

Effects of Electrolyte Impurities in Chlorate Cells

Presentation provides an introductory review of the role of electrolyte impurities in chlorate cells on DSA coating and chlorate cell performance. Provides a series of case histories discussing specific impurities that have initiated premature DSA failures in chlorate systems. Also touches on the impact of impurities on solution processes and cathode effects often mistaken for changes in anode performance. Presentation is specific to the chlorate cell industry.



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DSA[®] service life and performance have been greatly influenced on occasion by the impurities present in chlorate cell electrolytes. It can be safely observed that brine and electrolyte quality plays a crucial role on the long term economic performance of DSA technology. Recommended electrolyte quality specifications are usually a part of anode contracts and provide a reliable guide to achieving expected lifetime and voltage performance. Impurities impact chlorate cell DSA through the classical failure modes of **coating loss, passivation, and blinding deposits**. With cathodes, reduced operating efficiencies and increased operating voltages are observed. Each of these areas and the effect of specific impurities on chlorate cell DSA can be best reviewed through a series of case histories detailing specific field encountered problems.

First, it is appropriate to review some background on DSA anode technology. DSA are a unique combination of valve metal, precious metal oxides catalysts, chemically bound to a valve metal substrate (Figure 1). For most commercial applications the valve metal of choice is titanium. A valve metal is a metal that will passivate (form a protective oxide film on exposed metallic surfaces) upon anodic polarization in aqueous electrolytes. This property gives the valve metals a remarkable corrosion resistance in many operating environments, but also prevents the use of the valve metal, independently, as an anode without the addition of a properly formed catalytic layer. The protective action of this oxide film in many applications is sufficient to allow reuse of the substrate when catalyst failure has occurred. A Scanning Electron Microscope (SEM) surface view compares that of EC100 and EC120 (Figure 2). EC100 reveals the mudcracked, high surface area characteristic of chlorine/chlorate DSA. The EC120 has a smoother morphology, of which the benefits will be described later.

Examining a cross sectional view, there are four ways to interrupt the electrical circuit between the metal substrate and the electrolyte. The catalyst can be lost in service exposing the valve metal substrate which oxidizes and cannot accept electrons from solution without the presence of the catalyst (Figure 3). Secondly, the substrate can be chemically attacked at the coating interface, resulting in loss of adhesion of the coating (Figure 4). Thirdly, the interface between the catalyst and the substrate can become non-conductive preventing electron flow from the catalyst to the substrate (Figure 5). And finally, a foreign material can deposit on the surface of the catalyst effectively isolating the catalyst from the solution (Figure 6).

Coating Wear
Substrate Attack
Passivation
Blinding Deposits

Impurities in the electrolyte impact directly and indirectly on each of these failure mechanisms.

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COATING LOSS

Wear

Brine impurities directly and indirectly affect the catalyst wear mechanism. Normal DSA performance is characterized in Figure 7. Typically a 10-15% initial loss of catalyst is observed over the first six months to a year of operation, followed by a gradual wear with time throughout the useful life of the coating. No change in voltage performance is expected until below 20% of original loadings are present. As wear continues, a gradual increase in operating voltage will be observed as wear exposes uncoated areas of the substrate. Current will shift to remaining active areas, locally increasing current density and observed operating voltage.

Wear accelerating impurities can be broken readily into two groups. Those that attack the DSA directly when present in the electrolyte and those which have a secondary role by interacting with another part of the system causing subsequent effects on the DSA.

A list of secondary impact elements and compounds has been developed (Figure 8). These materials directly impact on cathodes allowing the alkaline condition of the cathode region to reach the DSA surface, directly attacking the coating matrix. In chlorate systems, hardness scales can grow from cathode surfaces to bridge the gap between anode and cathodes. The porous nature of these deposits works like a sponge, allowing caustic to directly attack the DSA matrix. Aluminum and silica are also frequently found within these hardness deposits adding to the growth rate above that expected from the hardness values alone. In systems where titanium cathodes are used there can be a synergistic effect between all of the above.

Chemical attack to the coating matrix is generally characterized by large variations in catalyst loading. In extreme cases, this can be observed visually. In regions where coating remains it will have developed a very powdery texture. If only chemical attack has occurred, the SEP's will be normal in the areas with coating remaining. Local regions can be passivated if flow blockage has taken place.

Accelerated Wear

The Effect of Cathode Scales

The wear accelerating effects of cathode scales were easily visualized with a slide of a failed chlorate cell DSA. Operators experienced difficulties in maintaining low hardness brine feed to the electrolyzer. Over the course of a year, hardness levels ranged between 80 - 100 ppm Ca. Within fifteen months serious voltage escalation were being observed. Sufficient DSA were chemically attacked by the cathode scales that recoating of the plant was required. Improvements in the brine system allowing routine operation below 25 ppm Ca and, eventually to less than 5 ppm Ca, have extended anode lifetimes well beyond 5 years.

Accelerated Wear Synergistic Effects

Emphasis on the use of low hardness brines is important but it is not the only source of problems in chlorate systems. At another plant site, traditional brine quality was very good but erratic cell voltage performance was encountered. A review of feed brine hardness, over the period of concern, revealed excellent control of calcium and magnesium, yet anodes removed from service were visually scaled. Cleaning of the parts revealed wide variations in appearance. Locally DSA coating was completely stripped from the surface of the anodes. The extent of damage ranged from no coating loss through 90% catalyst removal from the mesh. Effects were typical of caustic accelerated wear from cathode scales, with symptoms that include erratic cell voltages, light scales on DSA surfaces and random loss of catalyst, apparent when surface scales are removed. In areas with catalyst remaining voltages were normal.

Scale samples were initially analyzed by ICP techniques. The deposit was not typical of previously reported cathode scales but contained significant amounts of Al, Si and Ti with only small amounts of the traditional Ca and Mg. Referencing a summary of additional analysis conducted on the anode samples, TEFA analysis for heavy metals revealed catalyst components with trace levels of Fe, Sn and Ca. Finally, an analysis of the scale deposits using X-ray diffraction techniques demonstrated the scale to be a combination of titanium oxides and hydrides in addition to the aluminum and silicon. The combination of deposits was sufficient to allow caustic migration from the cathode to reach anode regions locally stripping the DSA. Had the deposits been typical of anode blinding, passivation would have been encountered instead.

Substrate Attack The Fluoride Factor

Fluoride ion directly attacks the titanium at the coating/substrate interface. The corrosion resistance of DSA depends on the stability of the oxide film. Fluoride ion can penetrate this film, destabilizing the titanium surface. Titanium dissolution results in loss of catalyst.

The symptoms of fluoride attack are characteristic of wear from titanium instability. Adhesion to the substrate is poor. Areas of removed coating are usually visible. Bare metal exposure occurs by adhesion testing but catalyst activity remains normal.

Laboratory testing of the effect of fluoride ion on EC100 DSA lifetime has been dramatic. At 10 ppm free F⁻ in pure electrolytes lifetimes in accelerated testing were reduced 64%. In the field, a chlorate manufacturer was mistakenly delivered sodium fluorosilicate instead of sodium chloride. Within hours of the delivery, the plant began experiencing short filter cycles and problems in salt recovery. No problems were observed with cell voltages or oxygen levels. Five or six days passed (over the holidays) before treatment to remove F was initiated. Within this time period free F⁻ peaked at 32 ppm. Within two days of treatment fluoride levels dropped to < 4 ppm but would periodically rise again to 30 ppm as pockets of contaminated salt were consumed. Anodes ranged in age from 8 months in one circuit to 39 months in another circuit. All had extremely poor catalyst adhesion but excellent single electrode potentials. Accelerated testing of affected anodes indicated at least a 50% reduction in life compared to new material of the same catalyst loading. That combined with a reluctance to risk a catastrophic failure because of the poor adhesion,

resulted in recoating of the anodes from the older circuit. Anodes from the circuit less than 8 months old were returned to service without recoating. Lifetime was four years. Anodes out of service at the time of the upset exceeded eight years of service.

At another plant site, a cooling system failure contributed serious fluoride upsets when Freon contaminated hydrogen was burned to supply acid for pH adjustment. A step increase in cell voltage was reported by the customer. Two anodes received for analysis had an orange surface deposit covering the entire anode, while an additional two anodes received had very little visible surface deposits. Surprisingly, the anodes with the heavy deposits had normal SEP's, while the clean anodes had elevated SEP's of >2.0 V vs. SCE. A microscopic examination of the high SEP anode revealed areas of substrate attack, as would be expected by the presence of fluoride. Tape tests removed more of the loosely bonded coating. Electrolyte analysis found fluoride levels of 50 ppm. The source of the fluoride was determined after the examination. The two anodes with the deposit had been removed from service prior to the contamination, thus the normal SEP. The voltage increase may also have been caused by organics, as thermal cycling the anodes lowered the SEP.

On yet other occasions, fluorides have entered chlorate liquors through water sources and accumulated in closed loop systems.

EC120 now has several years of commercial service at some locations where fluoride levels are 20 - 30 ppm, with no significant coating wear or substrate attack. This is due to the compact nature of the coating, resulting in a less porous coating compared to EC100. The stability of the EC120 may also be influenced by other elements/compounds in the electrolytes that are tying up the fluoride ion, inhibiting substrate attack.

PASSIVATION

Substrate passivation is defined as the growth of a non-conductive oxide layer between the DSA catalyst and the valve metal substrate. This is the primary failure mode for anodes designed for use in oxygen evolving applications such as electrogalvanizing. Passivation failures in chlor-alkali service have been rare but are being observed in diaphragm and membrane cell service. Some coatings with 15 to 20 years life in diaphragm service are experiencing passivation failures. When early passivation is encountered in chlor-alkali service it is a direct result of operating the chlorine DSA at conditions associated with increasing the rate of oxygen generation at the catalyst surface. Restricted levels of chloride ion associated with low electrolyte concentrations, surface deposits that interfere with the rapid diffusion of chloride to the catalyst surface, even changes in current density associated with poor current distribution will effectively increase the rate of oxygen evolution.

A typical potential time curve for DSA anodes operated to passivation failure is similar for both chlorine and oxygen type anodes (Figure 9). The difference between the two is reflected in the time axis. For oxygen coatings at 3 kA/m^2 the time axis can be years. For chlorine coatings, producing only oxygen, the axis is measured in hours.

In both cases, the time to failure can be directly related to the amount of oxygen produced and the rate at which it is generated. Studies involving chlorine DSA coatings run to passivation failure under low NaCl conditions have resulted in a mathematical relationship between life, catalyst loading, and the rate of oxygen generation at the DSA surface.

The exponential relationship between expected lifetime and the rate of oxygen production can result in rapid failure of a chlorine DSA when operation at conditions favoring increased oxygen production are encountered. If a catalyst loading is established for operation at a specified maximum rate of oxygen generation using 3 kA/m^2 but is operated at 4 or 5 kA/m^2 by design or through poor current distribution, the forecast life is significantly reduced as illustrated (Figure 10).

Passivation failure is characterized by a non-reversible increase in the single electrode potential when conventional surface cleaning concepts are employed. Failure of chemical etching, degreasing or mechanical cleaning methods to restore performance has traditionally been used as an indicator of passivation, prior to the introduction of AC Impedance concepts.

While surface cleaning techniques are ineffective in recovering the performance of passivated samples, thermal processing has been used to recover chlorine single electrode potentials. This is consistent with the concept of subtle changes in the interface region explaining the high voltage performance. Thermal processing can alter composition through diffusional processes reducing resistance and recovering for a short time the operating potentials.

In chlorine systems, passivation failure is usually preceded by a period of high cell voltage or unstable current distribution. Generally high levels of residual catalyst will remain, but operate at high potential.

Impurities that result in precipitation within the cell compartments can cause a loss of flow within the electrolyzer or locally between anodes and cathodes in unseparated systems. Indirectly, cathode scales can slump during outages and settle below or within the inter-electrode gap restricting flow to the electrode pair and depleting the chloride ion.

Impurities do not directly interact with the DSA to cause passivation failure but rather create conditions in which chloride ion is prevented from reaching the electrode surface in sufficient quantity to support the current passage. Water electrolysis takes over as the dominant reaction resulting in passivation. Passivation effects are more prevalent in chlorate systems because of the characteristically small inter-electrode gap, and the increase of concentration of impurities over time because of the closed loop systems. Any elements that can precipitate in sufficient quantity to block flow can lead to passivation effects.

Passivation

The Consequence of Loss of Flow

Inlet anode packs were exhibiting high voltage performance after short operating periods. A typical returned anode was covered with heavy scale deposits encrusting the surface. The mating titanium cathode retained the impression of the anode mesh design etched into its surface. Time on line was not sufficient to remove the mill finish from the cathode. Single electrode potential measurements were made on as received material and after a series of cleaning steps. Standard voltages in 300 gpl NaCl solution exceeded 4 V at 1.5 ASI vs. normal values of 1.12 V vs. SCE. Current reversal partially reduced voltages as hydrogen charging of the catalyst occurred during cathodic operation. This is an extreme procedure and can temporarily restore partially passivated materials for very short periods of time. Scale analysis revealed significant amounts of aluminum and silicon with a little iron and titanium. Atypical of previously encountered cathode scales containing various Ca, Mg and Ti compounds. Alkaline brine soluble aluminum and silicon impurities were precipitated as a sodium aluminum silicate on mixing with the acid used to adjust feed pH prior to the inlet cell. Blockage of anode /cathode assemblies occurred. Operation in a low chloride condition rapidly passivated affected anodes.

BLINDING DEPOSITS

The most frequently encountered effect of brine impurities on DSA performance is the formation of blinding deposits. Both organic and inorganic deposits have been encountered over the years. The inorganic deposits can be the result of chemical precipitation reactions when solubility product limits are exceeded or may be electrochemically oxidized at the anode. The high surface area DSA catalyst effectively binds the deposit, blocking solution access to the surface. Failure to remove gross surface deposits can lead to an acceleration of the passivation mechanism (Figure 11).

In general, these deposits form by both electrochemical and electrophoretic processes. As they form, they alter the current distributions within the cell and can result in locally high current densities in non-blinded regions. The first indication of a problem is usually rising cell potentials. Inorganic deposits are normally visible on inspection. High single electrode potentials that return to normal on proper cleaning, rule out passivation. Coating loading and appearance are normal after cleaning.

Each of these areas and the effect of specific brine impurities on chlorate cell DSA can be best reviewed through a series of case histories detailing specific field encountered problems. All of the histories presented involve EC100 coating. Because of the reduced mudcracking of EC120 coating, the number of binding sites for deposit formation are reduced, and the smoother surface will also result in ease of deposit removal.

Barium Sulfate

The role of barium sulfate has been reviewed many times. Barium sulfate precipitation occurs whenever the solubility product limit for this compound is exceeded. This effect was well documented in a test by a DSA customer who intentionally fed barium chloride into a chlorate reactor containing about 15 gpl sulfate. Over a period of about a week the voltage in the electrolyzer went up 400 mV from barium sulfate deposition on the anode surface. At the end of the week the barium addition was stopped and the electrolyte was allowed to mix with the rest of the cellroom. The voltage performance returned to normal as the barium sulfate redissolved. If upsets like this are caught quickly, little or no damage is done to the coating. If the DSA coatings are required to operate at higher potentials from blinded regions, the normal oxygen passivation mechanism can be rapidly accelerated and much shorter lifetimes can be observed.

Phosphates

Experience in a commercial chlorate system raised a red flag over the effect of phosphates on anode performance in chlorate applications. Action to avoid phosphate addition to the electrolyte was effective in avoiding deposits at the plant level, but the complete phenomena has yet to be duplicated in the ERC Laboratory. The problem was illustrated in slides where rapid voltage rise was observed over a two week period. Cleaning with dilute HCl solution recovered performance, but upon restart the voltage rise began again. Associated with the phenomena was an increase in oxygen levels as well. The only brine impurity outside normal practice was phosphate at levels of 1 to 5 ppm.

Lab simulation with lab electrolyte was conducted at ERC initially at 1000 ppm for gross effects then at the lower concentrations indicated. In lab electrolyte voltage escalation is apparent at 150 and 300 ppm but not at the 50 ppm level. Field reports suggest a synergistic effect between phosphate and iron, combine to magnify the problem but other priority work prevented this from being pursued at ERC. Although current work is not conclusive for low phosphate levels, the fact that voltage rise can be associated with the presence of phosphate in chlorate electrolytes is surprising based on membrane cell experience and should not be overlooked when recurring rapid voltage rise is encountered in the field.

Tin

The introduction of closed loop systems to the chlorate industry revealed a problem associated with tin accumulation. Tin stabilized piping was used in the electrolyte loop after a crystallizer was installed. Shortly thereafter a rapid rise in cell voltage was observed along with high oxygen levels in the hydrogen. Analysis of the plant electrolyte revealed tin levels above 30 ppm and rising with time. Analysis of feed brine solutions revealed tin levels below 1 ppm. Laboratory testing of chlorate electrolyte with the addition of tin chloride resulted in a rapid increase in anode potential when tin exceeded 20 ppm in the electrolyte. Solution sale was arranged to reduce the buildup of tin and resolve the problem. Plant electrolyte contamination peaked at 70 ppm Sn.

Laboratory cell testing was used to confirm the effect of tin on oxygen levels as well as voltage performance. Contamination of a lab cell electrolyte with 70 ppm Sn as SnCl_4 resulted in the oxygen level rising rapidly over a 6 hour period. Periodically samples of plant electrolyte were operated in a lab cell to confirm performance improvements as tin levels were lowered. Oxygen levels declined as tin was reduced in the electrolyte. High levels of tin were observed on returned anode samples. The material responded only to mechanical cleaning techniques, but continued operation of the contaminated anodes yielded self cleaning as tin levels in the electrolyte were reduced. Leaching declined to acceptable levels within six months of start up.

Titanium

In systems where Ti cathodes are used, anodes were examined after a steady increase in cell voltage was reported. The hydriding of the cathodes, coupled with the small inter-electrode gaps, provide a source and means for Ti based particles to electrophoretically deposit on the anode surface.

Microscopic analysis reveals that after 3 months service, the anode surface has started to be covered with discrete areas of Ti oxide particles. These particles are spherical shaped. After 6 months operation, large quantities of Ti oxide surface deposits are present, with porous areas in the deposit. These pores lead to the catalytic coating surface to supply chloride ions for electrolysis, as the SEP's are normal. The deposit thickness is 10-20 microns. With continued operation, the pores will be filled with other impurities as Al, Si and Fe, essentially blinding the coating surface. With 11-12 months operation SEP's are now elevated in the deposit areas. With additional operation of 4-6 months at these elevated potentials, the onset of passivation is possible.

In systems where steel cathodes are used, Ti tanks could be a source for electrolyte contamination, if corrosion of the tanks occurs.

Iron, Silicon

Fe and Si based anode surface deposits are very common with chlorate anodes. Sometimes phosphorous is also present with Fe.

In the case presented, cell voltages were increased. Surface deposits were visible on the anodes, and SEP's were elevated by 200 mV. Microscopic evaluation showed some deposit areas having Si as the major quantity present, while other areas of the same anode had Fe and P as the major elements, with only a trace of Si present. The appearance of the deposit is similar in both cases, and the coating is completely blinded in discrete areas. Cleaning methods had to be used that would successfully remove all contaminants. Fortunately, the anodes were cleaned in a timely manner, before the onset of passivation occurred.

In another case, a plant encountered Fe problems after 8 - 10 years of service. Throughout the course of a year, the anodes were chemically cleaned, with continued good service for several more years afterwards.

In still another case, anodes were operated for 5 years with routine maintenance cleaning and consistent cell performance. Increasing operating voltages and elevated k-factors were experienced throughout the course of the following year. Several anodes were removed from service and found to contain heavy amounts of deposits containing Fe, P and Si. These deposits covered approximately 10% of the anode surface layer. Laboratory testing indicated elevated SEP values of 2- 3 V in the deposited areas, with normal SEP's on the remainder of the anode. An aggressive cleaning protocol of NaOH/HCl was used to remove the deposits, with elevated, non-reversible SEP values still present. This is an indication of passivation, and was confirmed with Electrochemical Impedance Spectroscopy evaluation. The coating loadings remained high at >80% of original. Since only a small percentage of the anode was effected, recoating was not initiated, and the anodes are still in service currently.

Organics

Most organics found in the brines around pulp and paper facilities are easily oxidized to CO₂ and not a problem in cell operation. Periodically spills and accidents can introduce more stable materials into the electrolyte. Long chain aliphatic and fluorinated oils, designed for stability in the strongly oxidizing environment, can and do deposit on the surface of the DSA. The rate of voltage escalation depends on the nature of the deposit and the rate the impurity is added to the electrolyte. When present on DSA surfaces, a brown to yellow film is generally observed. Selection of the appropriate solvent cleaning technique is generally required to restore performance.

Cleaning Methods

Some deposits are easily removed with a water wash or dilute acid (<5 wt% HCl) cleaning at ambient conditions. These deposits are loosely adherent and are usually formed during reactor draining after a shutdown, caused by steel cathode corrosion residue in the electrolyte.

Other deposits are formed by electrophoretic deposition, and require more aggressive methods of removal. Again, 5 wt% HCl is a good cleaning agent for most iron based deposits. What is required are elevated temperatures (40-70°C), and prolonged contact times (1-4 hours) to fully remove the deposits. Other deposits, such as iron phosphates, and Al or Si based compounds, usually require an additional cleaning in 0.5-2.0 wt% NaOH (at elevated temperatures/time) to be completely removed. Anodes have been successfully cleaned in the lab under these various conditions, and field evaluations have also been successful.

Microscopic analysis after cleaning does not show any damage to the coating. It is important that these conditions not be exceeded to prevent damage to the coating. There may also be environmental/disposal and health restrictions at a commercial site preventing use of more concentrated chemicals. It must be emphasized that these cleaning methods have only been evaluated on ELTECH DSA coatings, and use of these methods with other coatings may damage them.

COMBINED ANODE/CATHODE EFFECTS

Cell Performance

Brine impurity effects are not restricted to the DSA alone. Published literature reference the effect of various metals on the catalytic decomposition of hypochlorite in solution. Cobalt, copper, iron, and manganese have been discussed by Coleman in a 1981 paper to the AIChE. The accumulation of deposits on the cathode is known to impact cell voltage performance. At times, both anode and cathode performance can be simultaneously affected yielding symptoms of elevated cell potential and elevated oxygen.

During evaluation of performance deficiencies for the EC-900 coating formulation designed to yield low oxygen performance during the period of initial new coating start-up, unexpectedly high oxygen levels were encountered. Evaluation of returned anode samples revealed surface iron deposits which elevated single electrode potentials slightly. Lab cell operation of anode samples revealed some elevation in oxygen levels when compared with an aged EC-100 standard and unoperated EC-900 retains but could not explain the reported plant oxygen levels of 3.5-4%.

The combination of an as received returned anode and as received steel cathode samples yielded oxygen levels of 4%. A comparison of cleaning tests involving both the anode and cathode samples reduced oxygen levels to expected values of 1.5%. The reduction of oxygen was traced to improvements in cathode efficiency as complete removal of iron deposits from the cathode surface was achieved. The iron scale deposits on the cathode surface interfered with formation of a complete chrome film necessary to prevent hypochlorite reduction. High levels of chrome were observed on the as received fouled cathode surface by XRF techniques, but it was ineffective in maintaining good hydrogen efficiency. The observed increase in oxygen levels was the result of decreased hydrogen production caused by cathode fouling from iron deposits from the electrolyte.

DIAGNOSTIC TOOLS

There are a variety of analytical techniques that are used for anodes which have encountered performance problems.

X-Ray Fluorescence: measures the amount of catalyst (Ru) remaining, and iron due to surface deposits

Measurement of Ru determines general wear rate and locates areas of increased wear. During the past several years, iron loading measurements have been made available to correlate iron amounts to SEP value. Developing an iron history can then lead to determining cleaning intervals to avoid passivation damage to the anodes.

Single Electrode Potential: measures the catalyst activity.

Used as a screening tool to determine elevated and non-reversible potentials.

Electrochemical Impedance Spectroscopy: a destructive technique that confirms the onset of passivation

This laboratory test has been used on several occasions to confirm passivation of commercially operated anodes.

Tube Excited Fluorescence Analysis: an XRF technique that identifies all surface deposits present and can be quantified to give relative percentages

This technique has been used extensively on both direct analysis of the anodes, or removing the deposits with tape, and analyzing the tape. Has also been used to determine changes in coating component concentrations.

Scanning Electron Microscopy: either surface or cross-section analysis can be used to take high quality, high magnification images of the coating morphology. Normally is combined with EDS (an XRF technique), to provide chemical information

Surface Science Techniques: these include Auger and XPS, which analyze 30 - 50 Å of the surface, eliminating substrate interference's.

Developed over the past several years as a tool that has been used on several customer operating issues.

SUMMARY

The importance of high quality brines cannot be overstated. Electrolyte impurities have been presented which impacted each of the DSA failure mechanisms in chlorate systems. **Passivation** occurred when loss of flow was locally created by aluminum silicate deposits. **Coating loss** through an attack on the titanium stability was encountered when fluoride ion entered the electrolyte. Caustic attack to the DSA matrix **accelerated wear**, when hardness scales and synergistic effects from aluminum, silicon and titanium oxides, and hydrides were encountered. BaSO₄, tin oxides and organics have created **blinding deposits**. Phosphate remains an open question at present. Finally iron compounds were shown to adversely affect both anode and cathode surfaces. There is no substitute for adhering to sound brine treatment practices that assure high quality electrolytes.

Figure 1

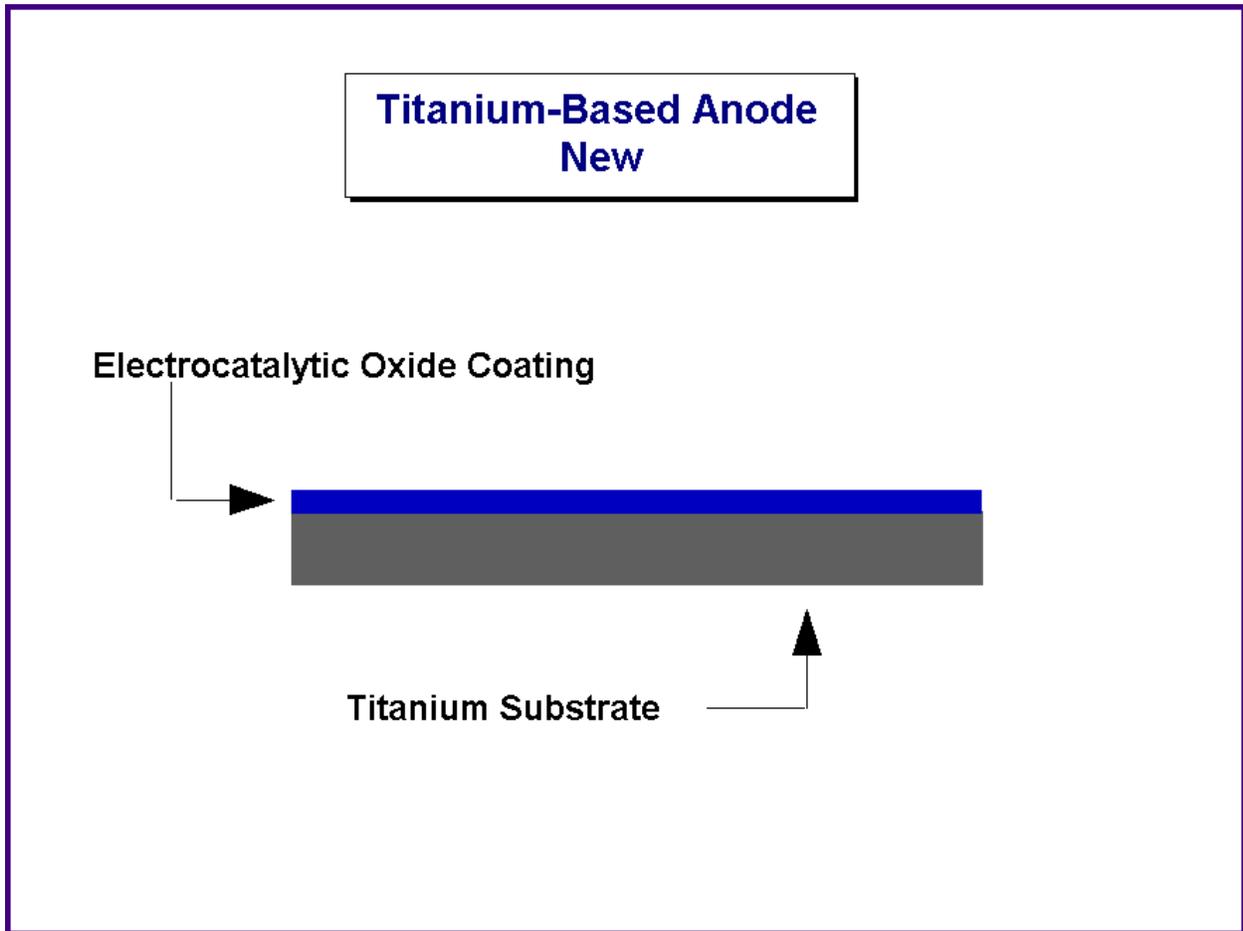
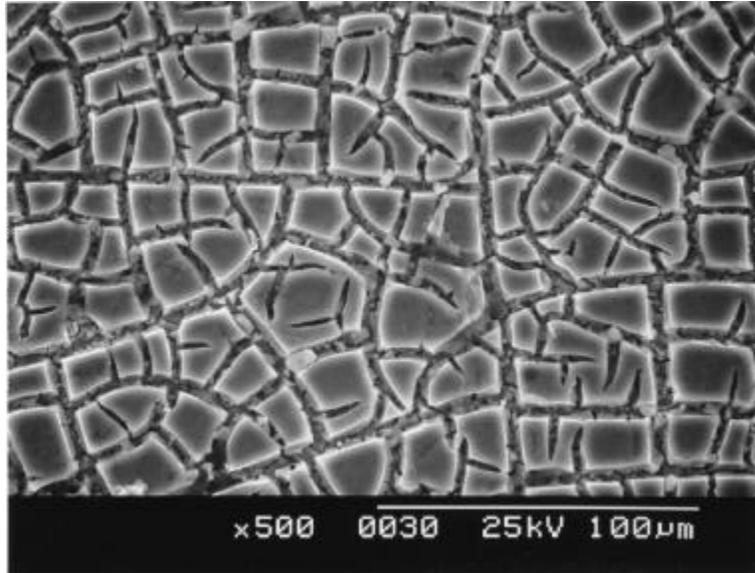


Figure 2

EC100



EC120

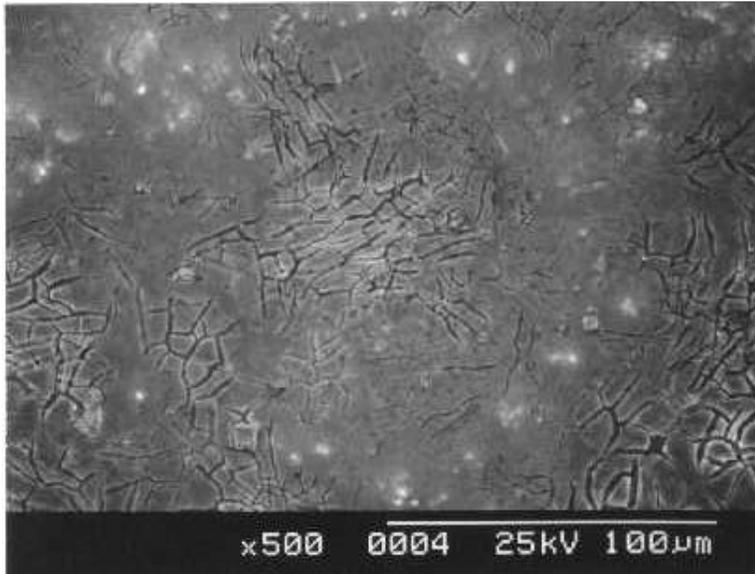


Figure 3

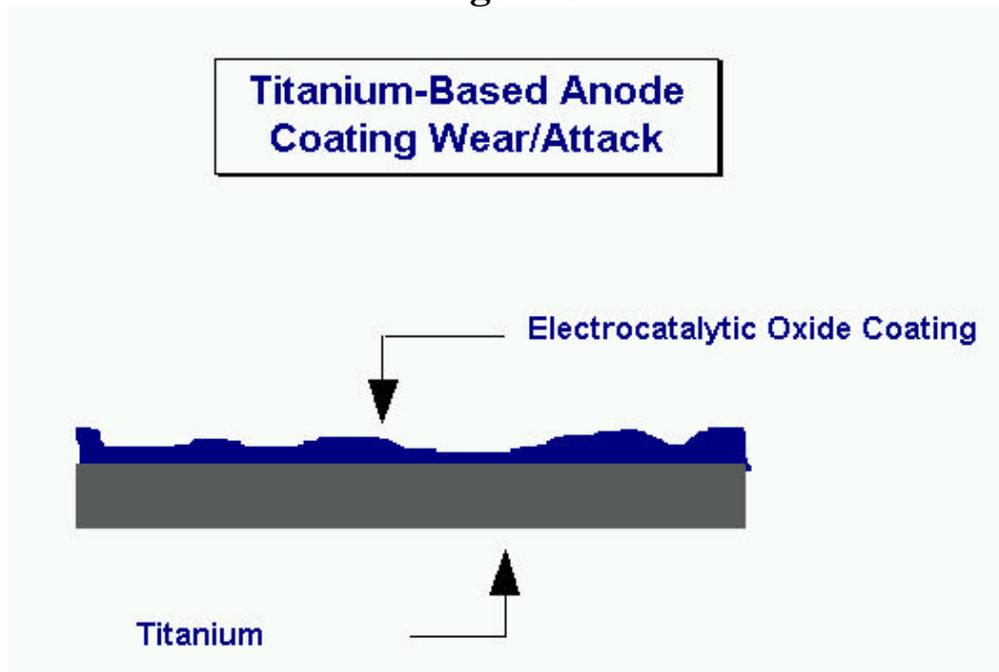


Figure 4

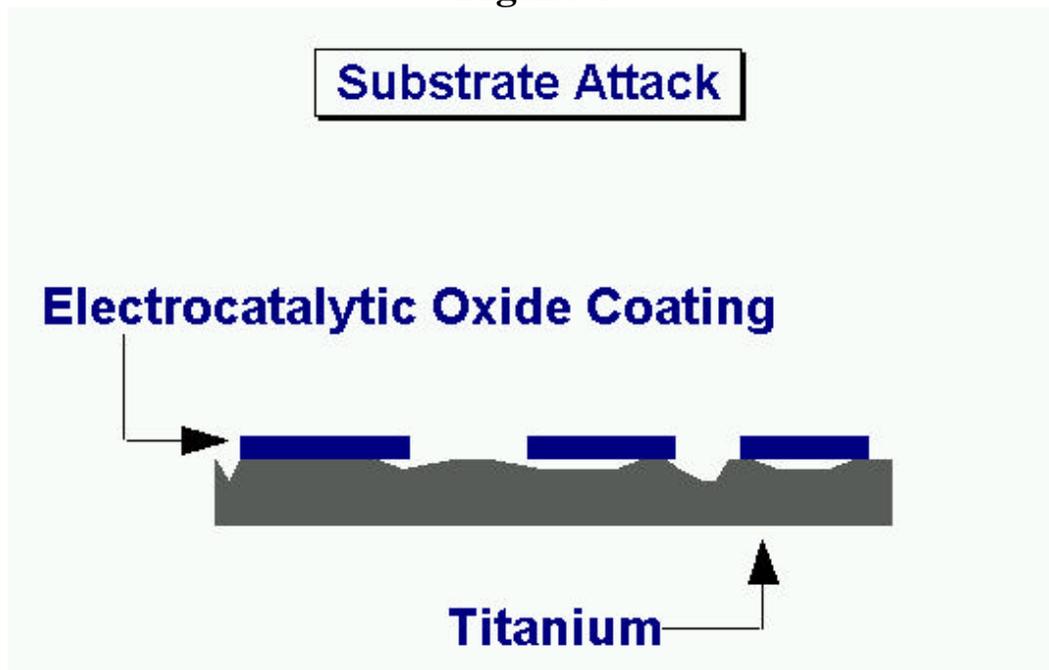


Figure 5

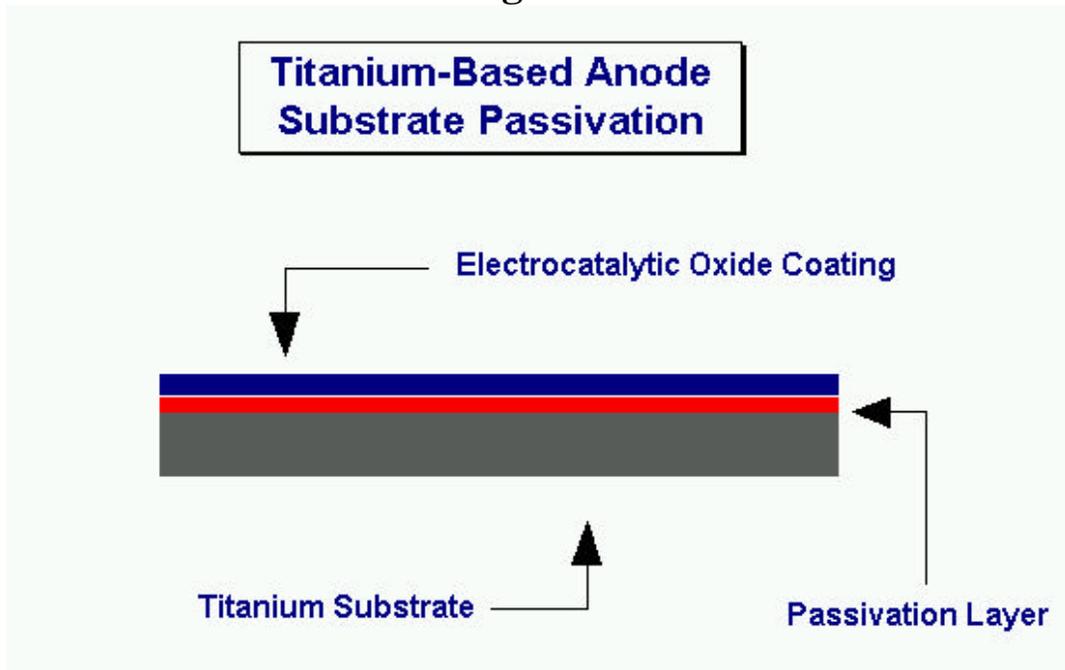


Figure 6

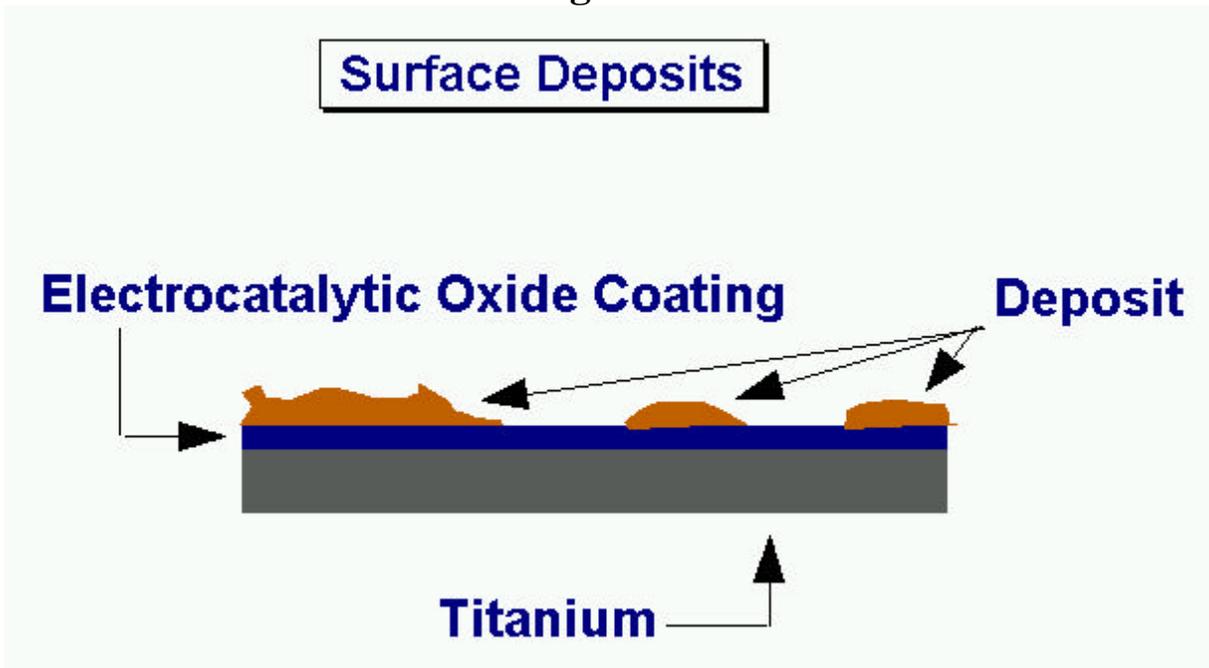


Figure 7

**Normal Coating Wear Rate
for Chlorate DSA**

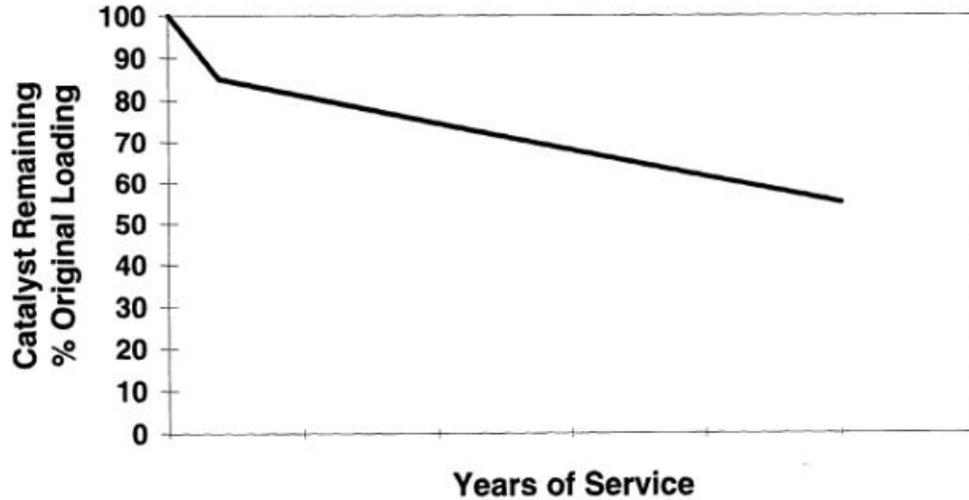


Figure 8

WEAR ACCELERATING IMPURITIES

SECONDARY IMPACT MATERIALS

CALCIUM

MAGNESIUM

ALUMINUM

SILICA

TITANIUM OXIDES

TITANIUM HYDRIDES

SUSPENDED SOLIDS

HEAVY METALS

Figure 9
TYPICAL POTENTIAL TIME CURVE

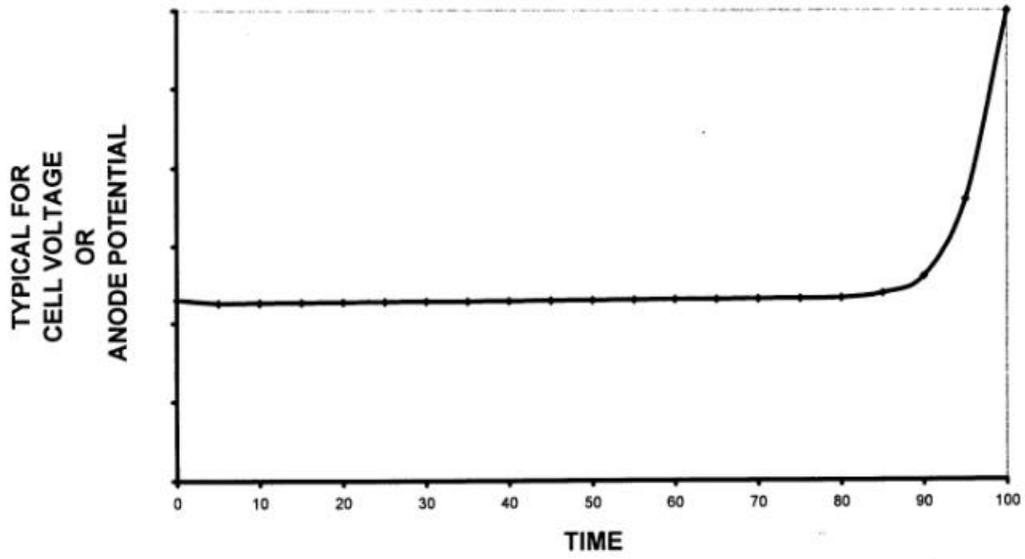


Figure 10
IMPACT OF EXCEEDING DESIGN CONDITIONS ON LIFE EXPECTANCY

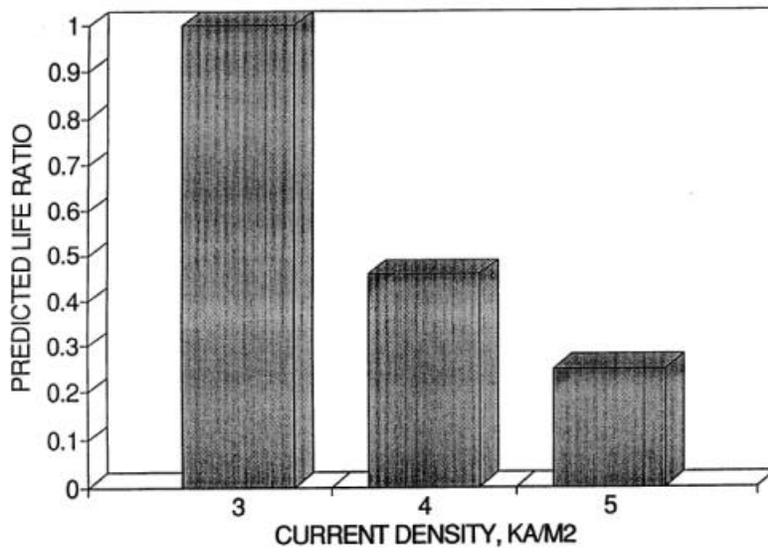


Figure 11

BLINDING DEPOSITS

