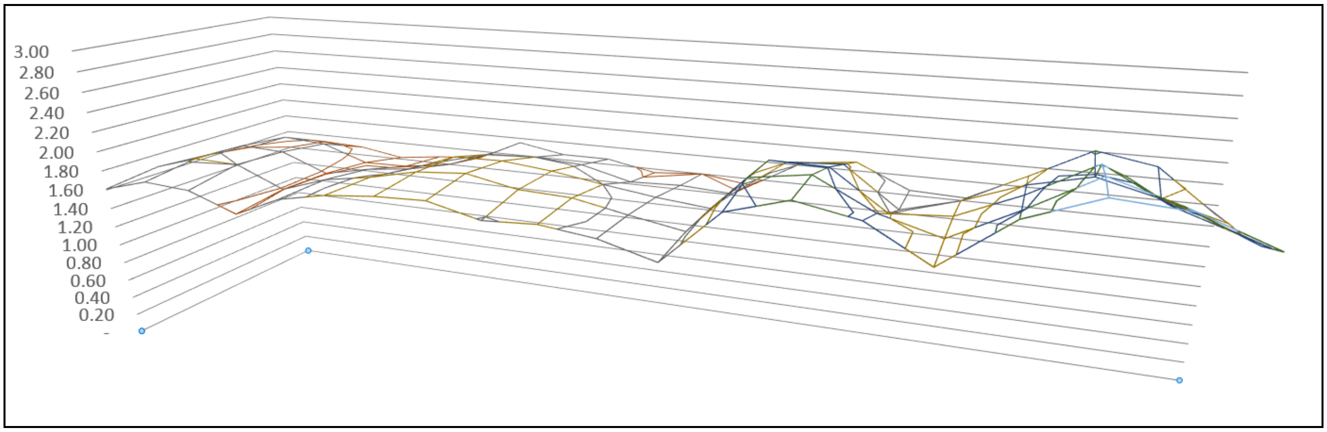

Figure 8: Worst Case Surface Distributions across Plating Flight Bar (21”x24”) Soluble Anodes.

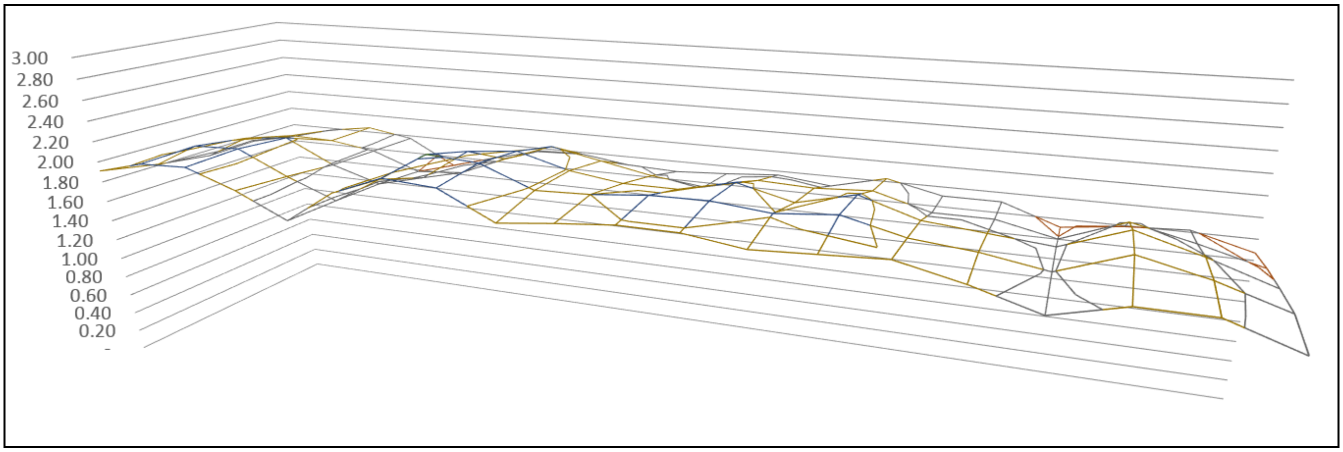

Figure 9: Best Case Surface Distributions across Plating Flight Bar (21”x24”) Soluble Anodes.

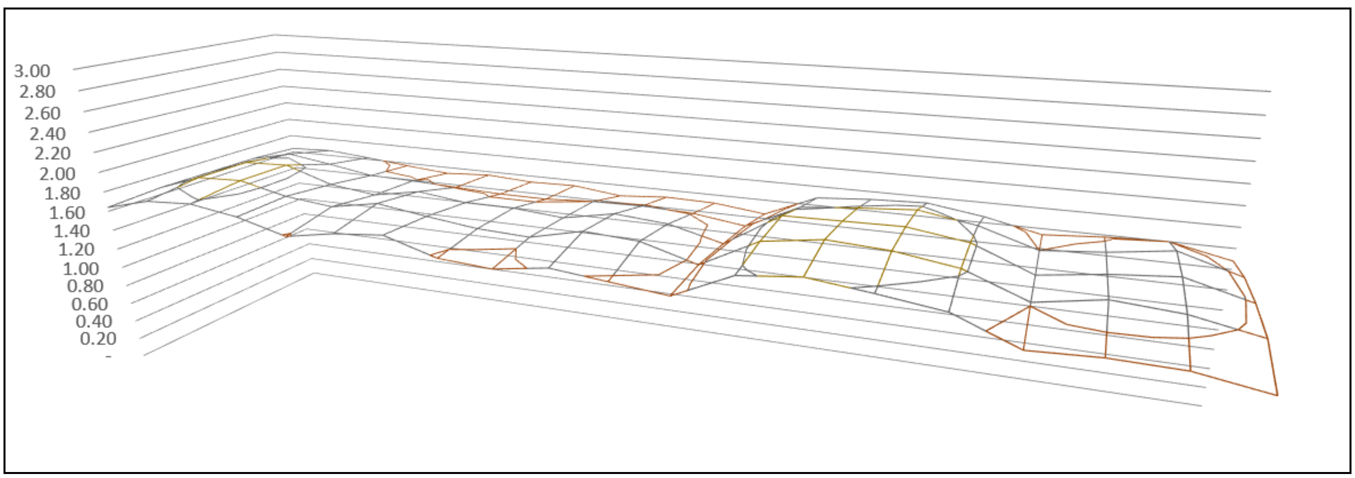

Figure 10: Surface Distributions across Plating Flight Bar (21”x24”) Insoluble Anodes.

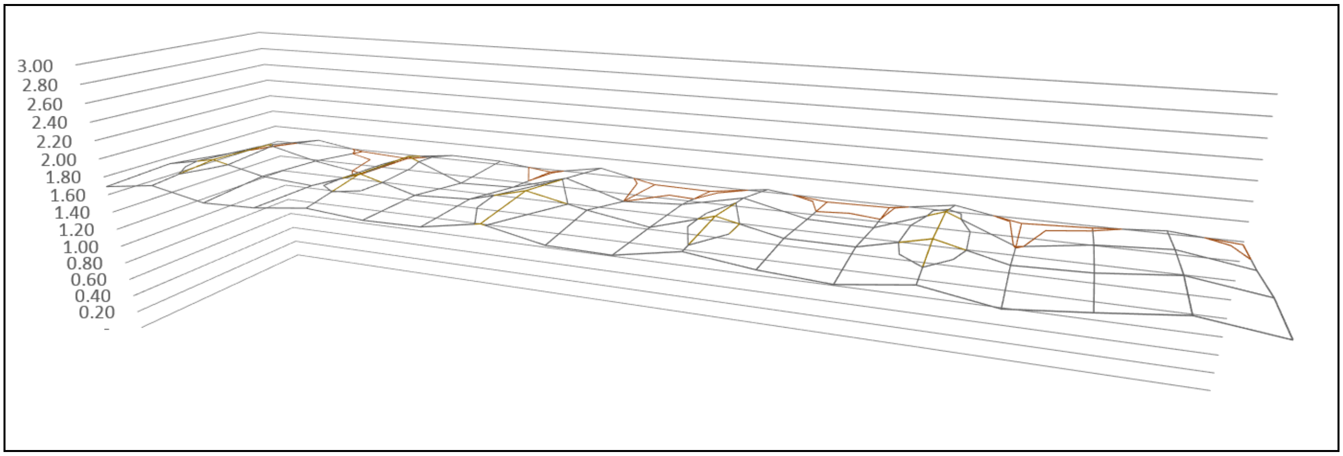

Figure 11: Best Case Results of Distributions across Flight Bar (18"x24") Insoluble Anodes.

By decreasing overall distribution of plating thickness (based on averages of position on the test vehicle of all test panels) by 40%, tighter control of plated through holes, vias and surface plating is observed and provides new business opportunities for advanced board configurations. Uniform distributions allow for tighter control of impedance and for tighter trace and space requirements to be met, as entrapped dryfilm (largely a result of uneven plating distributions) is often mitigated. However, board design is still a factor that has a large amount of influence over the tendency to overplate specific areas of a board and cannot be ignored. Isolated copper features will still plate unevenly due to the localized high current density attracted to these areas.

High Quality Copper Deposit

The physical properties associated with the copper deposit on a circuit board are extremely important. To have resilience and durability, a circuit board must be able to go through many forms of stress. Since plated copper forms the connectivity of the circuit board, it is important to have a deposit that can withstand both thermal and mechanical stress. To ensure the copper deposited on a circuit board meets the properties needed to withstand the stresses exerted upon them, tensile and elongation testing and copper purity analysis was performed. IPC Class 3A minimums are required to ensure the highest quality copper deposit.

Tensile and elongation testing was carried out in accordance with IPC standard TM-650 Method 2.4.18.1A. Three steel plates (21"x26") were procured, cleaned mechanically machine deburred, followed by chemical treatment with isopropyl alcohol. To obtain a usable sample, a 14" by 14" square was taped off on the center plate to make it easy to remove without being bent or otherwise deformed. The three plates were then loaded into the plating bath for 4 hours 25 minutes at 12 amps per square foot applied current. After plating approximately 0.05mm of copper, the stainless panels were removed from solution. The sample square was removed and packaged for transport to an outside testing laboratory. As per procedure, the outside lab selected a clean area (no nicks, pits, or holes) near the center of the large sample with which to evaluate smaller test coupons.

Copper purity testing was carried out in accordance with IPC standard TM-650 Method 2.3.15D. Copper foil was produced in the same manner as the tensile and elongation testing. The foil was packaged and shipped to an outside laboratory for testing. A five-gram sample was divided from the foil and cleaned with acid. The sample was weighed and then dissolved in concentrated acid. A platinum cathode was also weighed and then added into solution with an inert anode. Current was applied through the electrodes into solution and dissolved copper was then plated onto the platinum cathode. Since the current density for this test is relatively low, significant time is required to plate all copper from solution onto the cathode. After approximately 16 hours, the plating completed, and the cathode was, rinsed, dried and re-weighed. This new weight was compared to the original value and original copper weight to determine the purity of the copper.

Results from Tensile and Elongation as well as copper purity provide conforming results to IPC Class 3A standards, and exceed the minimum requirements. Figures 12-16 show the trending results of monthly testing over the course of 7 months with soluble and insoluble anodes. This data suggests fully compliant copper deposits with good quality physical properties achieved using insoluble anodes.

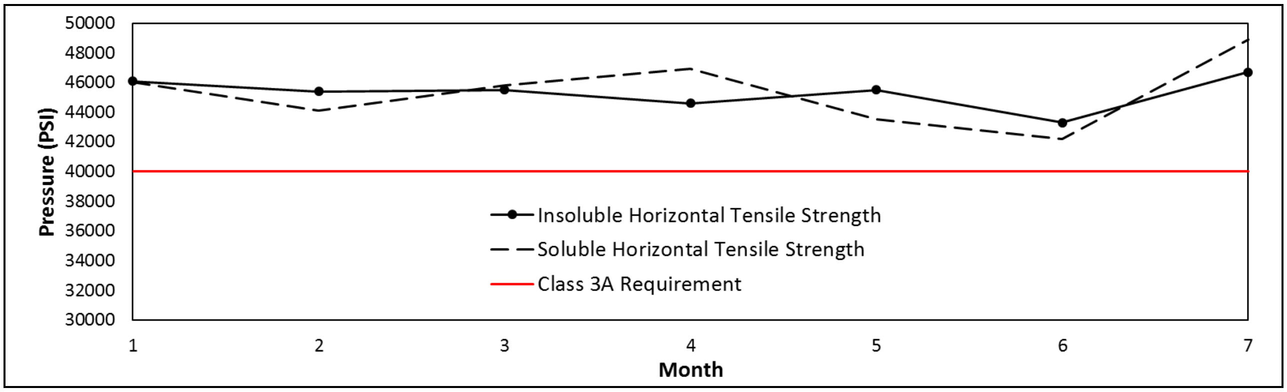

Figure 12: Horizontal Tensile Strength Monthly Results Trending.

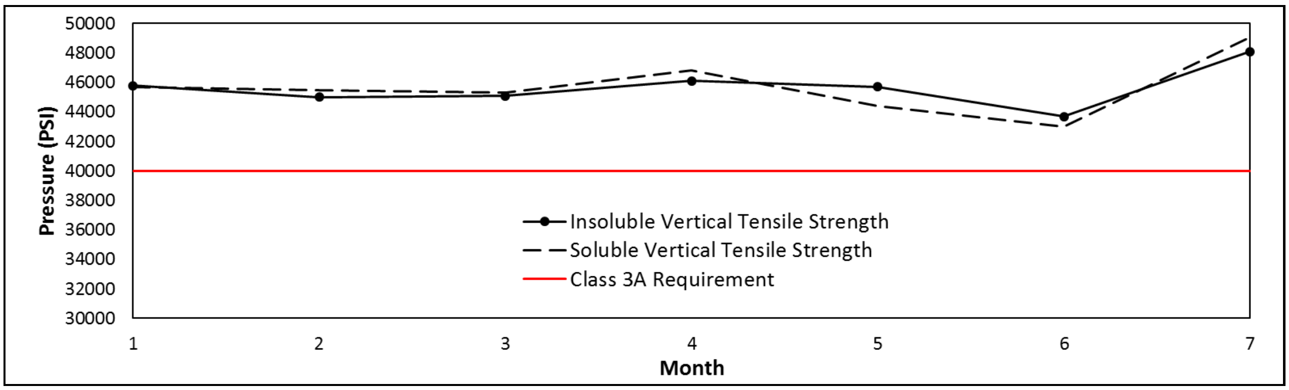

Figure 13: Vertical Tensile Strength Monthly Results Trending.

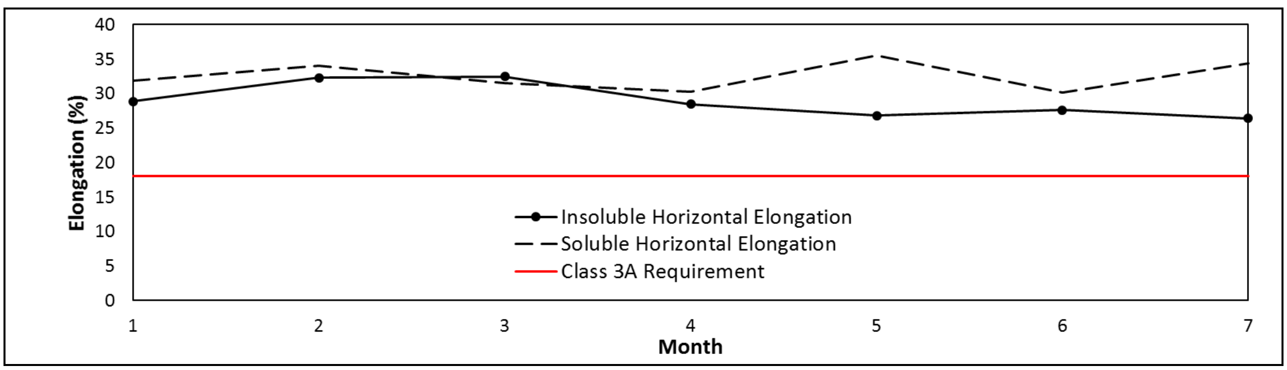

Figure 14: Horizontal Elongation Monthly Results Trending.

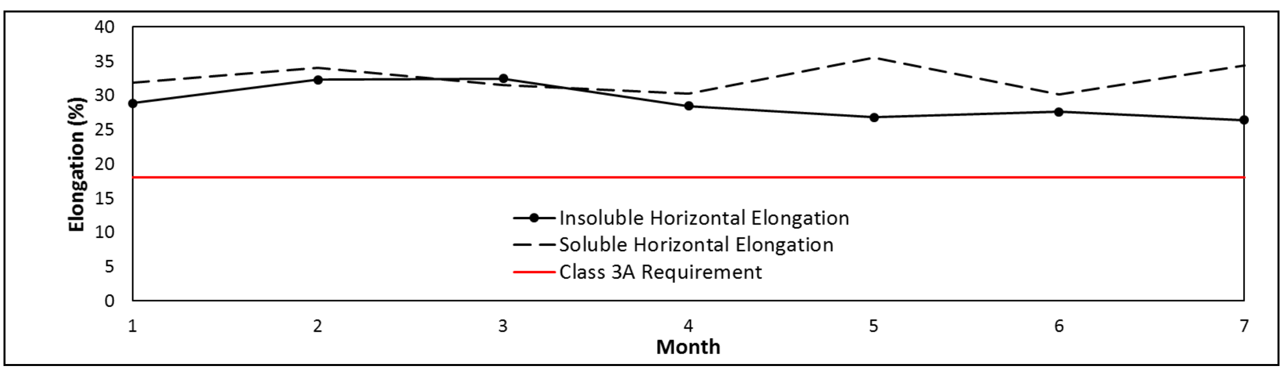

Figure 15: Vertical Elongation Monthly Results Trending.

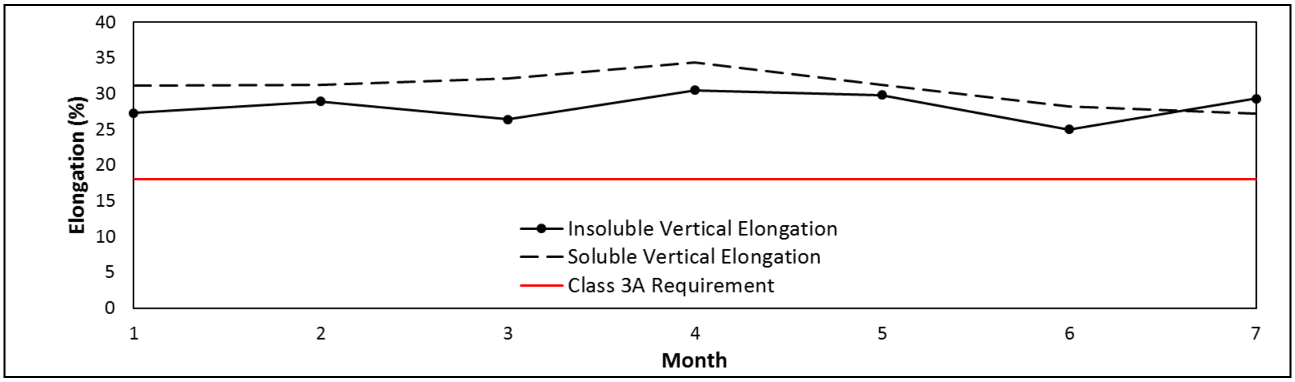

Figure 16: Copper Purity Monthly Results Trending.

Immediate Increase in Production Capacity

Dimensional stability means several things that benefit the production of printed circuit boards. As the MMO anodes maintain their electrochemical potential and do not change overtime, there is no need for routine maintenance like that of soluble anodes. Normally, with soluble anodes, the plating line needs to be shut down several times a week to allow for the operators to knock down the leftover copper to the bottom of the baskets and add new copper balls to the baskets. This maintenance accounts for a considerable amount of downtime and lost productivity of the plating line.

Along with the elimination of regular anode maintenance, insoluble anodes also eliminate the need to “dummy plate” to remove contaminates from the soluble anode sludge that form nodules and re-introduce the diffusion layer film on the copper balls. This eliminates the need to have pre-production plating requirements after extended periods of downtime, resulting in quick process startup. Overall with the elimination of downtime for anode maintenance and the removal of dummy plating requirement prior to startup, an overall increase of 12% in production is observed.

Process Controls

Soluble anode systems rely on the current efficiency of the anode reaction and the cathode reaction to be balanced to control the copper concentration. This is one of the reasons phosphorous is alloyed with the copper anode balls, as it helps to stabilize the corrosion rate of copper at the anode, since it is a more favored electrochemical reaction than that of the cathode. Using high quality copper balls allows for well controlled copper concentration, but impurities in the electrolyte and the changing anode structure creates small variations in copper concentration.

The copper replenishment system of the insoluble anodes employs a colorimeter to monitor copper concentration. The copper concentration determined by the colorimeter controls the feed addition of copper oxide and keeps the copper concentration within a range specified by the user. This control system has proven to keep copper concentration well-regulated, with better results than that of the anodic dissolution of the soluble anodes. Figure 14 shows copper concentration control charts of the soluble system versus the insoluble system for a 6-month period.

Chemistry Consumption

Overall chemistry consumption is not greatly affected using insoluble anodes. After testing the anodes and allowing for steady state of organic concentrations, dosing was found to be at roughly the same parameters of the dosing parameters of soluble anodes. The PWB formulated catalytic coating applied to the MMO anodes provides bath stability of the organic additives during the plating operation. The organic additive package used consists of 2 organic components for additions to the plating bath. For these purposes, we will refer to them as component “1” and component “2”. Table 4 shows a summary of dosing parameters of components 1 and 2 before and after insoluble anode installation. Slight variations can be attributed to swings based on bath age and CVS trending of component concentrations. Values this close together do not suggest large differences in chemistry consumption. Component 1 usage is seen to have increased slightly while component 2 usage has decreased slightly.

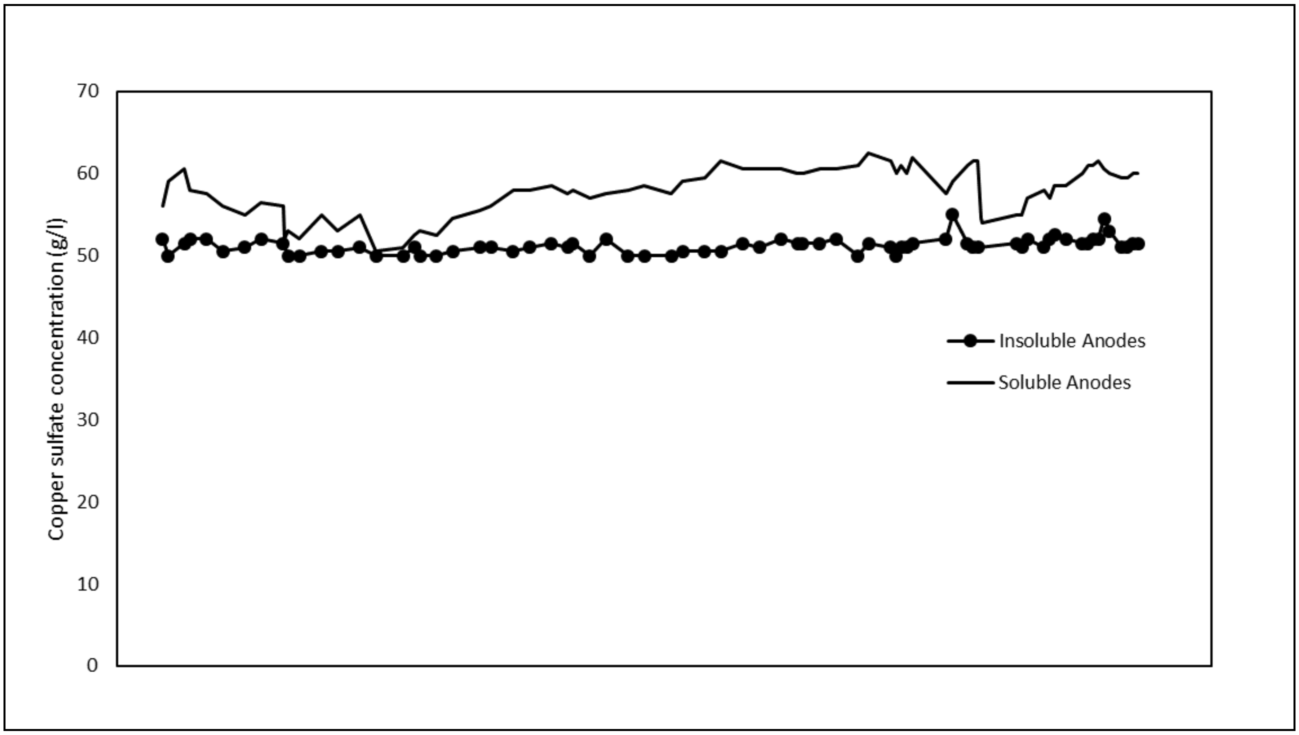

Figure 17: Copper Sulfate Concentration Control Chart for 6-Month Period.

Table 4: Chemistry Consumption Comparison.

	Before Insoluble Anodes	After Insoluble Anodes
Component 1	60 ml/1000 Amp Hour	80 ml/1000 Amp Hour
Component 2	330 ml/1000 Amp Hour	224 ml/1000 Amp Hour

Discussion

From a manufacturing perspective, the use of insoluble anodes as a replacement to the conventional copper ball anode system can provide several key benefits to the production of PCBs. Initial beneficial impact can be seen immediately in the production capacity gained from the conversion. The reduction in maintenance needed and lack of nodules generated during plating provided immediate increases in production capacity, as much of downtime can be eliminated. Along with these gains in manufacturing capacity comes gains in quality, which allows for plating of enhanced technology board products. Insoluble anodes have shown to decrease variation in plated copper distributions significantly allowing for reduction in scrap and increasing the likelihood of successful etching of fine line and space products.

Converting to an insoluble system can be trouble-free for the manufacturer as well. With proper planning, minimal downtime is observed and the drop-in-place ability of insoluble anodes means no need for changing parameters of the bath, or the bath itself during conversion. Once the system has been tested, anode placement has been verified and optimized through distribution analysis, production can begin immediately.

Conclusions

Acid copper plating is a key foundation in creating a high-quality PCBs. The copper plated on a circuit board is one of the most important aspects of the circuit's functionality. For decades, this has been done with the same conventional system of anodic dissolution of soluble copper-phos anodes. As technology demands increase in a growing North American and global market, it is becoming evident that higher quality plating technologies are required. The detrimental effects of a soluble anode system have become more obvious, as the need for tight copper distributions is fundamental to producing fine line circuits. Sludge created as a byproduct of copper-phos anodes and the ever-changing geometry/passivation loss of the anode itself requires extensive downtime to maintain and provides significant variations in plated copper, resulting in unpredictable copper deposits. With developments in anode technologies, MMO coated insoluble anodes have emerged as a long-term solution to these issues. These anodes have been put to the test in rigorous manufacturing environments and have shown the ability to provide the following toward the production of PCBs;

- Increased production capacity
- Decreased variation in plated copper.
- Decrease in plating related scrap
- Decreased likelihood of entrapped dry film based on plating variation
- Increase in plating technology capabilities as a result
- 100% plated copper utilization

Because of these attributes, the ability to produce high-technology circuit boards is increased. Through the application of the MMO anodes, a 12% production improvement is realized while copper plated board distributions were reduced by 50%. An advanced copper replenishment system allows for tighter control of copper concentration when compared to that of a soluble anode system. The electrolytic grade of copper oxide supplied is only marginally more expensive than the soluble copper-phos balls, providing little impact on the overall board costs. The copper content of the copper oxide powder is ~80%. However, the associated production costs only account for a small cost increase per panel produced when measured along with the increased production capacity benefit. As demand for high technology work in the North American and global PCB market rises, insoluble anodes with advanced MMO coatings are an important component of the solution.

References

1. M. Lefebvre, G. Allardyce, M. Seita, et al., "Copper Electroplating Technology for Microvia Filling", HKPCA, no. 14, pp. 1-13.
2. C. F. Coombs, H.T. Holden, "Printed Circuits Handbook", McGraw Hill, 2016.
3. G. Milad, "How to Set Up a Successful Blind Via Hole Fill DC Plating Process", February 2016, SMTA International Conference.

Mixed Metal Oxide "MMO" Insoluble Anode System for Enhanced Operational Acid Copper Plating of Printed Wire Boards "PWB"

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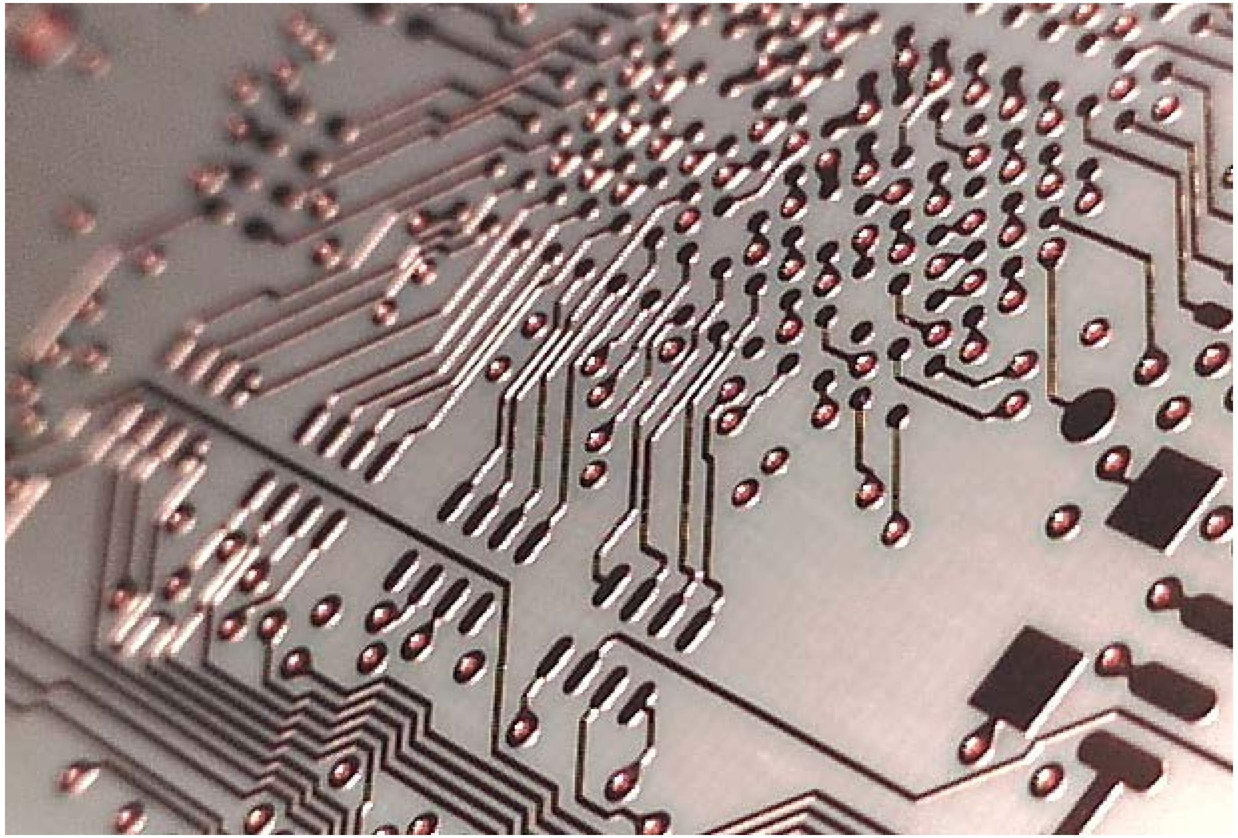
Outline

- Acid-Copper Electroplating
- Anode systems
  - *Soluble*
  - *Insoluble*
- Insoluble Anodes in Industry
- Installation
- Testing/Results
- Conclusions

Acid-Copper Plating

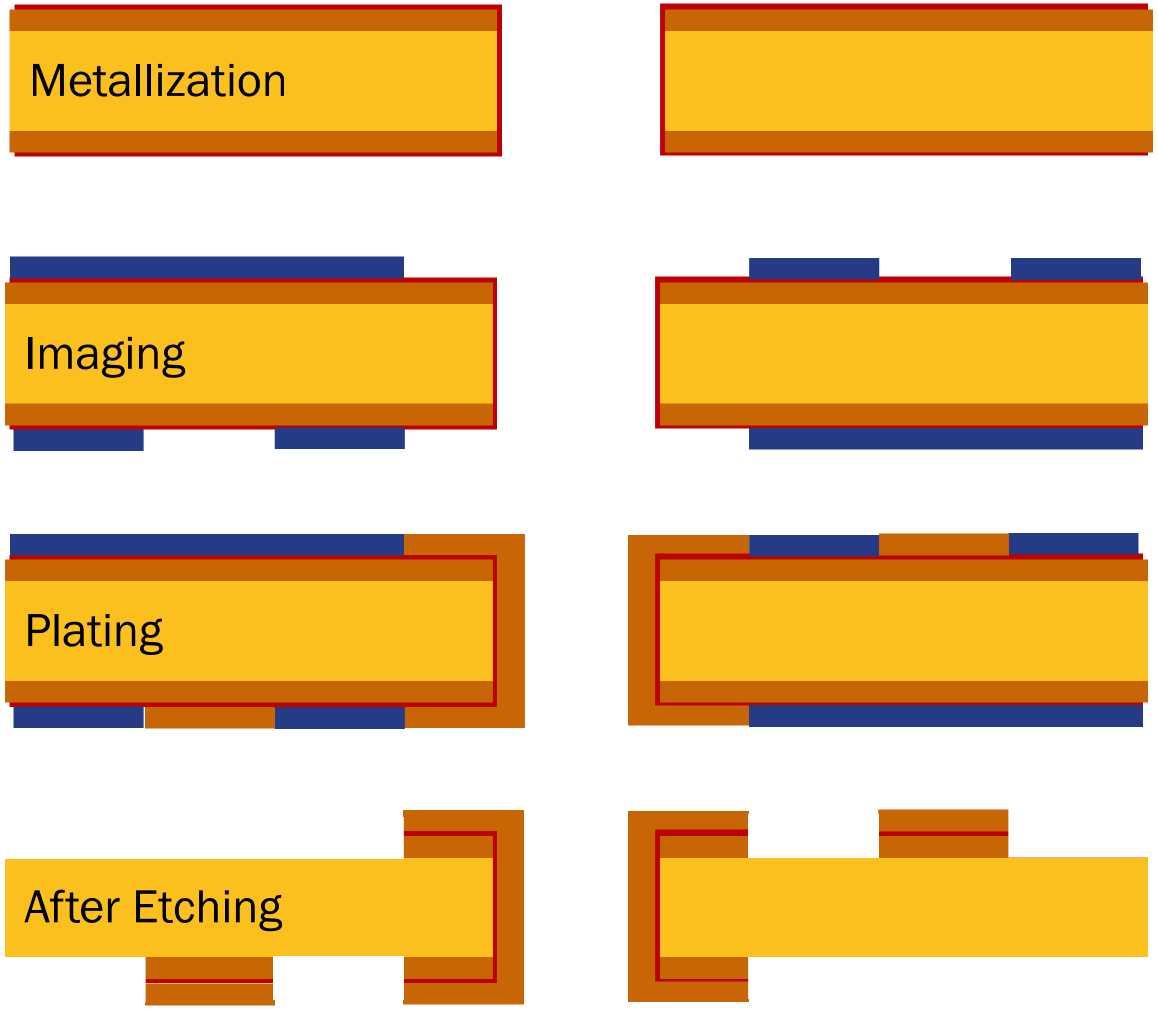
- Responsible for creating robust copper plated holes and conductors
  - *Key in withstanding stress*
- Consists of:
  - *Copper*
  - *Sulfuric Acid*
  - *Chlorides*
  - *Organics*



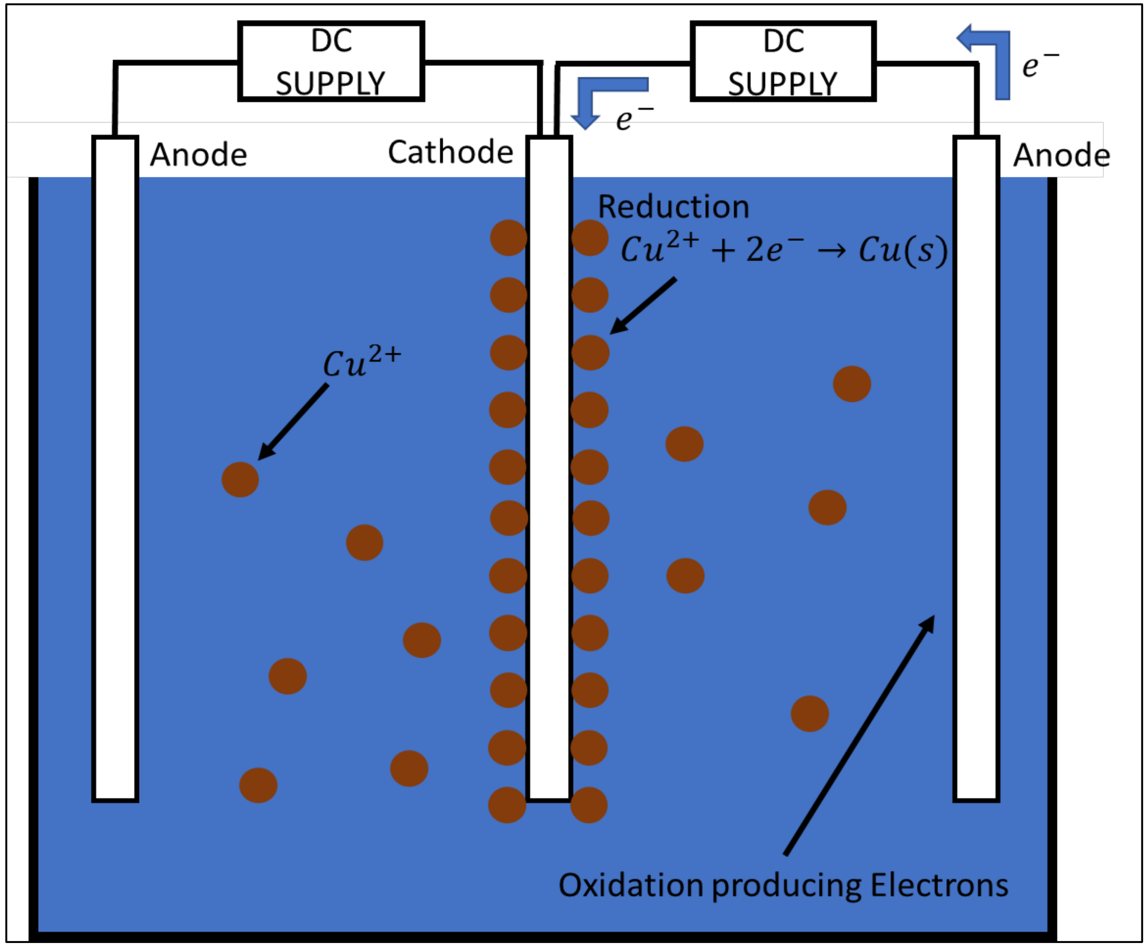
Electroplating

Desired Characteristics

- High throwing power
- Copper distribution (uniformity)
- High quality deposit (grain, purity, etc…)



Simple Copper Electroplating Cell



Soluble Anodes

- Traditional Cu-Phos anodes are 99.93% copper
- Relies on electrolytic dissolution of copper anode as source of copper ion in plating bath

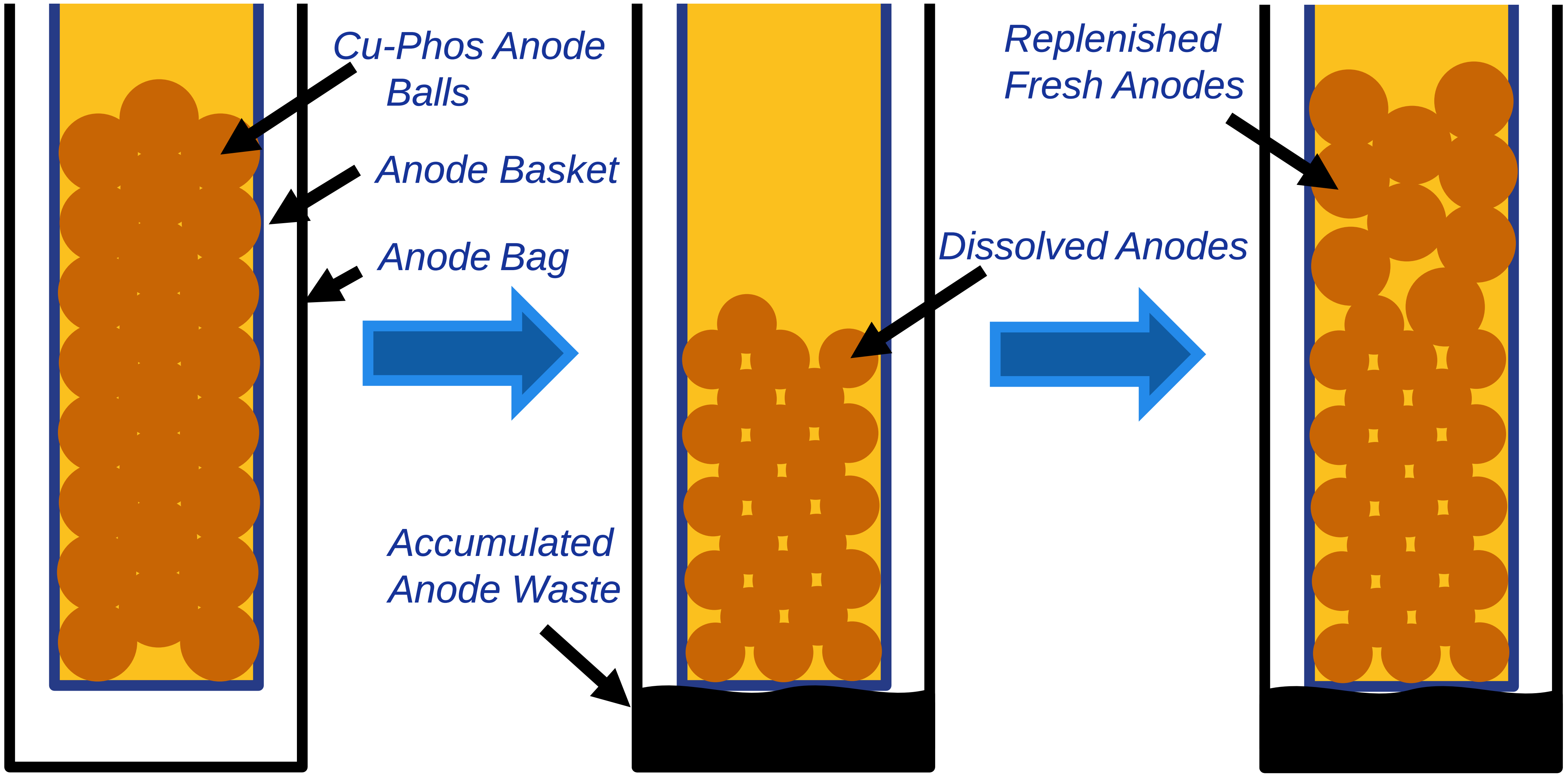
$$Reaction\ at\ the\ anode: Cu(s) \rightarrow Cu^{2+} + 2e^{-}$$

$$Reaction\ at\ the\ cathode: Cu^{2+} + 2e^{-} \rightarrow Cu(s)$$

Soluble Anodes

- As the copper dissolves into solution, the anodes change shape
- The anodes must then be refilled with new copper
- Impurities build and create sludge in bottom of anode bag
- Requires maintenance to refill, knock down and dummy plate anodes

Soluble Anodes



Soluble Anode Degradation

Insoluble Anodes

- Uses an electrocatalytic layer and conductive surface to transfer electrons
- Is not consumed by the reaction
- Evolves oxygen as a result

Insoluble Copper Plating System Reactions

$$Reaction\ at\ Anode: H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

$$Reaction\ at\ Cathode: Cu^{2+} + 2e^- \rightarrow Cu(s)$$

$$Reaction\ at\ Cu\ Dissolution\ Unit:\ CuO + H_2SO_4 \rightarrow Cu^{2+} + {SO_4}^{2-} + H_2O$$

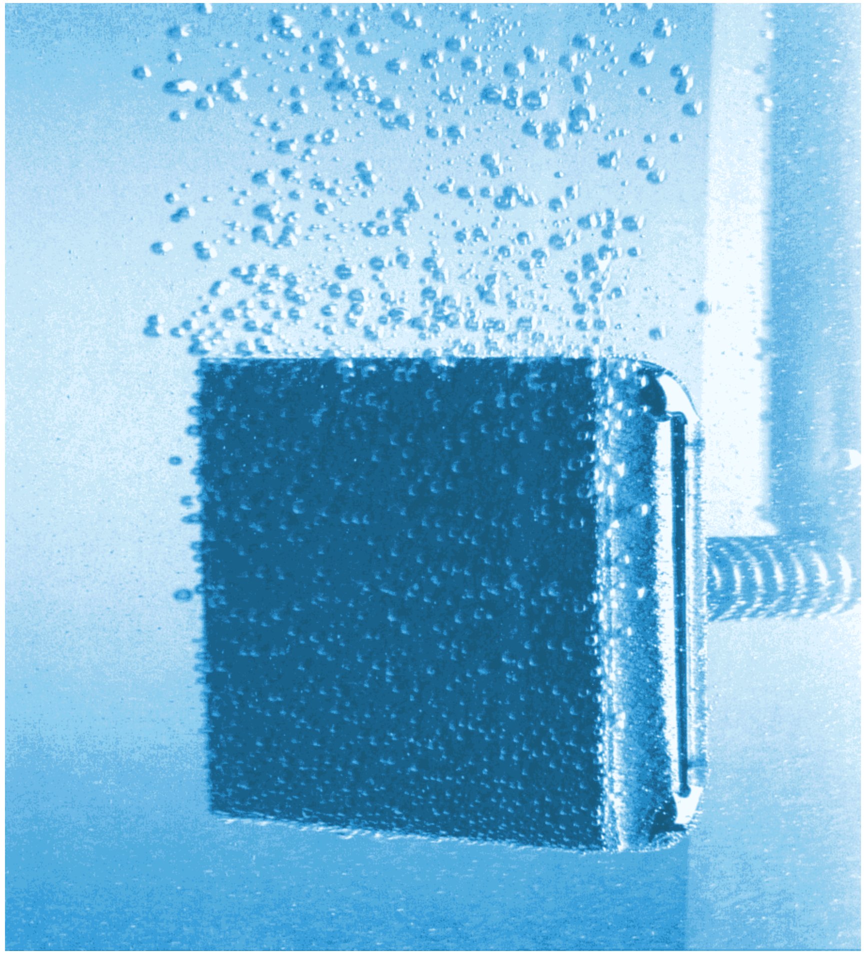
Dimensionally Stable Anode Mixed Metal Oxide (MMO)

Valve Metal Substrate

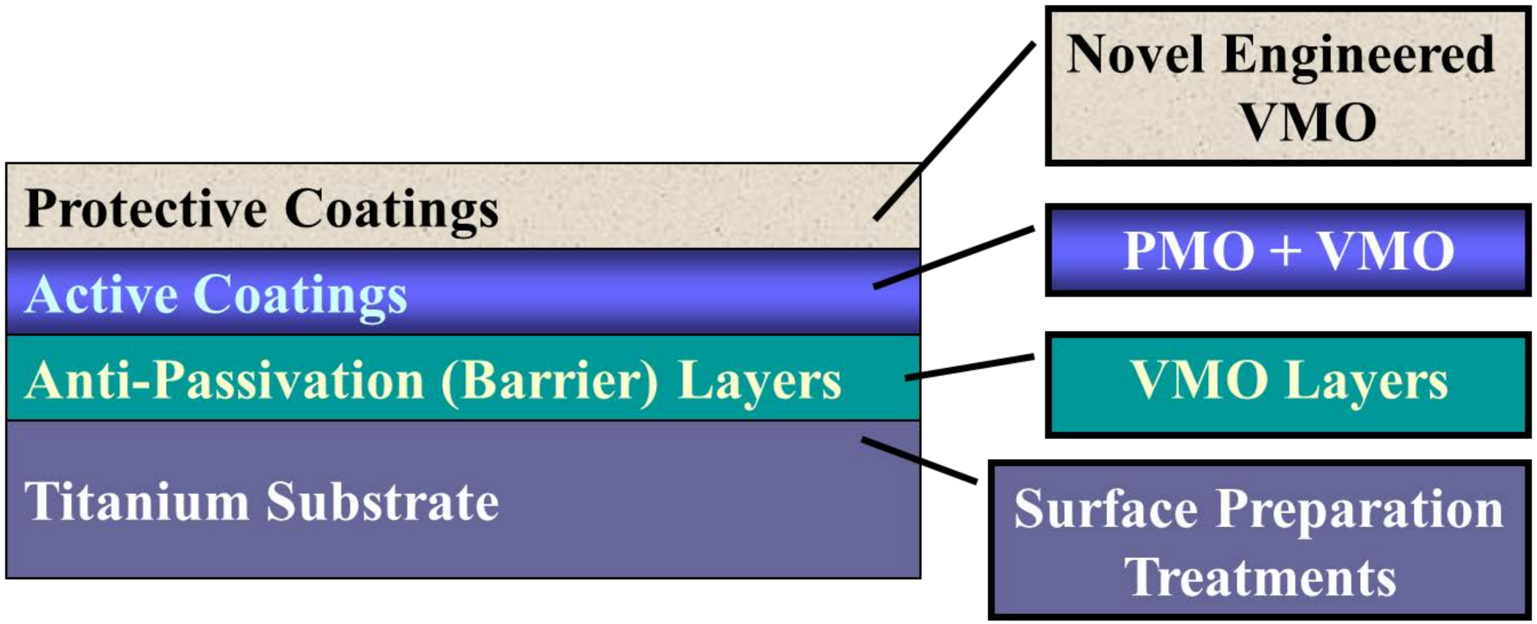
- Titanium

Electrocatalytic Coating

- Platinum group metal oxides
  - *RuO_2 and IrO_2*
- Valve metal oxides
  - *TiO_2 and Ta_2O_5*



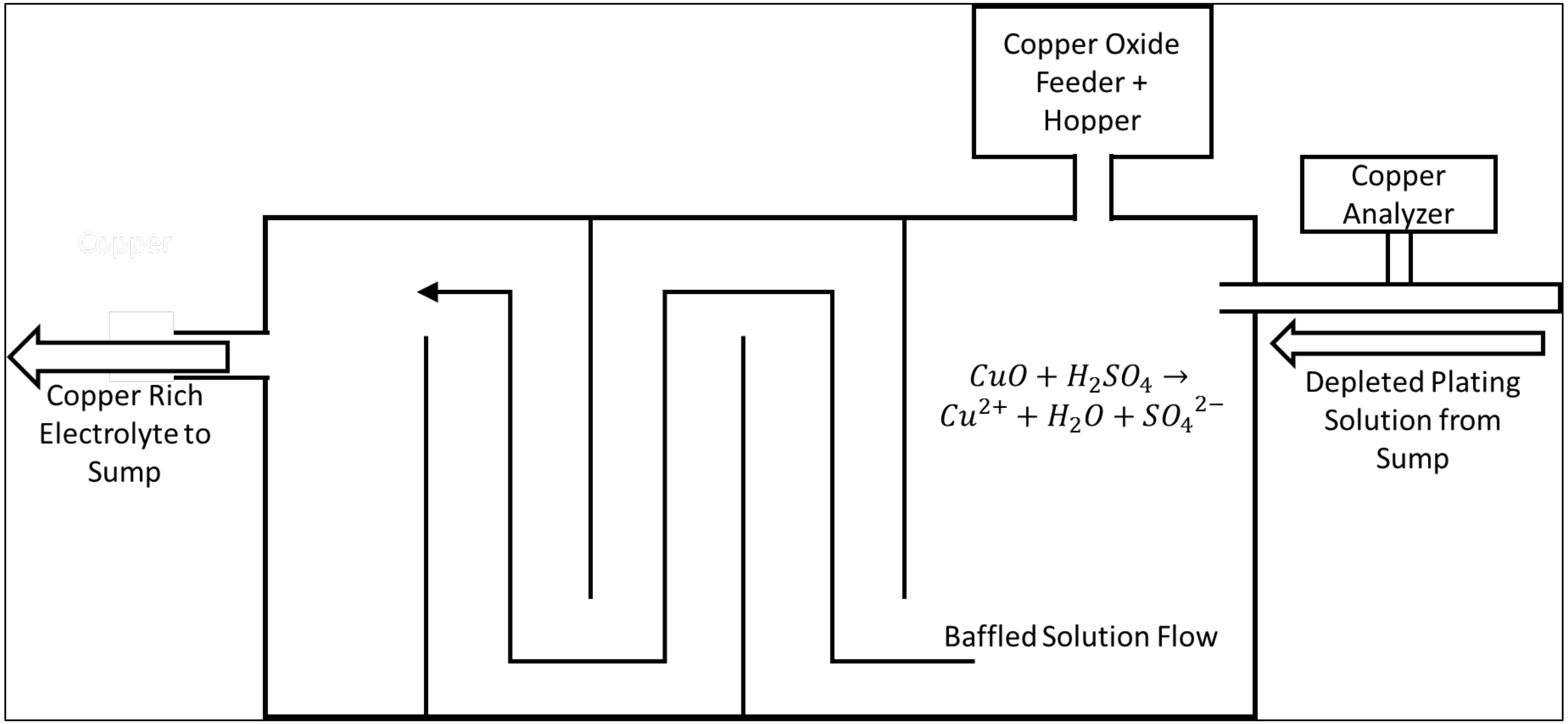
Dimensionally Stable Anode Components
Mixed Metal Oxide - MMO



Copper Oxide Feeder System

- CuO Powder Feeder Control Loop Methods
  - *Continuous Feedback Control Loop employing Inline Colorimeter*
  - *On-Demand AmpHr Control Loop Using Rectifier Output Signal*
- Associated Mixing Tank is Designed to Facilitate CuO Dissolution
  - *Mixing Tank ~10% Volume of Plating tanks*
  - *Internal Tank Design includes Baffles for Increased Electrolyte Residence Time for Improved CuO Dissolution*
  - *Incorporates Internal Mixers and Pump Electrolyte Recycle*
  - *Can be Plumbed to Support Feed to Multiple Plating Tanks of Common Chemistries*
- Copper Oxide – CuO
  - *Electronic-Technical Grade High Purity, 99+% CuO*
  - *Specified for Quick Full Dissolution*

Diagram Depicting Action of Copper Oxide Dissolution Feeder Unit (Copper Replenishment System)



Comparison of MMO Titanium Anode to Soluble Anodes

Insoluble Anode

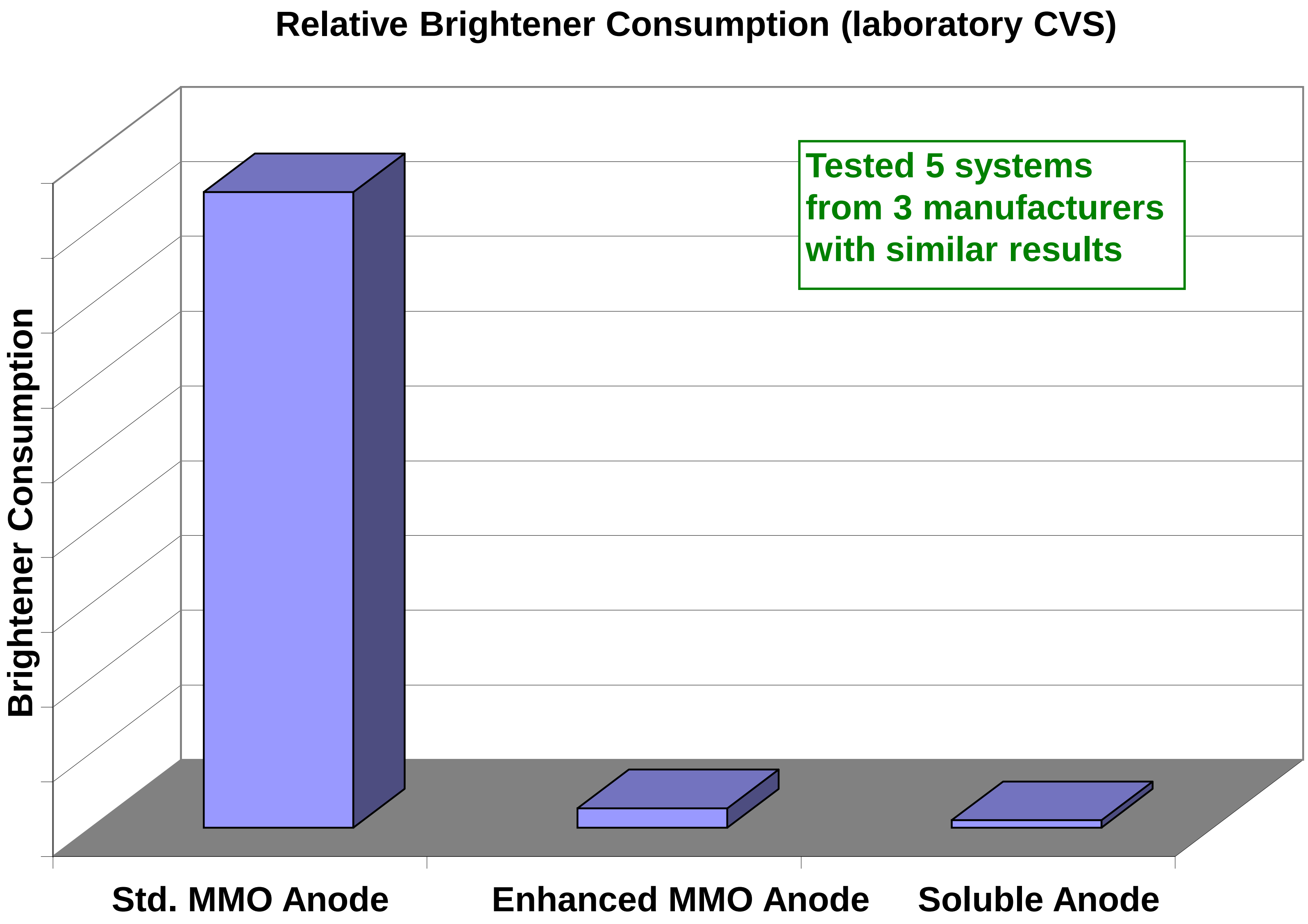
- Stable substrate
  - *No contamination*
  - *No change in gap*
- Recoatable Ti Substrate
  - *15+ yr, 3+ yr coating*
- Low Operational Potential
- Needs Copper Replenished
- High Design Flexibility

Soluble Anode

- Continuous dissolution
  - *Adds impurities*
  - *Req. balancing anodes*
  - *Req. dummy plating*
  - *Changing surface/gap*
- Replace continuously
- Very low potential
- Little design flexibility

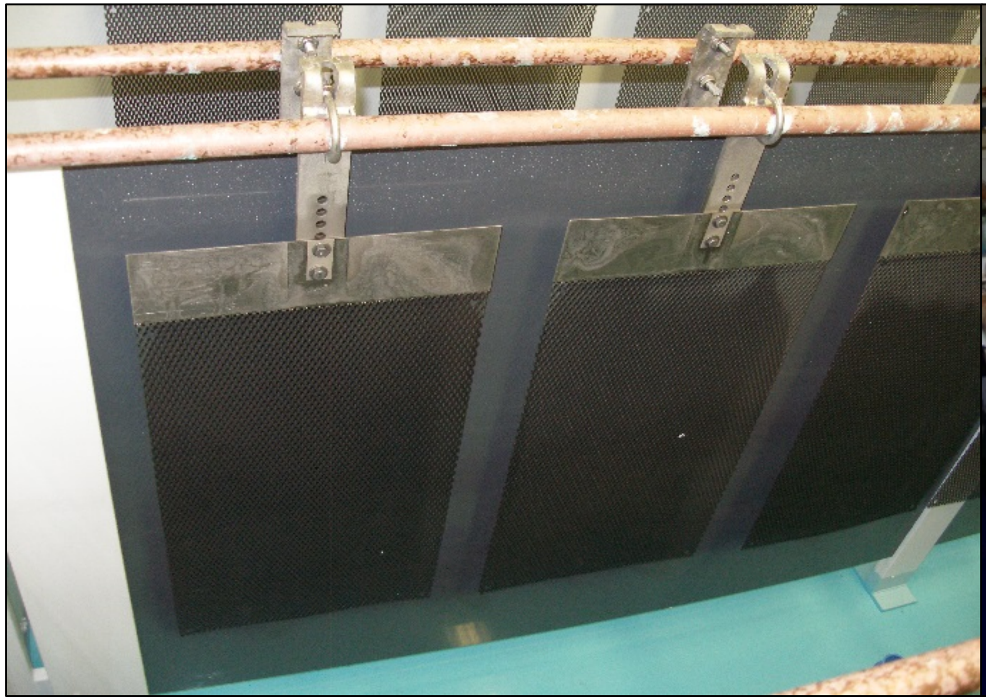
MMO Insoluble Anode in PWB Industry

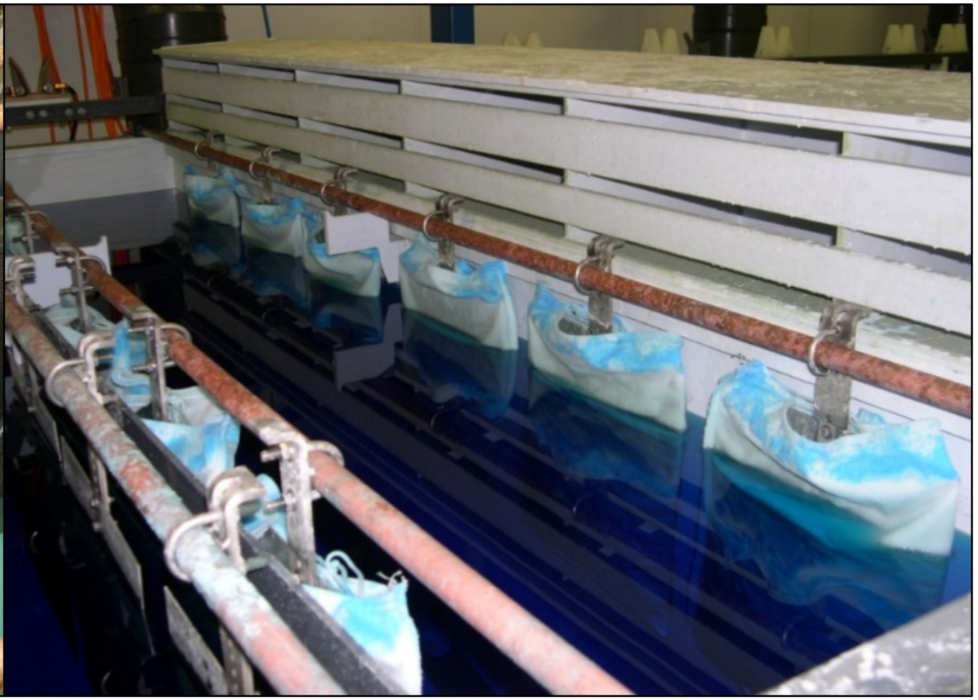
- Replaces soluble Cu anodes
- Addition of protective VMO topcoat minimizes oxidation of organic components (brighteners, levelers, carriers) in plating path
- Additional protection provided by utilizing bags over anodes to keep oxygen bubbles from main plating solution
- Advantages;
  - *Improves uniformity in thickness of plated layer*
  - *Improves throwing power*
  - *Provides reproducible performance*
  - *Eliminates need to dummy plate*
  - *Eliminates routine operator maintained to replenish anodes*
  - *Eliminates copper waste*


Relative Brightener Consumption (laboratory CVS)
Brightener Consumption
Tested 5 systems
from 3 manufacturers
with similar results
Std. MMO Anode
Enhanced MMO Anode
Soluble Anode

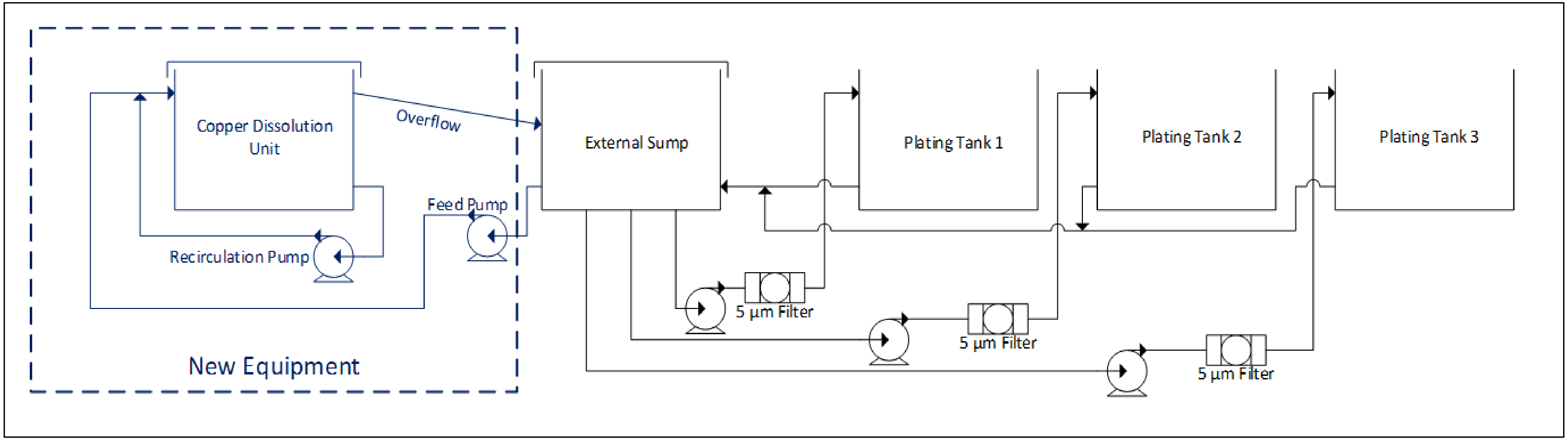
Installed MMO Anode in Plating Tank

(Before and After Oxygen Capture Bag Installation)





Simplified Diagram of Vertical Racked Plating Set-up

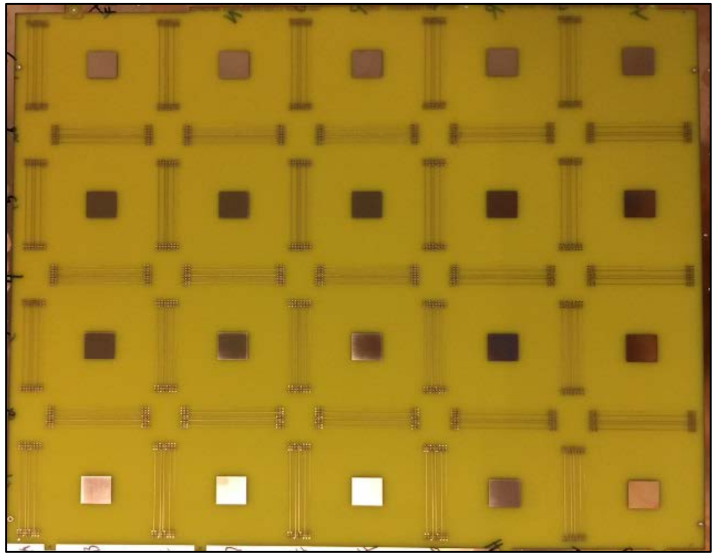


Plating Cell Volume (2 Cells per Tank)	550 Gallon
Anode to Cathode Spacing	10.5 in.
Filter Replenishment Rate (per cell)	45 gal/min
Bath solution turnover (refresh rate)	5/hour
Eductor Flow rate (per cell)	35 gal/min

Improved Distributions Results – Gateway to Advanced Technology Products

Test Vehicle Parameters for Distribution Analysis

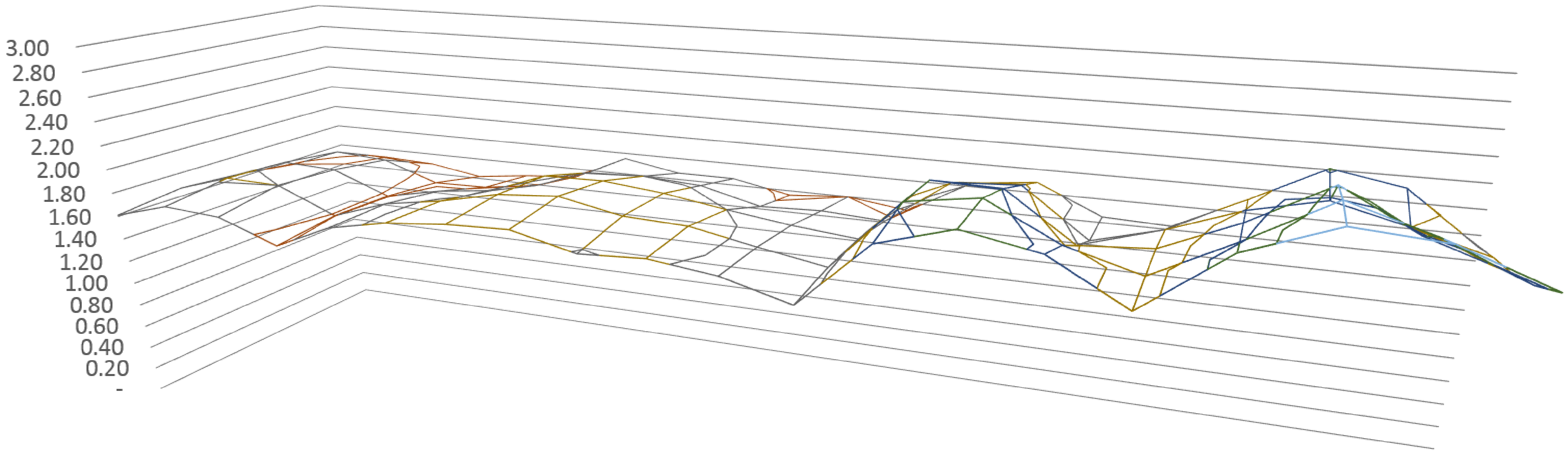
	18" Test Vehicle	21" Test Vehicle
Surface Area/Side	0.371 ft^2	0.495 ft^2
Total Surface Area	0.742 ft^2	0.99 ft^2
Current Density	14 amps/ft^2	14 amps/ft^2
Plating Time	90 minutes	90 minutes



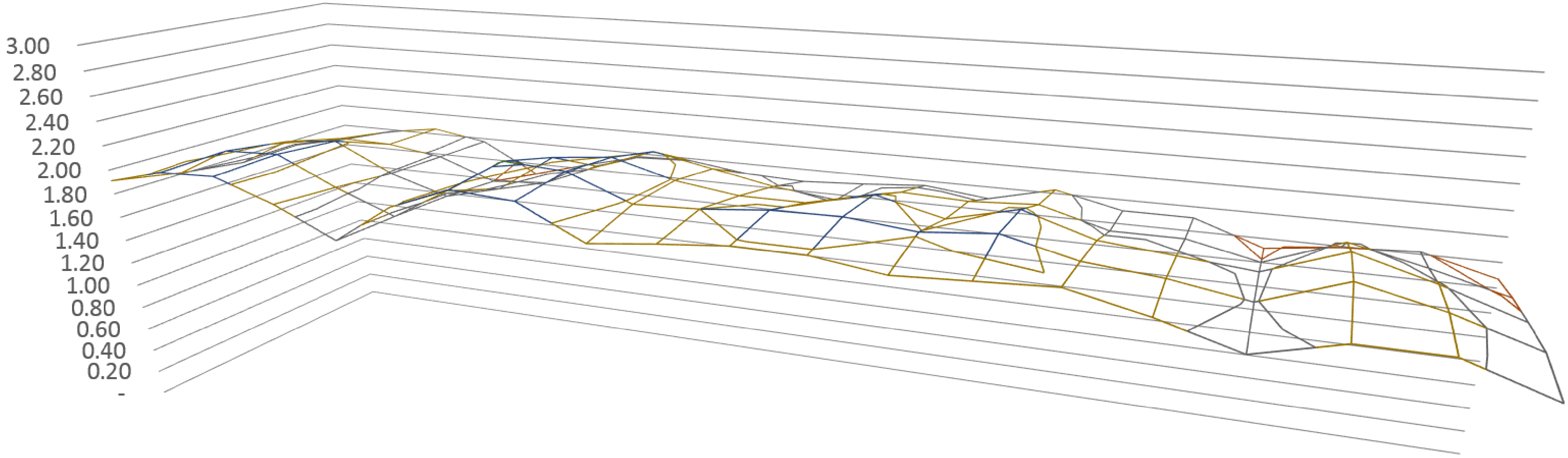
Reductions in Range and Standard Deviation of Plating Thickness.

	All Data Points	Averaged by Position
Range	55% Reduction	38% reduction
Standard Deviation	50% reduction	42% reduction

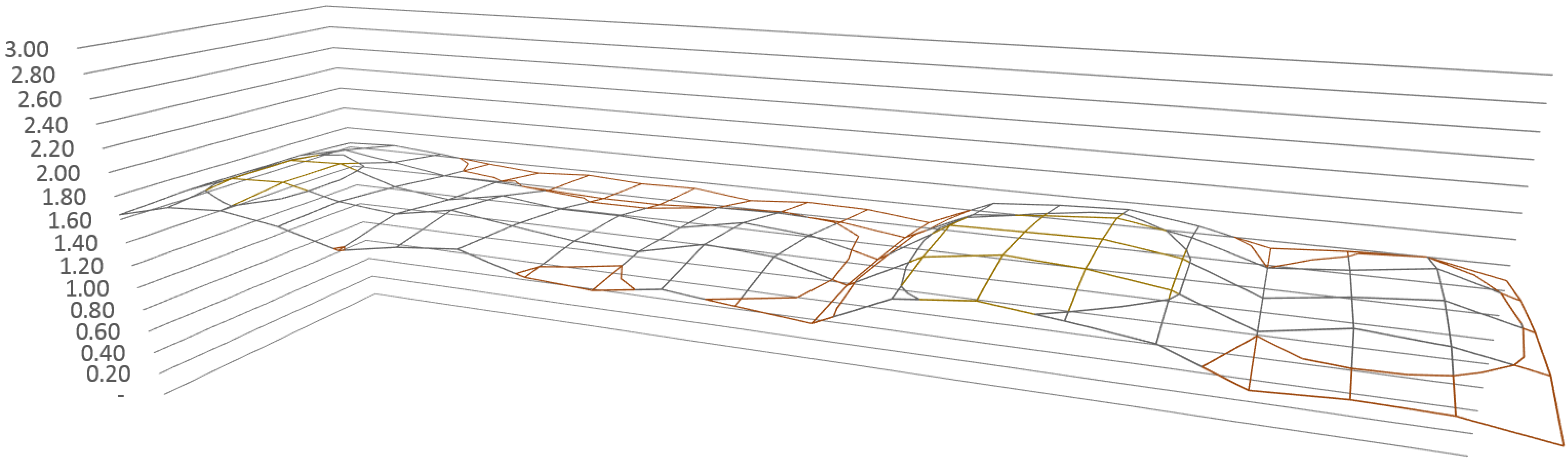
Flight Bar Surface Distribution Soluble Anodes: Worst Case



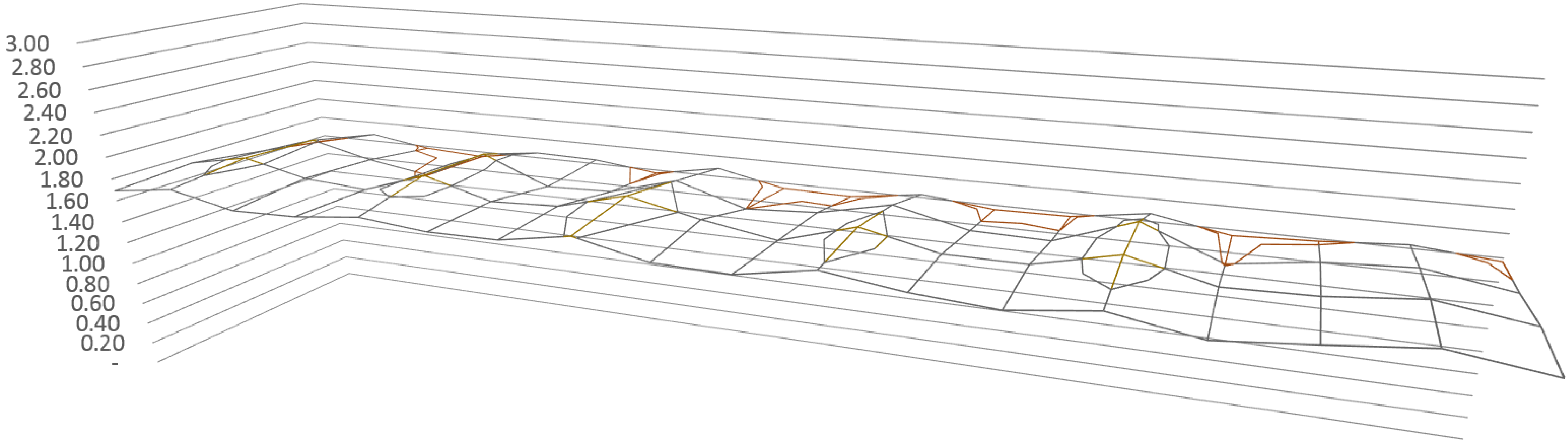
Flight Bar Surface Distribution Soluble Anodes: Best Case



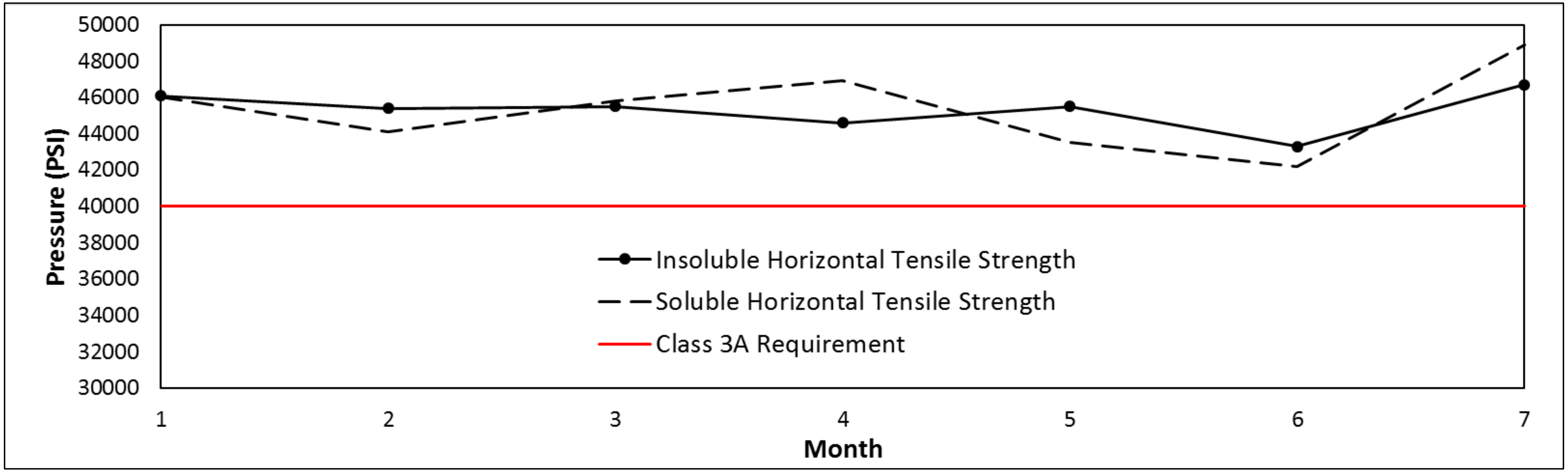
Flight Bar Surface Distribution Insoluble Anodes: Worst Case



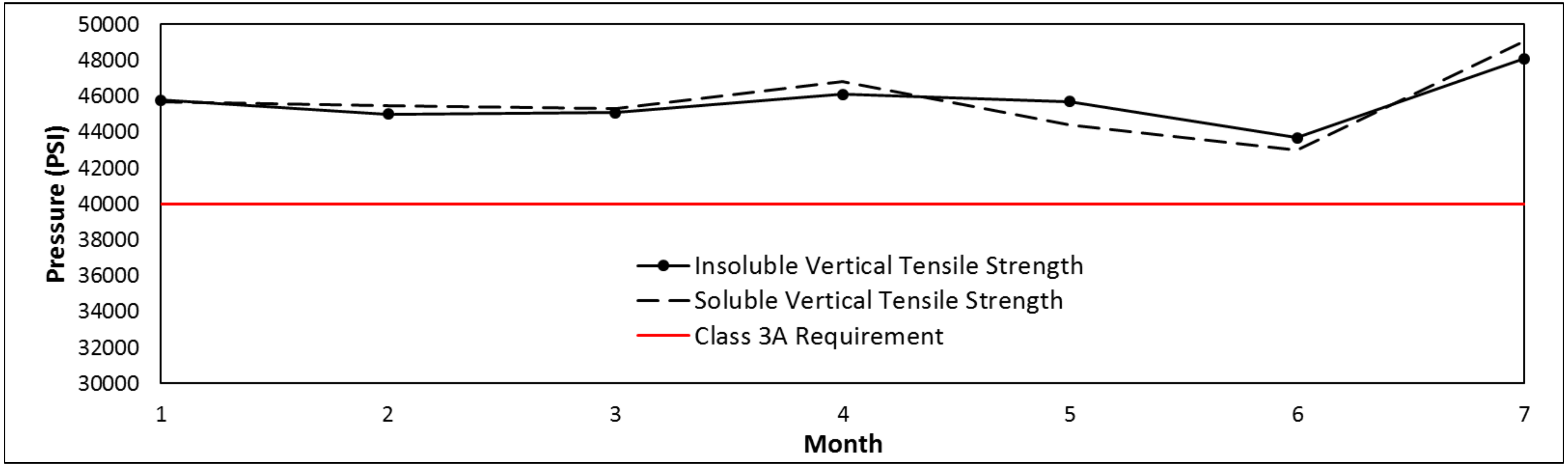
Flight Bar Surface Distribution Insoluble Anodes: Best Case



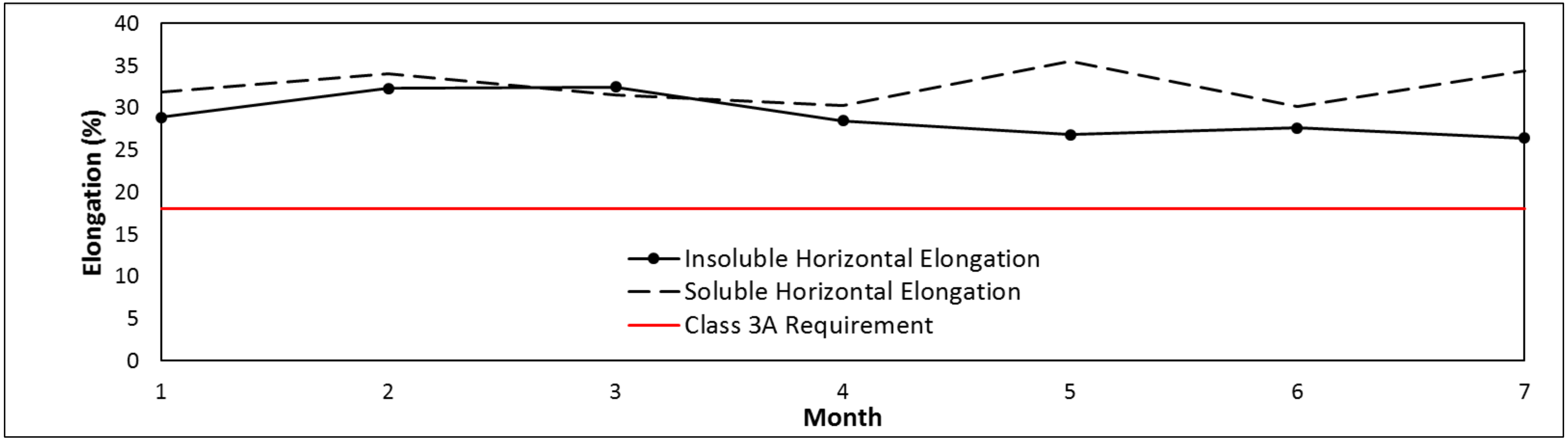
Horizontal Tensile Strength Monthly Results Trending



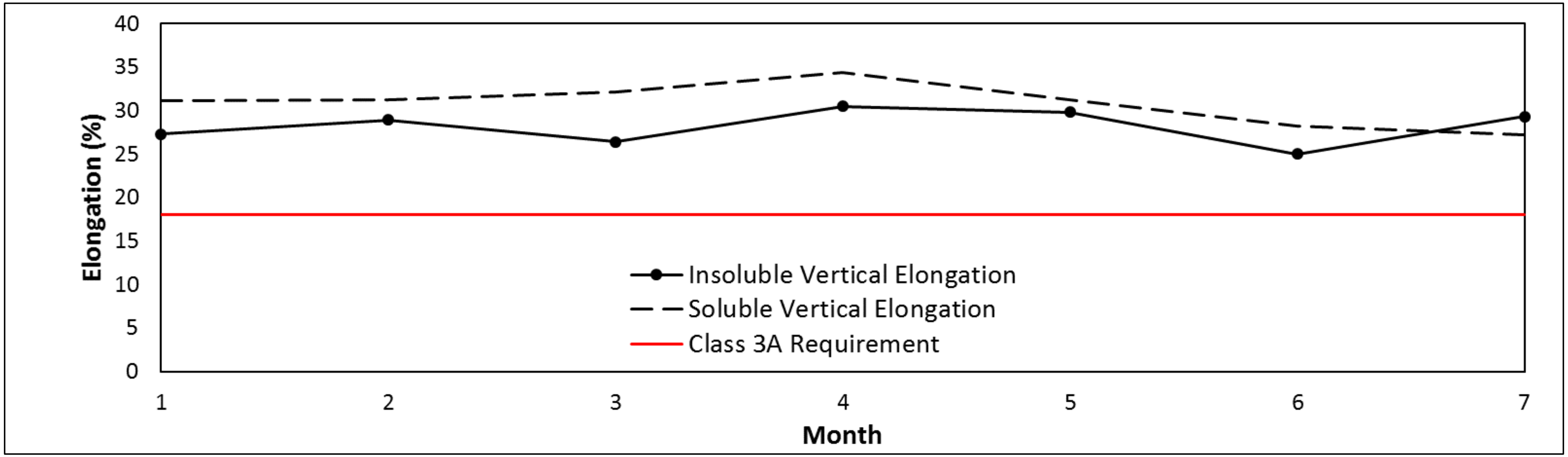
Vertical Tensile Strength Monthly Results Trending



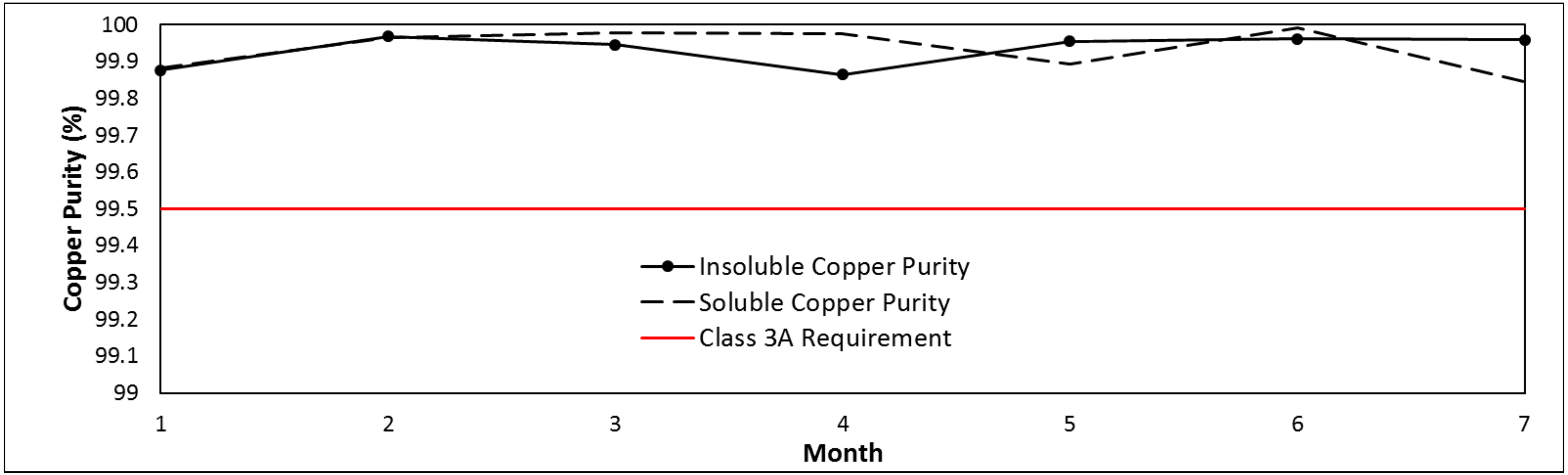
Horizontal Elongation Monthly Results Trending



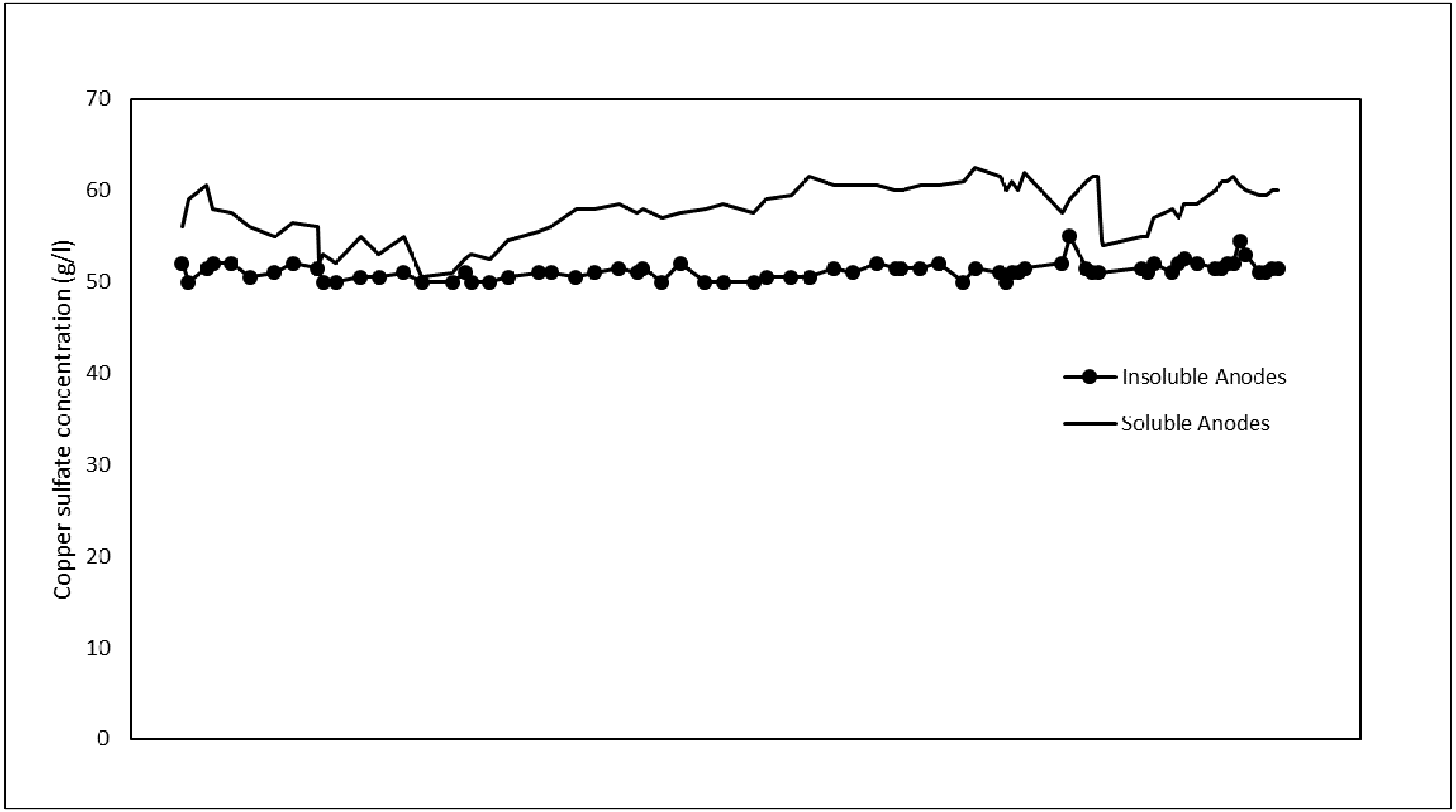
Vertical Elongation Monthly Results Trending



Copper Purity Monthly Results Trending



Copper Sulfate Concentration Control Chart for 6-Month Period



Chemistry Consumption Comparison

	Prior Operation with CuP Soluble Anodes	Operation with Enhanced Insoluble MMO Anodes
Component 1	60 ml/1000 Amp Hour	80 ml/1000 Amp Hour
Component 2	330 ml/1000 Amp Hour	224 ml/1000 Amp Hour

Near equivalency suggests continuity in chemistry consumption with change to enhanced MMO system

MMO Automatic Vertical Hoist Line Conclusions

- Increased production capacity
- Decreased variation in plated copper
- Decrease in plating related scrap
- Decreased likelihood of entrapped dry-film based on plating variation
- Increase in plating technology capabilities as a result
- 100% plated copper utilization

Questions?