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TITANIUM ANODES IN CATHODIC PROTECTION.(U)

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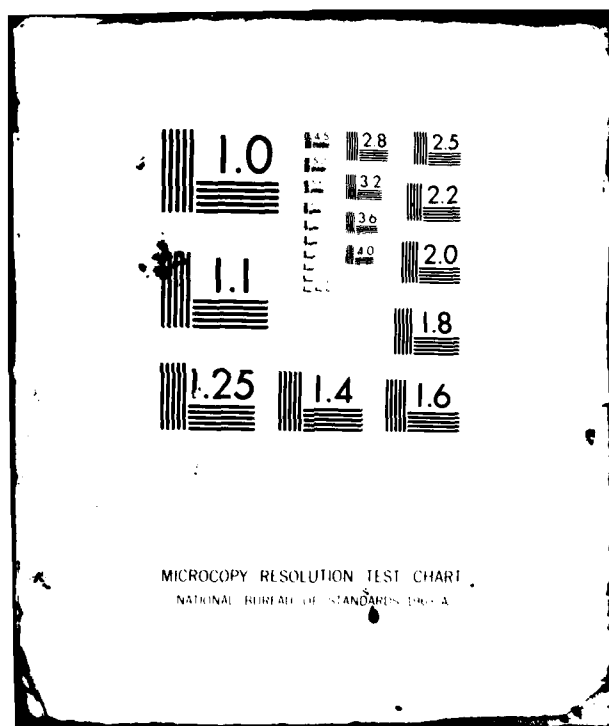
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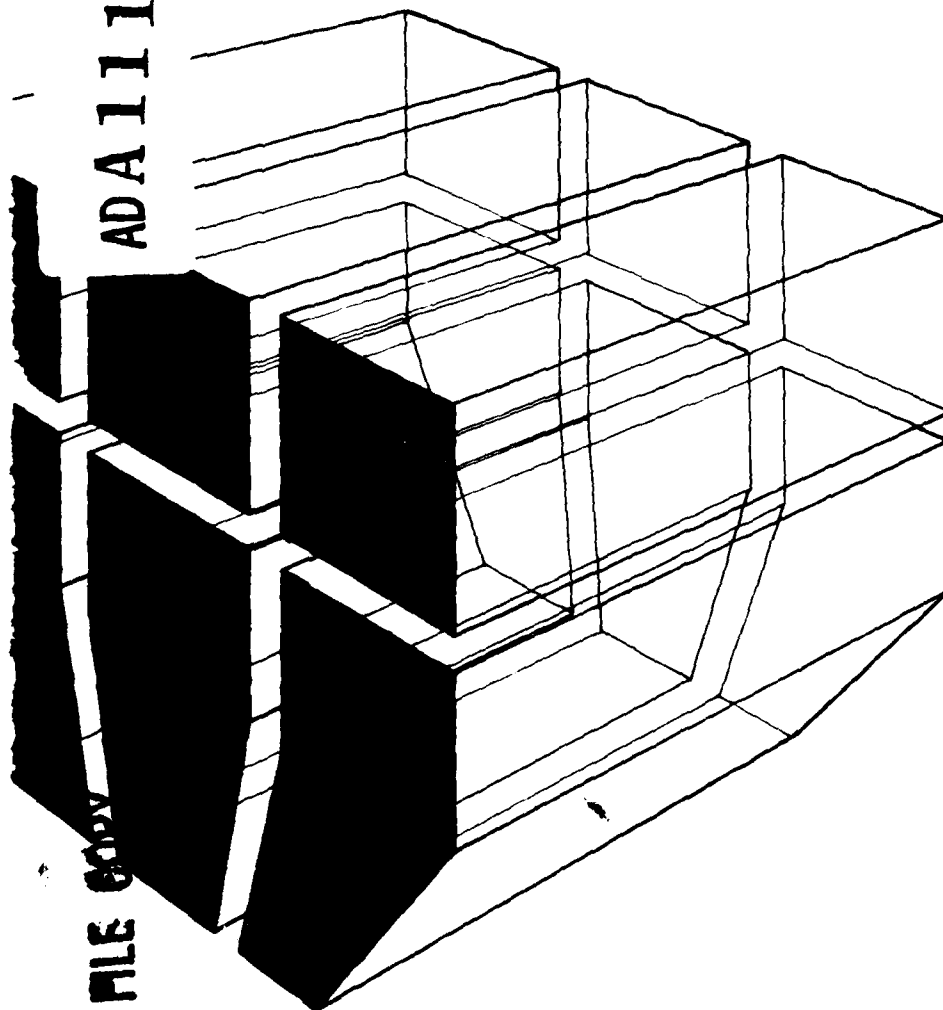


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January 1982

TITANIUM ANODES IN CATHODIC PROTECTION

by
E. G. Segan
J. Bukowski
A. Kumar



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At NaCl concentrations of up to 0.0055 percent, the breakdown voltage of titanium was found to be in excess of 80 V in tap water. It is recommended that anodic potential not exceed 9.17 V (SCE)* when platinum- or ceramic-coated titanium anodes are used for impressed current cathodic protection. This voltage reflects the worst case pitting behavior encountered in high chloride solutions (3.5 percent or 35,000 ppm NaCl) and operation of anodes below this potential insures that pitting of titanium anodes will not occur in fresh water such as the Ohio River, which has much lower chloride content (28 ppm).

*Volts vs. saturated calomel electrode.

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FOREWORD

This study was conducted for the Directorate of Civil Works, Office of the Chief of Engineers (OCE), under CWIS 31204 (Corrosion Mitigation in Civil Works Projects). The OCE Technical Monitor was Mr. J. Robertson. The research was conducted by the Engineering and Materials (EM) Division, U.S. Army Construction Engineering Research Laboratory (CERL). Dr. R. Quattrone is Chief of EM.

COL Louis J. Circeo is Commander and Director of CERL and Dr. L. R. Shaffer is Technical Director.

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TITANIUM ANODES IN CATHODIC PROTECTION

1 INTRODUCTION

Background

Cathodic protection has been used by the U.S. Army Corps of Engineers (CE) on metallic structures to extend the effective life of paint coating by reducing undercutting and to provide supplemental protection to defects in the paint film on immersed surfaces. The paint film, which is a hydraulic structure's primary protection against corrosion, is never perfect; defects and holidays are always present in hard-to-paint areas such as edges, rivet heads, and weld beads. In addition, paint film is scratched by debris carried by the river and barge traffic in the waterways; the exposed steel then corrodes until it is repainted or repaired.

The first CE cathodic protection systems were introduced in the 1950s and were experimental. Cathodic protection is now used on all the new lock gates on the Tennessee-Tombigbee Waterway. Some of the older lock gates on the Columbia River are being retrofitted with an impressed current cathodic protection system; in addition, designs for new locks on the Red River (Arkansas) include sacrificial cathodic protection systems.

The use of platinized titanium and niobium as an anode material was first attempted in 1958 in commercial installations in England. The usefulness of platinum as an inert electrode material for many other electrolytic processes is well known. In cathodic protection, the useful properties of platinum are exploited, but its volume and cost are minimized by using titanium as a substrate. Electrically conducting ceramics, such as ferrites (i.e., Fe_3O_4 and NiFe_2O_4) may be used in the future in place of platinum coatings on anodes, thereby reducing their cost. Titanium, niobium, tantalum, and other metals exhibit active-passive anodic behavior. These materials are commonly called valve metals. Titanium has exceptional resistance to most aqueous corroding media because it forms an inert oxide film during anodic polarization. However, because of this oxide film, titanium will not readily pass current when used as an anode in water. A deposition of an extremely thin layer (.0005-in. [.013-mm]) of platinum on a surface will allow current to flow from the substrate through the platinized area and into the water. If the platinum surface is scratched, the anode stops passing current from the scratched area. This

occurs because the protective oxide film which forms on the surface of titanium breaks down at voltages of about 60 V in fresh water with low chloride content.

The limitations of titanium have not been clearly identified and the mechanisms for breakdown are not fully understood. Before new Corps applications for platinized titanium anodes are developed, the electrical potential limits of the anodes in specific environments must be evaluated.

Objective

The objective of this investigation is to determine the pitting and breakdown potential of commercial titanium substrates for cathodic protection anodes in chloride-containing aqueous solutions. The characterization of pitting behavior will determine the suitability of using platinum- or ceramic-coated titanium anodes in cathodic protection of hydraulic structures. (Guidance in the installation and the use of platinized titanium anodes will be presented in a future report.)

Approach

For this investigation, CERL reviewed the state of the art of platinum- or ceramic-coated titanium anodes. Next, potentiodynamic tests were run to determine the pittings and breakdown voltages of titanium anode substrates in distilled and tap water in which the concentration of sodium chloride (NaCl) was varied from 0.005 percent to 3.5 percent. Finally, CERL analyzed the significance of the results to determine the suitability of using titanium anodes for cathodic protection of hydraulic structures.

Mode of Technology Transfer

This study will impact the proposed CE guide specifications for cathodic protection of hydraulic structures.

2 LITERATURE SURVEY

Corps of Engineers Cathodic Protection

The following discussion summarizes some of the cathodic protection techniques commonly used on Corps structures. The Corps' impressed current cathodic protection systems use graphite and high-silicon, chromium-bearing, cast-iron (HSCBCI) anodes. The graphite anodes have deficiencies. They are brittle and cannot withstand the mechanical damage caused by ice

and debris. In addition, they contain an organic binder material which, in aerated waters, especially near the water surface, is attacked by the oxygen liberated at the anode; as a result, the anodes eventually become porous and soft. Therefore, the use of graphite slab anodes is not recommended because they cannot be replaced without dewatering the lock. However, the New Orleans District has successfully used rod-type, sausage anodes of graphite in protected split pipes; these anodes can be repaired without dewatering by splicing with new anodes.

HSCBCI anodes are available in many sizes and shapes. One shape which has been developed for the Corps of Engineers is a 6-in. (152.4-mm)-diameter button anode (see Figure 1). The body of the anode provides the electrical connection; the anchoring bolt is electrically isolated from the body of the anode during installation. When the locks on the Tennessee-Tombigbee Waterway were constructed, it was discovered that installing button anodes is a rather tedious process; also, many problems (such as providing electrical

isolation of the anode from the gate and mounting and the anode) were encountered. Once installed, faulty button anodes on lock gates cannot be replaced without dewatering the lock.

However, the HSCBCI 6-in. (152.4-mm)-diameter button anodes, if properly installed, have performed extremely well on the skin side of miter gates; a grid of button anodes every 10 to 15 ft (3 to 4.5 m) provides adequate protection. One button anode is required in each compartment to prevent electrical shielding and to provide complete coverage. These compartments are enclosed on three sides and open on one side. Since the compartments are coated, cathodic protection current will spill over and protect the structure on the open side.

The cost of the cathodic protection system can be reduced somewhat by using sausage-type anodes made of HSCBCI in the compartments of the miter gate. In most cases, plastic-lined, steel split pipes will protect these anodes from mechanical damage caused by de-

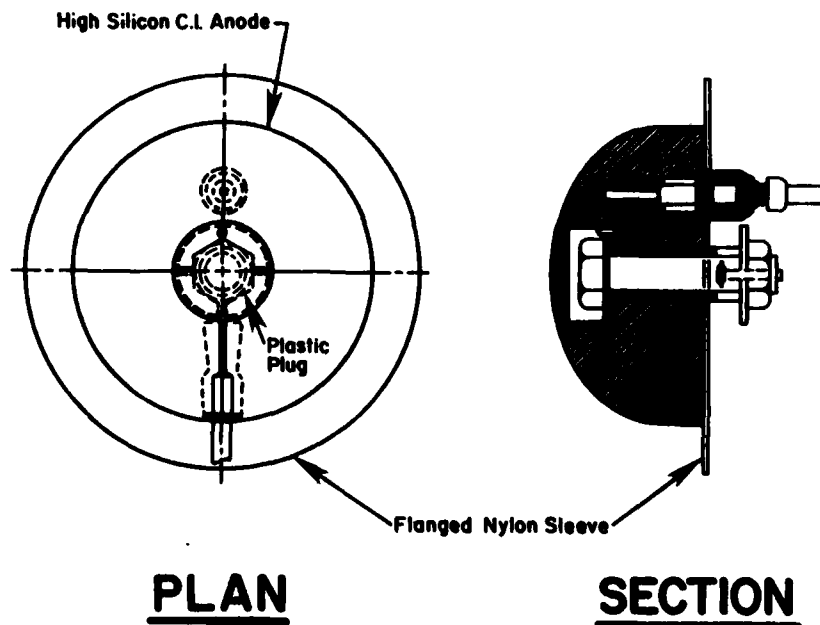


Figure 1. Silicon button anode design.

bris. However, severe ice and debris has damaged cables, pipes, and anodes on the Ohio River lock gates. A tough, durable anode material which can be mounted on the lock gate and protected from ice and debris would be a great improvement, but so far a satisfactory solution has not been found.

Platinized Anodes

History

Baboian¹ has reviewed the historical development of platinized anodes. The first platinized anode, developed in 1901, was made of a "cheap" metal like lead and clad with platinum. Later, copper, silver, and other substrate materials were used. Thick platinum coatings that were free of pinholes had to be used on the anodes to prevent contact of the substrate with corrosive environments; thus their use was severely limited because of the cost of platinum.

In 1913, platinized anodes with "valve metal" substrates such as titanium, niobium, and tantalum were introduced. A stable oxide film that forms on the valve metals prevents the flow of corrosion current from anode regions where the platinum coating is not continuous. Today lead-platinum bielectrodes, platinized-titanium, platinized-niobium, and platinized-tantalum are used a precious metal anodes. Breakdown voltages of tantalum and niobium exceed 120 V, while titanium can be used at voltages of up to 6 to 12 V in saltwater.² The passivating behavior of substrate materials is discussed in detail on p 10.

Coatings

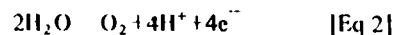
Both substrate and coating behavior affect the performance of platinized anodes. Factors such as platinum surface structure and electrochemical parameters such as potential and a.c. ripple, current density, IR drop, and solution parameters have been associated with the corrosion rate of platinum coatings. Development of clad platinum coatings about 5 μm thick which are continuous and nonporous has improved the

performance of platinized anodes. The recently developed coatings thin uniformly and exhibit good electrochemical properties.³

Investigation of electrochemistry of platinum in aqueous environments has shown that the most important reaction in seawater is:⁴



Other reactions involving formation of hypochlorous and hydrochloric acid have also been observed in seawater. In dilute saltwater, where chloride availability is limited, hydrolysis of water was observed at the platinum electrode according to the following reaction:⁵



Oxidation of hydroxyl groups to form oxygen was noted in alkaline seawater. Film formation occurred on platinum surfaces in solutions containing NaCl, and this appeared to affect the performance of platinized anodes. The current density obtained with platinized anodes is initially high and decreases with time under constant current conditions in chloride-containing environments.⁶

The predominant mechanisms of platinum consumption are uniform thinning and localized degradation. Uniform thinning of the platinum has been attributed to dissolution of the films formed on the platinum surfaces. The thinning rate increases rapidly as current density increases and temperature decreases and when oxygen evolution becomes the primary anodic reaction. Superimposed a.c. ripple can also adversely affect platinum's dissolution rate. Platinum dissolution is aggravated as the $I_{r.m.s.}$ * ripple exceeds 70 percent of

¹R. Baboian, "Performance of Platinum Anodes in Impressed Current Cathodic Protection," *Proceedings of the Fourth International Congress on Marine Corrosion and Fouling* (June 1976, Antibes, France), pp 51-56.

²E. W. Dreyman, "Precious Metal Anodes: State-of-the-Art," *Materials Protection and Performance*, Vol II, No. 9 (September 1972), pp 17-20; R. Baboian, "Platinum Consumption in Cathodic Protection Anodes," *Materials Performance*, Vol 16, No. 3 (March 1977), pp 20-22.

³M. A. Warne and P. C. S. Haywood, "Platinized Titanium Anodes for Use in Cathodic Protection," *Materials Performance*, Vol 15, No. 3 (March 1976), pp 39-42; M. A. Warne, "Precious Metal Anodes - The Options for Cathodic Protection," Paper No. 142, 1978 Corrosion Conference, Houston, TX (March 1978).

⁴R. Baboian, "Performance of Platinum Anodes in Impressed Current Cathodic Protection," *Proceedings of the Fourth International Congress on Marine Corrosion and Fouling* (June 1976, Antibes, France), pp 51-56.

⁵T. Fugii, T. Kodama, H. Baba, and S. Kitahara, "Anodic Behavior of Ferrite Coated Titanium Electrodes," *Boshoku Gijutsu*, Series 29 (1980), pp 180-184.

⁶R. Baboian, "Performance of Platinum Anodes in Impressed Current Cathodic Protection."

*Root mean square.

the direct current flowing from the anode. Localized degradation has been observed to depend on properties of the substrate material and the degradation rate of platinum. Platinum coatings applied by vapor deposition, sputtering, and roll bonding are better than those applied by electrodeposition, which chip and spall.⁷

Platinum coatings alloyed with noble metals such as rhodium, ruthenium, and palladium did not exhibit substantially improved durability. However, recently developed conducting oxide coatings for electrolytes may provide a new generation of anodes.⁸ These anodes appear to exhibit good electrochemical properties and may be more cost-effective than platinum.

Substrate Materials

Valve Metals

Many materials exhibit active, passive, and transpassive anodic behavior. Figure 2 shows typical potentiodynamic scans of titanium with some regions of interest labeled. Corrosion current increases with increasing potential (vs. reference) from the corrosion potential (E_{corr}) to the primary passivation potential (E_p). Primary passivation of titanium occurs at low anodic potentials and is associated with low currents. This peak is not visible in Figure 2. At E_p , a passivating film begins to form on the sample and the current decreases, with increasing voltage reaching a relatively constant value. However, as voltage increases, the passivating film eventually breaks down at the breakdown voltage (E_{BD}) at a current of I_{BD} . Pits form and rapid corrosion of the specimen occurs, as shown by an increased corrosion current. If the scan direction is reversed, a hysteresis effect is observed, as repassivation of the sample, commonly called the pitting potential (E_B), occurs at a lower voltage (at current I_B) than the breakdown voltage initially observed.

This behavior shows that at voltages between E_{BD} and E_B , one of two distinct corrosion currents may be observed, depending on the condition of the specimen's surface. In this voltage range, a sample will corrode rapidly if a pit already exists, but will not corrode much if the surface film is continuous. This is of practical importance because it establishes E_B as the maximum voltage (vs. reference) which will prevent rapid corrosion, regardless of surface condition.

⁷R. Baboian, "Performance of Platinum Anodes in Impressed Current Cathodic Protection"; Warne and Haywood.

⁸Warne; Fugii et al.

The uses and limitations of platinized anodes depend on the properties of substrate materials. The technically important "valve metals" exhibit passive behavior, but suffer pitting attack in chloride solutions. Palit and Elayaperumal⁹ noted that pitting resistance of some pure valve metals decreases in the following order: Ta>Nb>Ti>Cr>Zr>Al. Tantalum and niobium (columbium) were stable over a large range of environments, while zirconium and chromium required sufficient water for passivity and titanium required both water and oxygen. In the absence of sufficient water,¹⁰ all the passive metals were prone to pitting in chloride solutions.

Rabboh and Boden have investigated the pitting of pure titanium, zirconium, and tantalum in halide environments. Halides were particularly aggressive to passivating films on these metals; however, the mechanism of film breakdown is not fully understood. Adsorption of halides appeared to be associated with film breakdown on titanium and tantalum, and it was found that detrimental effects increased from chloride to bromide to iodide ions. Tantalum films could not be broken down in chloride solutions in the laboratory. The breakdown voltage of zirconium decreased from iodide to bromide to chloride (reversed dependence on halide ion); however, there was evidence of mechanical cracking of the film which appeared to be associated with breakdown. A common electrochemical mechanism involving halide adsorption on the films of titanium, zirconium, and tantalum was proposed to account for this phenomenon; the mechanical cracking of films on zirconium appeared to be associated with these anomalous results.¹¹

The three types of substrates most often used for platinized anodes – titanium, niobium, and tantalum – are best suited for impressed current cathodic protection anodes. Tantalum and niobium exhibit excellent physical, electrical, and electrochemical properties. Niobium anodes may be operated at voltages as high as 40 to 50 V, and tantalum may be used at up to 200 V in saltwater; the resistivities of tantalum and niobium

⁹G. C. Palit and K. Elayaperumal, "Passivity and Pitting of Corrosion Resistant Pure Metals Ta, Nb, Ti, Zr, Cr, and Al in Chloride Solutions," *Corrosion Science*, Vol 18 (1978), pp 169-179.

¹⁰Palit and Elayaperumal.

¹¹M. F. A. Rabboh and P. J. Boden, "The Breakdown of Passivity on Titanium, Zirconium, and Tantalum in Halide Media," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 653-660.

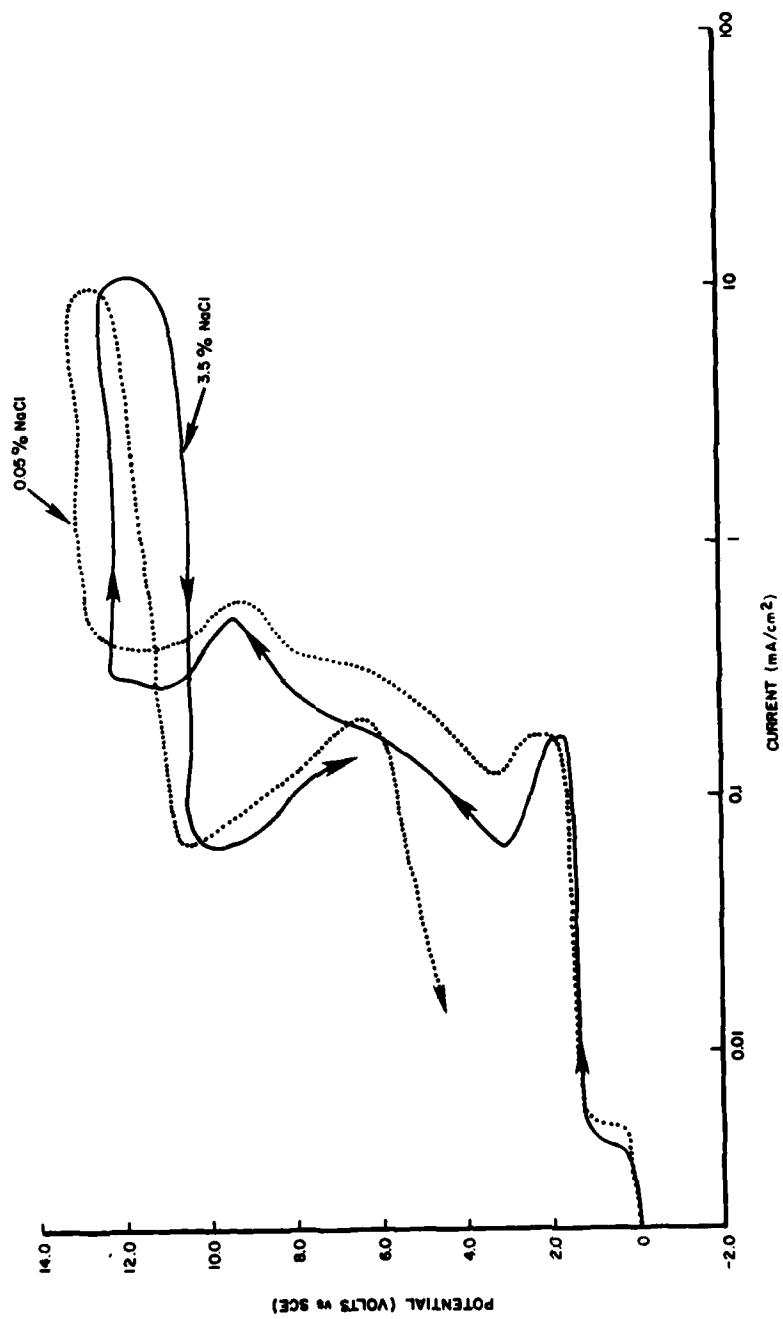


Figure 2. Potentiodynamic scans of titanium in distilled water solutions containing 3.5 and 0.05 percent NaCl.

are only one-third that of titanium. Titanium may be used at up to 9 to 10 V in saltwater. However, niobium can cost 18 times more than titanium, while tantalum can cost 30 times more.¹² Therefore, tantalum and niobium are used only in aggressive environments requiring excellent corrosion resistance.

Platinized niobium anodes have been used as platinized anodes for seawater environments (high current loading), heat exchangers (operation at high voltages), wet deep wells, and soil burial. They exhibit stability and high current carrying capability, and they are lightweight.¹³

Titanium Substrates

One of titanium's unique properties is its high strength-to-weight ratio, which makes it useful under demanding conditions. Commercially pure titanium has tensile strength of 60,000 to 95,000 psi, elongation of 25 to 28 percent, fatigue limit of 40,000 to 60,000 psi, density of 0.163 lb/cu in. (4.51 g/cm³) and resistivity of about 50 micro ohm-cm at room temperature. Commercially pure titanium has lower strength, higher corrosion resistance, and is less expensive than titanium alloys. The pure metal is used in applications where strength is not the main requirement. Titanium is available in a variety of forms, and several welding techniques may be used for joining it.¹⁴

Because of their high tensile strength, high strength-to-weight ratio, passivating behavior, availability in different forms, and relatively low cost,¹⁵ platinized titanium anodes have been successfully used to protect many types of structures, including: docks and offshore structures, ship hulls, heat exchangers, cooling water lines, water towers, treatment equipment, sewage treatment plants, sea grounding cells, deep anode beds, and food industry equipment.

¹²E. W. Dreyman, "Precious Metal Anodes: State-of-the-Art," *Materials Protection and Performance*, Vol II, No. 9 (September 1972), pp 17-20.

¹³R. Baboian, "New Developments in Platinum Type Anodes," *Materials Performance*, Vol 18, No. 1 (January 1978), pp 9-15.

¹⁴R. Baboian, "Performance of Platinum Anodes in Impressed Current Cathodic Protection," *Proceedings of the Fourth International Congress on Marine Corrosion and Fouling* (June 1976, Antibes, France), pp 51-56; R. A. Wood and R. J. Favor, *Titanium Alloys Handbook*, MC1C-HB-02 (Air Force Materials Laboratory, Wright-Patterson Air Force Base, December 1972).

¹⁵Dreyman.

However, titanium suffers from localized crevicing, pitting, and filiform corrosion under various corrosive conditions.¹⁶ Once begun, localized attack is severe and can extensively damage the anode, even in a short time. After a short time, loss of substrate may undercut the platinum coatings, and even if the localized corrosion ceases, the platinum surface area may be greatly reduced. Extensive pitting can result in loss of the physical integrity of the anode, or in severe cases, loss of an anode. Therefore, environments favorable to localized attack of titanium and design cathodic protection systems must be identified. However, localized attack appears to be unpredictable and erratic, even under controlled testing conditions, and its mechanisms are not fully understood. Safe limits for anodic potentials of 9 to 10 V in saltwater are generally reported, but pitting potentials of "pure" (the chemical composition was not reported) titanium as low as 2 V in water containing 5 percent NaCl have been reported.¹⁷

Cotton,¹⁸ Beck,¹⁹ and Gleekman²⁰ have reviewed the history of localized attack of titanium. The primary reported forms of titanium anode failure are crevicing and pitting in corrosive media. The possibility of catastrophic failure as a result of localized corrosion was realized after several titanium anodes located in aggressive environments failed. This possibility was partially due to the uncommon environments and unpredictable and erratic failures.

Dielectric breakdown of films on titanium is possible at high voltages (above 80 V), but this type of breakdown is usually associated with sparking and does not result from an electrochemical process. There is

¹⁶J. B. Cotton, "A Perspective View of Localized Corrosion of Titanium," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 676-679.

¹⁷R. Baboian, "Platinum Consumption in Cathodic Protection Anodes"; M. A. Warne and P. C. S. Haywood, "Platinized Titanium Anodes for Use in Cathodic Protection," *Materials Performance*, Vol 15, No. 3 (March 1976), pp 39-42.

¹⁸J. B. Cotton, "A Perspective View of Localized Corrosion of Titanium," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 676-679.

¹⁹T. R. Beck, "A Review: Pitting Attack of Titanium Alloys," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 644-653.

²⁰L. W. Gleekman, "Historical Industrial Developments with Crevice Corrosion of Titanium," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 669-675.

usually a clear distinction between pitting and crevice corrosion of titanium. Crevice corrosion may occur at low voltages. Pitting of a sample at a high anodic voltage will cease if the voltage is lower than the repassivation potential (E_B). Current density in a pit usually exceeds $1\text{A}/\text{cm}^2$, while the current density in a crevice is low. Pitting has only been observed in halide solutions and has been reported to produce Ti^{4+} ions, while crevice corrosion has been observed in both halide salt and sulfate solutions and appears to produce Ti^{3+} ions. Finally, crevice corrosion occurs predominantly at high temperatures, while pitting can occur at room temperature or below. However, the solutions in both pits and crevices are acidic with respect to the bulk solution.²¹ It is generally agreed that the film formed on titanium during anodic polarization is an oxide film of titanium. Formation of both amorphous oxide films and non-stoichiometric forms of TiO_2 have been reported under different conditions.²²

Crevice Corrosion of Titanium in Corrosive Environments

Crevice corrosion of titanium is very unpredictable and can lead to catastrophic failure. It is severe in dry chlorine environments and has been observed in wet chlorine gas at 200°F .²³ Cerquetti, Mazza, and Vigano²⁴ investigated the role of the passive film in the crevice process. Localized attack due to crevice was found to involve nucleation and growth of a crevice. They suggested that ionic conductivity of films is the major rate-controlling factor for nucleation of crevice corrosion processes, while electronic conductivity of the films is the rate-controlling process for crevice growth. Crevice corrosion may be inhibited by alloying titanium with 0.2 percent palladium or 2 percent nickel.²⁵ Recently, titanium and other metals have

been surface alloyed to improve their corrosion resistance properties.²⁶

Cotton²⁷ has summarized some observations on the crevice behavior of titanium:

1. Commercially pure titanium did not suffer from crevice corrosion in neutral seawater at temperatures up to 130°C .
2. Lowering the water's pH had little effect until it reached 3; at temperatures of 130°C , there was evidence of attack. Conversely, increasing the pH improved crevice resistance; no crevice was observed at a pH of 9 at 150°C .
3. Increasing the chloride concentration from 3 to 6 percent had little effect on crevice behavior.
4. The presence of metallic iron in the crevice was detrimental to corrosion resistance.
5. Titanium 0.15 percent palladium exhibited crevice attack resistance up to temperatures of 170°C . Lowering the pH to 3 was deleterious.
6. Application of a passivation potential of 2 V prevented crevice corrosion at temperatures as high as 170°C .
7. Hydrides were present in metal surfaces suffering crevice attack.

Pitting of Titanium in Corrosive Environments

Beck²⁸ has reviewed pitting attack on titanium and its alloys. The potentials that initiate pitting are notably higher than those below which cessation of pitting occurs (pitting potential). Values for pitting potentials

²¹T. R. Beck, "A Review: Pitting Attack of Titanium Alloys."

²²E. W. Dreyman, "Precious Metal Anodes: State-of-the-Art," *Materials Protection and Performance*, Vol II, No. 9 (September 1972), pp 17-20; A. Cerquetti, F. Mazza, and M. Vigano, "Crevice Corrosion of Titanium in Contact with PTFE and Properties of the Surface Oxide Films," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 661-668.

²³L. W. Gleckman.

²⁴A. Cerquetti et al.

²⁵A. Cerquetti et al.

²⁶N. D. Tomashov, G. P. Chernova, and T. A. Fedoseeva, "Cathodic Alloying of the Surface of Titanium, Chromium, and Stainless Steel as a Method of Increasing Their Passivation and Corrosion Resistance," *Corrosion - NACE*, Vol 36, No. 4 (April 1980), pp 201-207.

²⁷J. B. Cotton, "A Perspective View of Localized Corrosion of Titanium," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 676-679.

²⁸T. R. Beck, "A Review: Pitting Attack of Titanium Alloys," *Proceedings of the International Conference on Localized Corrosion* (6-10 December 1971, Williamsburg, VA, NACE-3), pp 644-653.

of commercially pure titanium are generally about 9.0, 0.9, and 1.8 V in chloride, bromide, and iodide solutions, respectively. Although pitting and crevicing are distinct phenomena, the presence of crevices severely reduces the pitting potential of titanium.²⁹

Temperature has a pronounced effect on the pitting potential of titanium in halide solutions. Cotton noted that in 1M NaCl solution, the pitting potential drops nearly linearly from about 9.2 V at 20°C to 7 V at 55°C. Solution agitation improved pitting behavior at high velocities for circulation rates of about 5000 rpm. Pitting current densities ranging from 1 to 23 A/cm² have been observed during corrosion of titanium.

Pitting of titanium has been associated with dissolution of titanium to form Ti⁴⁺ ions. Corrosive environments in a pit are very different from those on the bulk of a specimen. The pH of solutions with a pit growing in neutral environments has been reported³⁰ to be lower than 1.3; in fact, pitting potentials exhibit limited dependence on pH except in very basic environments. The potential inside a pit does not equal the applied voltage; the voltage within a growing pit moves in a negative direction with respect to the nonpitted area surrounding it. Different models have been proposed to explain pit nucleation and growth.³¹ The pitting of titanium is complicated and does not fit a simple model. A mechanism involving formation of a salt film on the metal surface and reactions involving the electrolyte diffusion layer has been proposed to explain the pitting of titanium qualitatively.³² Cotton has noted that electrolytic reactions occurring at high impressed voltages are different from those encountered in natural environments. In natural environments, the dissolution reaction of titanium may involve the formation of a Ti³⁺ solvated stage and subsequent formation of oxides or oxyhalides; however, at high impressed voltages, titanium may react directly to form TiO₂.³³

²⁹Cotton.

³⁰Beck, "A Review: Pitting Attack of Titanium Alloys."

³¹Cotton; Beck, "A Review: Pitting Attack of Titanium Alloys"; Beck, "Pitting of Titanium I, Titanium-Foil Experiments," *J. Electrochem Society: Electrochemical Science and Technology*, Vol 120, No. 10 (October 1973), pp 1310-1316; Beck, "Pitting of Titanium II, One-Dimensional Pit Experiments," *J. Electrochem Society: Electrochemical Science and Technology*, Vol 120, No. 10 (October 1973), pp 1317-1324.

³²Beck, "Pitting of Titanium I, Titanium-Foil Experiments"; Beck, "Pitting of Titanium II, One-Dimensional Pit Experiments."

³³Cotton.

Methods to increase the pitting resistance of titanium have been investigated.³⁴ One technique involves adding 0.15 percent palladium, which shifts the anodic potential of a pit or crevice into the passive region. However, this technique can increase the corrosion rate under certain conditions.³⁵ Organic compounds that inhibit titanium corrosion in sulfuric acid and that form permanent complexes with the titanium have been developed.³⁶

Application of Titanium for Platinized Anodes

It is obvious from the preceding discussion that predicting the behavior of platinized titanium anodes based on prior research is difficult, at best. Therefore, before developing new applications for platinized titanium anodes, the electrical potential limits of the anodes must first be evaluated in the environment of interest.

Anode Evaluation

Electrochemical techniques such as anodic polarization, polarization resistance, corrosion current, field potential, and metal conductance are useful for studying the corrosive behavior of materials in aqueous environments. The following list gives some of the advantages of these electrochemical techniques noted by Walker and Rowe:³⁷

1. Considerable corrosion information can be obtained quickly.
2. Corrosion rates can be measured instantaneously without disturbing the metal.
3. Very low corrosion rates can be measured.
4. Many environmental conditions can be investigated during a single test.
5. Reproducibility of results is very good.

³⁴O. L. Riggs, Jr., K. L. Morrison, and D. A. Brunzell, "Inhibitor Development for Titanium Corrosion," *Corrosion - NACE*, Vol 35, No. 8 (August 1979), pp 356-360.

³⁵Cotton.

³⁶Riggs, Jr., et al.

³⁷M. S. Walker and L. C. Rowe, "The Use of Electrochemical Techniques for Corrosion Research in the Automotive Industry," *Electrochemical Techniques for Corrosion*, R. Baboian, ed. (National Association of Corrosion Engineers [NACE], 1977).

6. Methods are applicable to service testing in an evaluation of how changes affect operation conditions.

7. New insights into corrosion mechanisms are provided.

Electrochemical techniques have been used to study alloy development, corrosion resistance of metals to various environments, corrosion resistance of thin film coatings on metals, and other corrosion processes.³⁸

For example, the anodic polarization technique enables measurement of corrosion parameters over short periods of time. This technique uses a Greene Cell, in which the sample (working electrode), a counter electrode, and a reference electrode are immersed in a liquid corrosive environment. Voltage is applied externally between the sample and counter electrodes. The resulting potential difference between the sample and a reference electrode is measured with a high impedance potentiostat or electrometer, the current flowing through the counter electrode/working electrode circuit is also measured. Corrosion data may be extracted in several ways; for example, by fixing sample versus reference voltage (potentiostatic) or by fixing the rate of increase of the sample vs. reference voltage and measuring the resulting current (potentiodynamic).

3 EXPERIMENTAL PROCEDURE

Samples

CERL obtained platinized titanium anodes and titanium substrate rods 1/2 in. (12.7 mm) in diameter for testing from the Harco Corporation.* The rods were machined into samples 0.375 ± 0.003 in. ($9.525 \pm .076$ mm) in diameter and 0.500 ± 0.003 in. ($12.7 \pm .076$ mm) in length. Each sample was drilled and tapped to accept a 3-48-UNC-2A screw at 5/16-in. (7.95-mm) minimum thread depth and polished to a mirror finish. Samples for this investigation were obtained from three rods.

Table 1 lists the nominal compositions of the rods. Samples from Rods 1, 2, and 3 were comparatively examined by spectrographic analysis. Rods 1 and 2 were found to be essentially identical, containing only traces of tin, iron, aluminum, manganese, nickel, chro-

Table 1
Nominal Composition of Grade 2 Titanium Rods*

Nitrogen	0.03 percent
Carbon	0.10
Hydrogen	0.015
Iron	0.3 max
Oxygen	0.25 max
Others	Each 0.05 percent max (total does not exceed 0.3 percent max)
Titanium	Remainder

*Supplied by Harco, Inc., 1055 Smith Road, Medinah, OH 44256.

mium, and silicon. Both rods qualified as commercially pure titanium. However, quantitative analysis of Rod 3 revealed high concentrations of aluminum (0.31 percent), iron (0.11 percent), and chromium (0.01 percent).

Each sample was hand polished to a 600-grit surface finish, and the length and the diameter of each were measured with a micrometer. Samples were boiled under benzene for about 10 minutes to remove surface contaminants and then placed immediately in the Greene Cell for testing. Care was taken to avoid contaminating samples after degreasing.

Corrosive Environments

Solutions were prepared by adding appropriate amounts of analytical-grade NaCl to distilled and tap water. The NaCl content of the solutions ranged from 0.005 to 3.5 percent* total chloride content. Analysis of Champaign, IL, tap water (Table 2) revealed approximately 5 ppm chloride and 40 ppm sulfate ions. The high sulfate content results from the water softening process.

A YSI Model 31 Conductivity Bridge was used to determine solution resistivity at a frequency of 1K Hz. Figure 4 shows resistivities of distilled and tap water containing varying amounts of NaCl. The curves shown in Figure 3 reflect the water's total chloride content.

*Solution concentrations in this report are expressed as weight/volume; i.e., 1 percent NaCl solution contains 1 gr NaCl/100 ml solution. However, the specific gravity of the chloride-containing solutions used in this investigation is nearly unity so that percent weight by volume is synonymous with percent weight by weight.

³⁸Walker and Rowe.

*Harco Inc., 1055 W. Smith Road, Medinah, OH 44256.

Table 2
Chemical Analysis* of Champaign, IL, Tap Water

pH	8.8 to 9.0 units
Total Alkalinity	100 to 120 mg/L as CaCO ₃
Calcium	30 to 35 mg/L as CaCO ₃
Magnesium	45 to 50 mg/L as CaCO ₃
Hardness	75 to 85 mg/L as CaCO ₃
Fluoride	0.90 to 1.20 mg/L
Iron	Less than 0.02 mg/L
Sodium	Less than 40 mg/L
Sulfate	Less than 40 mg/L
Nitrate	Less than 2.0 mg/L
Chloride	Less than 5.0 mg/L
Total Solids	Less than 180 mg/L
Ammonia	Less than 2 mg/L
Chlorine	Combined residual 2.5 ± 0.1 mg/L
Turbidity	Less than 0.1 JTU
Color	0 units
Odor	0 units

*Analysis supplied by Northern Illinois Water Corporation, Champaign, IL.

Corrosion Studies

A Princeton Applied Research corrosion system consisting of a Model 175 Universal Programmer, a Model 173 Potentiostat/Galvanostat with a Model 376 Logarithmic Current Converter Module, and a standard three-electrode Greene Cell was modified for this investigation. The standard system can measure voltages (vs. a reference) only up to about 10 V. Since the breakdown voltage of passive films formed on titanium can be higher than 10 V in many corrosive environments, equipment modification was necessary.

Figure 4 shows a schematic diagram of the platinum electrode designed and made for this investigation; it simultaneously served as a counter and as a potentiostat reference electrode. The electrode consisted of a sealed glass tube with 20 cm of 10-mil platinum wire extending through it. The wire was wrapped around the circumference of the tube to provide an electrode

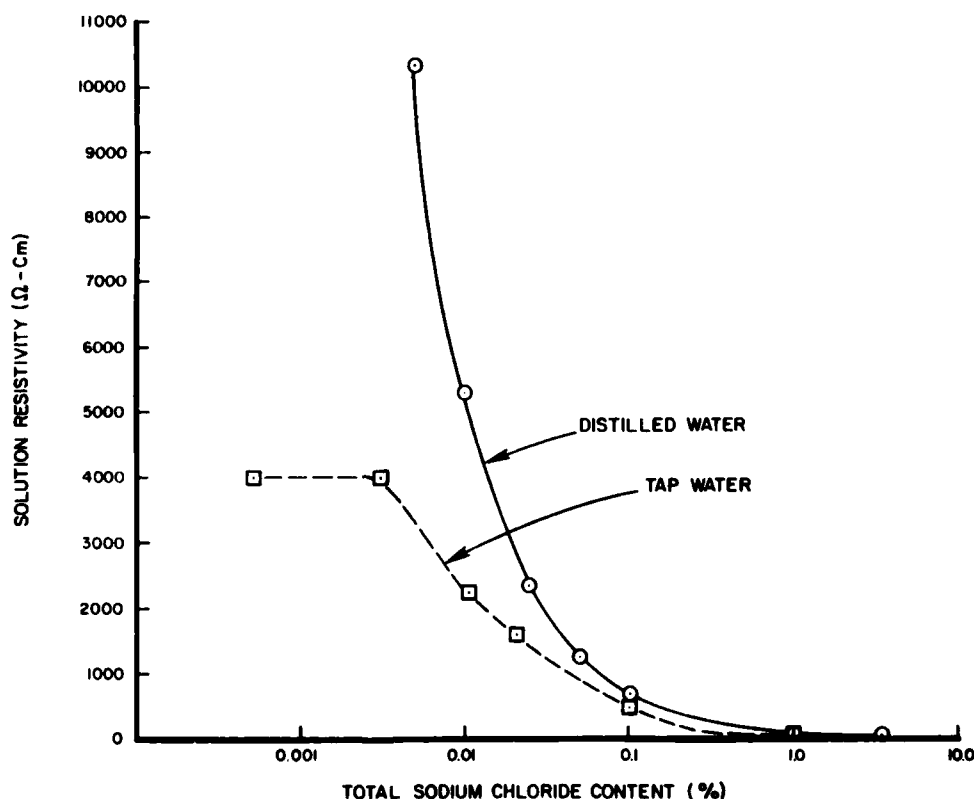


Figure 3. Resistivity of tap and distilled water solutions used to provide corrosive environments.

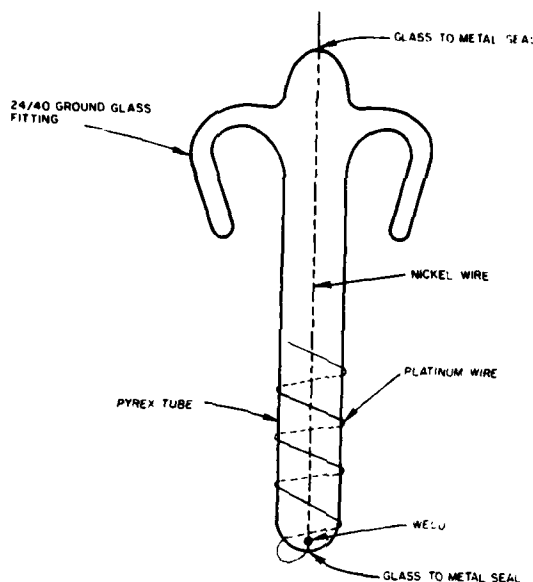


Figure 4. Schematic diagram of platinum electrode.

with a fixed surface area. Within the tube, the platinum wire was welded to a nickel rod several inches long. The top of the glass tube was sealed to the rod, leaving about 1 in. (25.4 mm) of the rod exposed for electrical connection. A 24/40 ground glass fitting was jointed to the glass near the top of the tube, allowing for immersion of the electrode to a fixed depth in the cell. The Greene Cell was filled with a fixed volume of solution (about 850 ml) for each run. The sample, saturated calomel electrode (SCE), and gas bubbler were installed in the standard fashion, and the remaining port on the cell was sealed with a closed-top 24/40 ground glass fitting. Oxygen was used as a purge gas for all experiments and a magnetic stirrer was used to maintain constant solution velocity for all potentiodynamic runs.

Figure 5 is a schematic diagram of the experimental setup used to obtain potentiodynamic scans for this investigation. The voltage was applied between the sample and the platinum electrode. A 10:1 voltage divider consisting of a $20\text{k}\Omega$ and a $100\text{k}\Omega$ resistor was constructed. The electrometer probe was connected between the resistors, and the potentiometer ground lead was connected to the $20\text{k}\Omega$ resistor. In this configuration, the potentiometer measured only one-tenth of the applied voltage, and the resulting rate of applied voltage increase was ten times the programmed scan rate. Unless otherwise noted, a programmed scan rate of 0.1 mV/sec was used for this investigation.

A DANA Digital Multimeter Model 5900 with an analog output and an input impedance of 10^7 to $10^{10}\ \Omega$ (depending on scale selection) was used to externally measure the voltage at the sample relative to a saturated calomel electrode. The rate of voltage (SCE) change varied with the IR drop of the current-carrying circuit, and voltage (SCE) scan rates deviated substantially from the expected 3.6 V/hr only at voltages (SCE) above the breakdown voltages of the samples. Analog outputs from the Logarithmic Current Converter and DANA Multimeter were provided to the X and Y axes of a Houston Instruments Omnigraphic 2000 Recorder.

Figure 2 shows a typical titanium potentiodynamic scan. Applied voltages were ramped at a constant rate; eventually, the passive layer on the titanium samples broke down and was shown on the potentiodynamic scan by a rapid increase in the current. The voltage (SCE) at which breakdown (i.e., the onset of rapid corrosion during an upward scan) occurred (E_{BD}) was determined graphically. After breakdown, the applied voltage was ramped until the corrosion current reached a level of 10^{-2} A/cm^2 of sample. At this current level, the scan direction was reversed to determine the pitting potential (E_B). The pitting potential was determined graphically as the voltage where the reverse voltage (SCE) vs. log current curve crossed the upward ramped curve (see Figure 2). The breakdown voltages and pitting potentials were tabulated, and plots of E_{BD} and E_B as a function of NaCl content were prepared.

4 RESULTS AND DISCUSSION

Behavior of Titanium in 3.5 Percent NaCl in Distilled Water Solutions

Figure 2 shows a potentiodynamic scan obtained for titanium in a 3.5 percent NaCl in distilled water solution (solid line). The curve is characterized by current maxima of 0.17 and 0.58 mA/cm^2 at about 1.75 and 9.34 V (SCE) , respectively. Breakdown of the passive film occurred at 12.2 V (SCE) , and the pitting potential observed during the reverse scan was 10.3 V (SCE) .

Several potentiodynamic scans were obtained for titanium in 3.5 percent NaCl solutions in distilled water; Table 3 tabulates the results. Four scans were conducted at an applied scan rate of 3.6 V/hr , and the breakdown voltage observed was $11.2 \pm 0.96\text{ V (SCE)}$. Potentiodynamic scans at 5.2 and 1.8 V/hr resulted in film breakdown at 10.25 and 10.8 V (SCE) , respectively. These voltages are within the error reported for

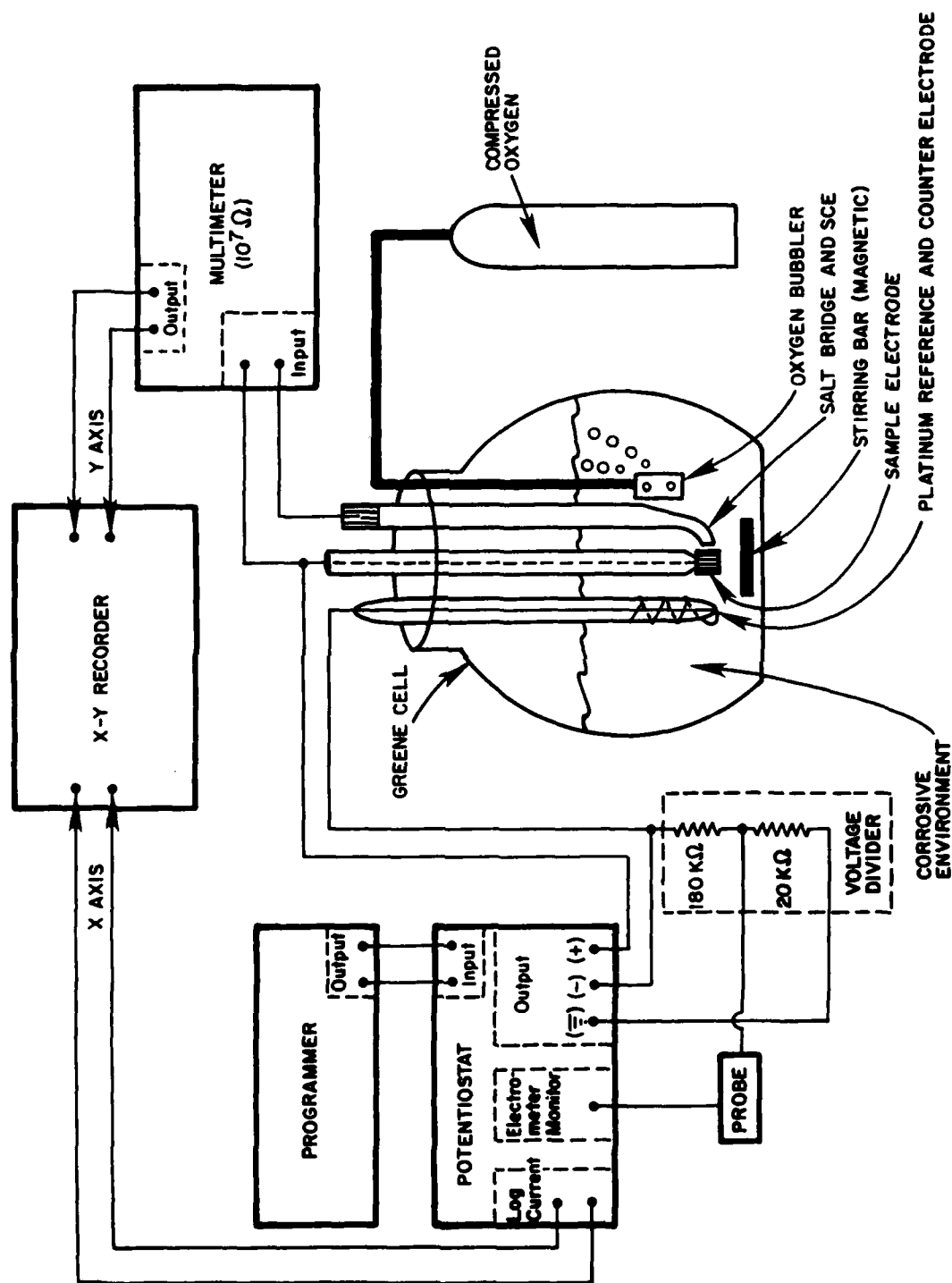


Figure 5. Schematic diagram of experimental apparatus used for modified potentiodynamic scans.

Table 3
Breakdown Voltages and Pitting Potentials of Titanium Samples
Immersed in 3.5 Percent NaCl in Distilled Water

Run No.	Applied Voltage Scan Rate (V/hr)	Breakdown Voltage (Volts vs. SCE)	Pitting Potential (Volts vs. SCE)
1	3.6	12.25	10.3
2	3.6	10.5	9.6
3	3.6	10.3	9.3
4	3.6	11.8	10.4
5A	5.2	10.25	9.4
5B	5.2	10.4	9.2
7	1.8	10.8	9.4
Runs 1 through 4: $E_{BD} = 11.21 \text{ V (SCE)}$ $E_B = 9.9 \text{ V (SCE)}$ $\sigma_{BD} = 0.96 \text{ V (SCE)} = 8.6 \text{ percent}$ $\sigma_B = 0.54 \text{ V (SCE)} = 5.5 \text{ percent}$			
Runs 1 through 7: $E_{BD} = 10.90 \text{ V (SCE)}$ $E_B = 9.66 \text{ V (SCE)}$ $\sigma_{BD} = 0.80 \text{ V (SCE)} = 7.4 \text{ percent}$ $\sigma_B = 0.49 \text{ V (SCE)} = 5.1 \text{ percent}$			

the 3.6 V/hr scans and represented no trend; thus, it is apparent that the variation of the applied scan rate from 1.8 to 5.2 V/hr has no effect on the breakdown voltage of the samples. Similarly, pitting potentials for four samples obtained at an applied scan rate of 3.6 V/hr were $9.9 \pm 0.54 \text{ V (SCE)}$, while pitting potentials of 9.4 V (SCE) were observed at scan rates of both 1.8 and 5.2 V/hr. Thus, the pitting potential and breakdown voltage are insensitive to the scan rates used in this investigation.

Figure 6 shows consecutive potentiodynamic scans obtained at an applied scan rate of 5.6 V/hr for a titanium sample immersed in a 3.5 percent NaCl in distilled water solution (runs 5A and 5B in Table 3). The corrosion potential was -0.05 V (SCE) at the start of the first run (solid line in Figure 6). During the scan, the sample exhibited typical voltage vs. current behavior, as shown by the characteristic current maxima of 0.072 and 0.76 mA/cm² at 1.6 and 9.7 V (SCE). Breakdown of the passive film occurred at 10.5 V (SCE), and the pitting potential was 9.4 V (SCE). No current maxima were observed during the downward scan, and the current was highest during the upward scan. The downward scan was terminated at zero V applied potential. The corrosion potential was measured again and found to be -0.55 V (SCE) , 1/2 V lower than during the first scan. A second anodic scan was then initiated. During this scan (dotted line in Figure 6), currents at a given voltage were generally lower than those observed during the first scan. The previous current maximum of 1.6 V (SCE) was not observed, and the second current maximum (previously observed at 9.7 V) appeared to be displaced to higher voltages. The passive films broke

down at 10.4 V (SCE), within 0.15 V of the initial scan. The pitting potential was 9.2 V (SCE), within 0.2 V of the initial breakdown.

Figure 6 shows that although the breakdown voltages and pitting potentials after breakdown are reproducible, the shapes of subsequent potentiodynamic scans are not. The current maximum at 1.7 V (SCE) was not observed during the second potentiodynamic scan of a pitted and repassivated sample. Furthermore, the corrosion potential shifted by -0.50 V after the first scan, and corrosion current levels during the second scan were generally lower. This suggests that preferential "leaching" of impurities near the surface during the first scan may have left behind relatively pure titanium at the sample's surface.

The breakdown and passivation potentials were insensitive to the condition of the passivated surface, as shown by only slight changes (less than 2 percent) in these values for consecutive potentiodynamic scans on the same specimen (see Figure 6). However, variations in these parameters among samples could be as high as 8.6 percent; the reason for this behavior is unclear.

Figures 2 and 6 show that current densities as high as 0.9 mA/cm² were observed before film breakdown began. It is not apparent whether these relatively high current densities are associated with dissolution of metallic ions from the electrode, an oxygen reaction, or other processes. A dissolution reaction could be detrimental to the long-term use of titanium as an anode material.

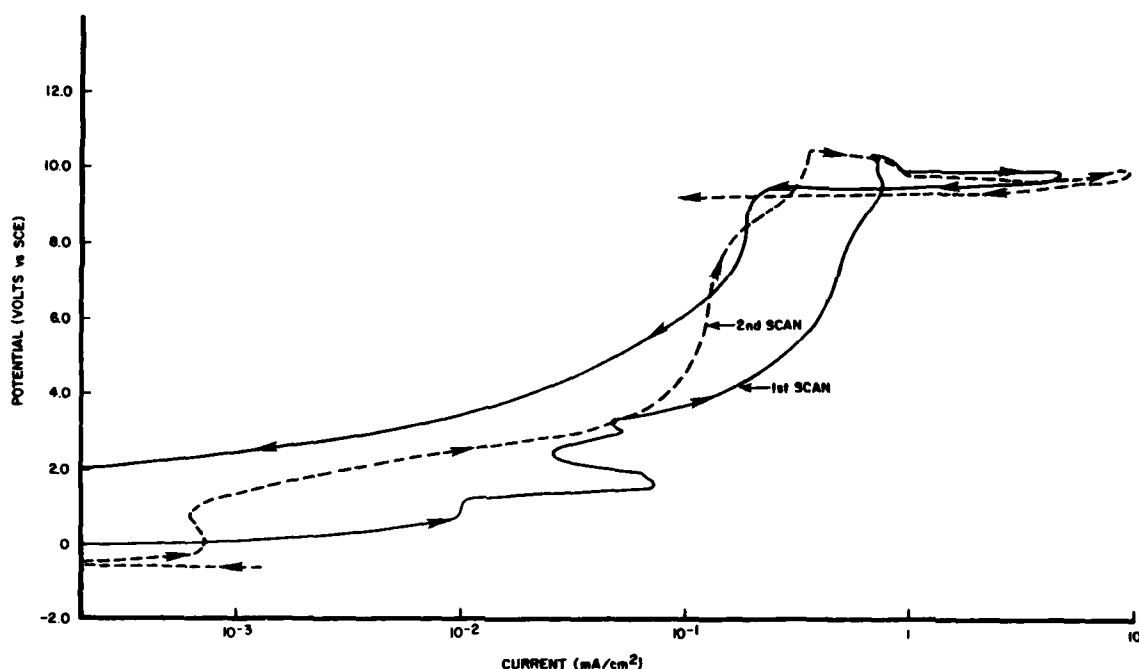


Figure 6. Consecutive potentiodynamic scans of titanium in 3.5 percent NaCl at an applied scan rate of 5.6 V/hr.

There was no evidence of sparking, which could be expected during dielectric breakdown at relatively high voltages. The breakdown mechanism appears to be dominated by electrochemical attack of the film by aqueous species, specifically the chloride ions.

The breakdown voltages and pitting potentials of titanium immersed in 3.5 percent NaCl solutions were within previously reported values.³⁹ No preferential attack was observed near the teflon sample support where crevicing might be expected to occur. There was no evidence that crevicing preceded pitting of the samples; pits appeared to initiate under stagnant bubbles (oxygen) on the specimen's surface.

Effect of NaCl in Distilled Water on Corrosion of Titanium

Figure 2 shows potentiodynamic curves of titanium

immersed in distilled water containing 3.5 percent (solid line) and 0.005 percent (dotted line) NaCl. The current at a given voltage in the 0.05 percent NaCl solution was higher than that observed in the 3.5 percent solutions, but this effect appears to be relatively minor, since the curves shown in Figure 2 exhibit the same general characteristics.

Figure 7 shows breakdown voltages and pitting potentials of titanium immersed in distilled water containing varying amounts of NaCl. A plot of solution resistivity vs. NaCl content is also shown. Table 4 lists the breakdown voltages, pitting potentials, and solution resistivities plotted in Figure 7. Data at 3.5 percent NaCl are plotted as an average showing error bars (see Table 4). Corrosion potentials measured at the beginning of each run varied from -0.2 to 0.5 V (SCE). The breakdown voltage decreased from 18.2 to 10.90 ± 0.80 V (SCE) for solutions containing from 0.005 to 3.5 percent NaCl, while the pitting potential decreased from 16.4 to 9.66 ± 0.49 V (SCE) for these solutions. The curves of breakdown voltage and pitting potential of titanium versus NaCl content exhibited about the same slopes, and both appeared to be relatively insensi-

³⁹M. A. Warne and P. C. S. Haywood, "Platinized Titanium Anodes for Use in Cathodic Protection," *Materials Performance*, Vol 15, No. 3 (March 1976), pp 39-42.

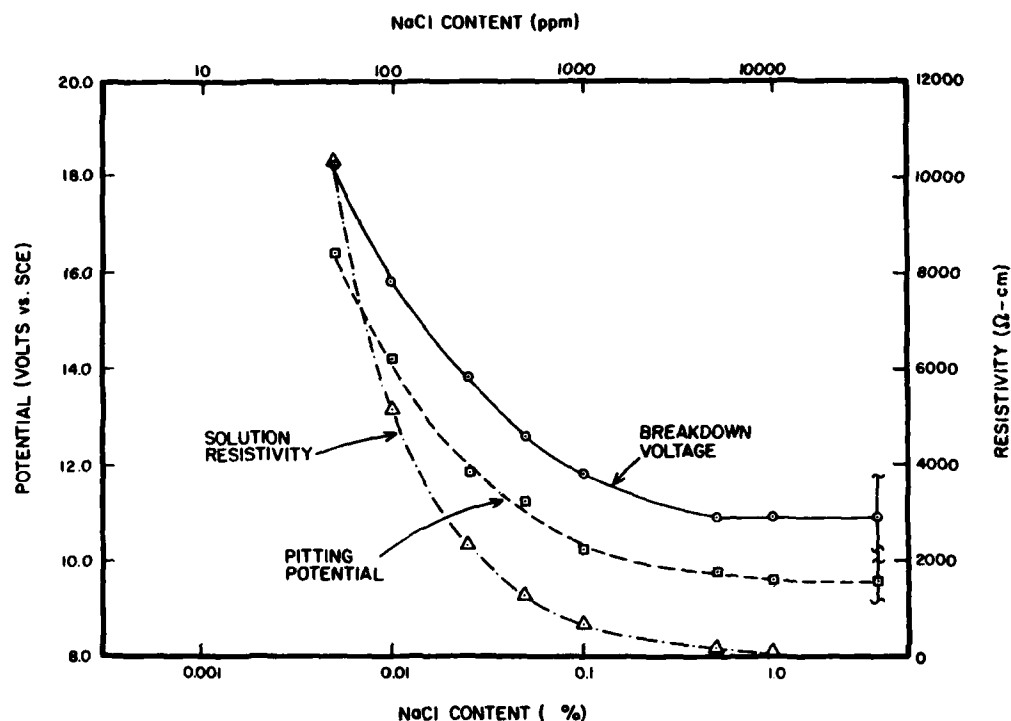


Figure 7. Breakdown voltages and pitting potentials of titanium immersed in distilled water containing varying amounts of NaCl.

tive to the NaCl content at concentrations above 0.5 percent. At low concentrations, the breakdown voltage and pitting potential increased with decreasing salt concentration. In very low chloride content solutions, the maximum working voltage (i.e., pitting potential) was just over 16 V (SCE). Again, there was no evidence of dielectric breakdown or crevice corrosion.

Potentiodynamic scans of titanium in solutions containing less than 0.005 percent NaCl are not reported. Resistivities of these solutions exceeded 10,000 Ω -cm, and scans in these solutions could not be obtained because the potentiostat could not apply enough voltage to the corrosion circuit to break down the passive films. This occurred because a large part of the applied voltage was lost in the IR drop of the solution.

Table 4
Breakdown Voltages, Pitting Potentials, and Solution Resistivities for Titanium Samples in Distilled Water Solutions Containing Varying Amounts of NaCl

NaCl Content (%)	Breakdown Voltage (Volts vs. SCE)	Pitting Potential (Volts vs. SCE)	Solution Resistivity (Ω -cm)
3.5	10.90 $\pm$ 0.80	9.66 $\pm$ 0.49	--
1.0	10.9	9.6	68
0.5	10.9	9.7	150
0.1	11.8	10.2	630
0.05	12.6	11.2	1,250
0.025	13.8	11.8	2,350
0.010	15.8	14.2	5,200
0.005	18.2	16.4	10,300

Significant IR drops may occur across the high resistivity solutions. As a result, potentials measured relative to the SCE may be reduced significantly. This effect can be estimated. The voltage drop across the solution (V) may be expressed as:

$$V = \rho \frac{l}{A} \cdot I \quad [\text{Eq 3}]$$

where: ρ = solution resistivity, Ω -cm

l = distance from specimen to SCE, cm

A = area $\approx 1 \text{ cm}^2$

I = corrosion current (total).

Currents of about 10^{-3} A were observed in high resistivity solutions ($\rho \approx 10000 \Omega\text{-cm}$) prior to sample breakdown, and sample-to-SCE distances were about 0.1 cm.

Substituting these values into Eq 1 and solving reveals that about a 1-V (SCE) voltage drop across the electrolyte occurs, significantly reducing the measured potential (SCE). However, this analysis shows that breakdown voltages and pitting potentials are at least as high as those reported⁴⁰ and that IR drops across the solution did not affect result trends.

Effect of NaCl in Tap Water on Corrosion of Titanium

Figure 8 shows potentiodynamic scans for titanium immersed in tap water containing 1.0 percent (dotted line) and 0.1 percent (solid line) NaCl. The corrosion potentials were 0.2 and -0.2 V (SCE) for the 0.01 percent and 1.0 percent solutions, respectively. The two curves exhibit the characteristic current maxima previously observed in the distilled water solutions, but these maxima were displaced to lower voltages. In the 1.0 percent NaCl solution, the maxima were observed

at 1.2 and 8.25 V (SCE), while in the 0.01 percent NaCl solution, maxima occurred at 1.6 and 9.0 V (SCE). Breakdown of the passive film in the 1.0 percent NaCl solution occurred at 11.0 V (SCE), while breakdown in the 0.01 percent NaCl solution occurred at a substantially higher voltage - 29.5 V (SCE). Voltage drops across the solution at high current levels occurred in both samples, although this effect was more pronounced in the 0.01 percent NaCl solution. Pitting potentials of 9.5 and 14.8 V (SCE) were observed in the 1.0 and 0.01 percent solutions, respectively. Lowered currents at a given voltage again occurred after film repassivation.

Figure 9 shows plots of the breakdown voltage and pitting potential of titanium in tap water containing varying amounts of NaCl and a plot of solution resistivity vs. NaCl content. Table 5 gives values of the breakdown voltage, pitting potential, and solution resistivity. It should be noted that the curves shown in Figure 9 reflect the total chloride content of the water. Corrosion potentials for titanium in tap water containing NaCl varied from 0.5 to 0.1 V. Breakdown voltages decreased from 29.5 to 11.0 V (SCE), and pitting potentials decreased from 14.8 to 9.5 V (SCE) for solutions whose total NaCl content ranged from 0.01 to 1.0 percent.

Potentiodynamic scans for titanium were also obtained for 0.001, 0.0025, and 0.0055 percent NaCl

⁴⁰R. Baboian, "Platinum Consumption in Cathodic Protection Anodes," *Materials Performance*, Vol 16, No. 3 (March 1977), pp 20-22; M. A. Warne and P. C. S. Haywood, "Platinized Titanium Anodes for Use in Cathodic Protection," *Materials Performance*, Vol 15, No. 3 (March 1976), pp 39-42.

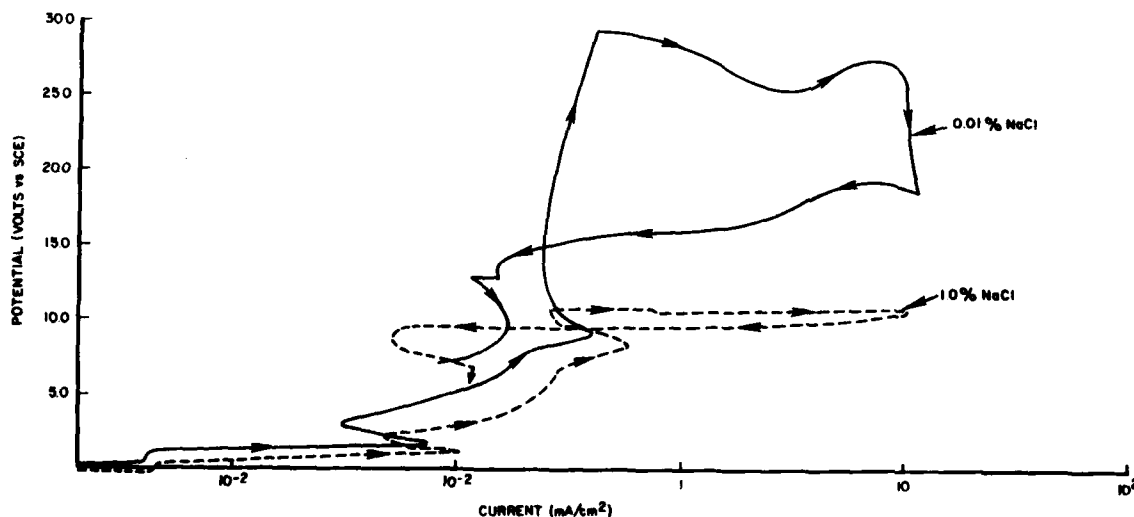


Figure 8. Potentiodynamic scans of titanium in tap water containing 1.0 and 0.01 percent NaCl.

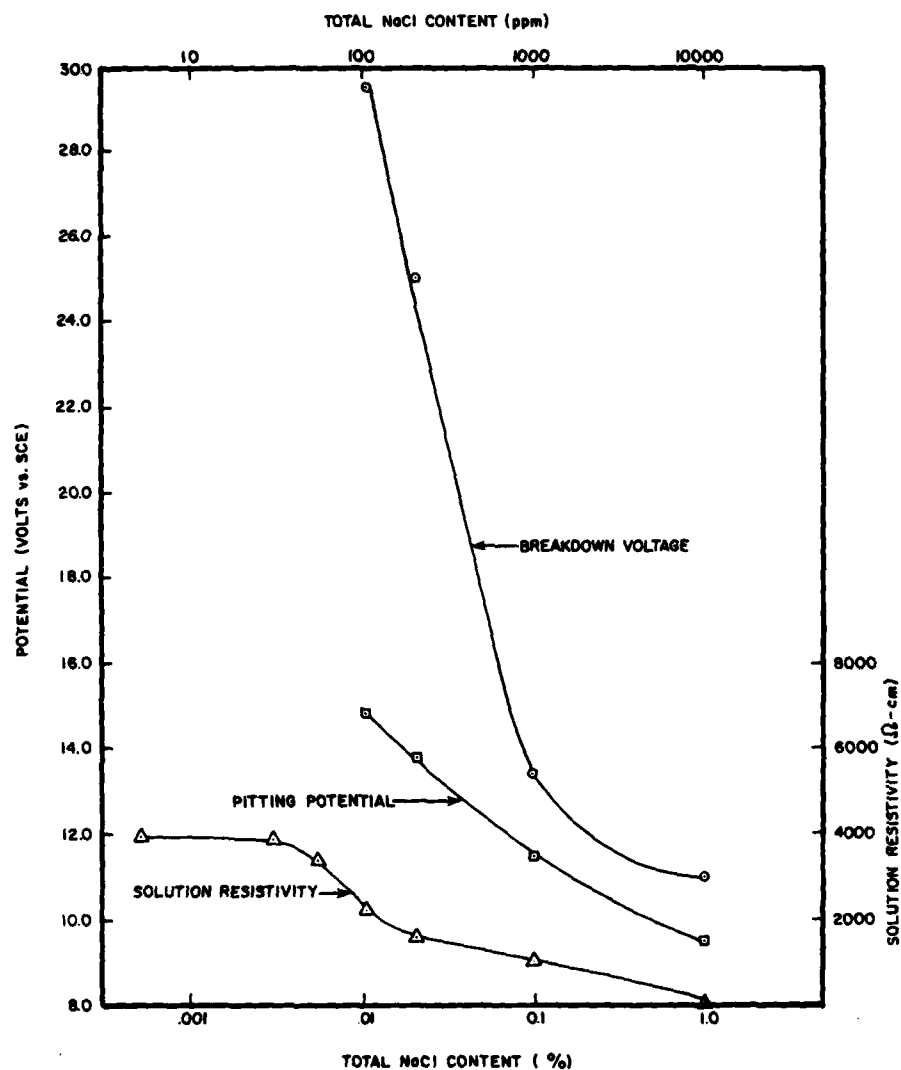


Figure 9. Breakdown voltages and pitting potentials of titanium immersed in tap water solutions containing varying amounts of NaCl.

solutions. The breakdown voltage of passive films formed on titanium in solutions containing as much as 0.0055 percent NaCl was more than 80 V (SCE), and could not be measured with experimental apparatus used in this investigation.

The breakdown voltage vs. NaCl content curve (see Figure 9) rises sharply at NaCl contents below 0.01 percent and the breakdown voltage curve rises much more steeply with decreasing NaCl content than the pitting potential curve. The breakdown voltage increased from 11.0 to 29.5 V (SCE) (a 168 percent

improvement) in solutions having from 1.0 to 0.01 percent NaCl, while the pitting potential only increased from 9.5 to 14.8 V (SCE) (a 55 percent improvement) in these solutions. Although the breakdown voltage is much higher in low chloride content tap water than distilled water, it is apparent that pitting potentials are only slightly improved.

IR drops that reduce the measured voltages in tap water may be again calculated using Eq 1. In 0.01 percent NaCl in tap water, solution resistivity was about 2500 Ω -cm, and currents on the order of 10^{-3} A/cm²

Table 5
Breakdown Voltages, Pitting Potentials, and Solution Resistivities for Titanium Samples Immersed in Tap Water Solutions Containing Varying Amounts of NaCl

NaCl Content (%)	Breakdown Voltage (Volts vs. SCE)	Pitting Potential (Volts vs. SCE)	Solution Resistivity (Ω -cm)
1	11.0	9.5	65
0.1	13.4	11.5	510
0.02	25.0	13.8	1600
0.01	29.5	14.8	2250
0.005	—	—	3400
0.0025	—	—	3800
0.001	—	—	3800
0.005 (tap water)	—	—	400

were observed prior to breakdown. Solving Eq 1 gives a voltage drop of about 0.25 V. Breakdown occurred at nearly 30 V in 0.01 percent NaCl in tap water, and although the 0.25-V drop was significant, there was very little effect on the data trend. Furthermore, actual voltages were again at least as high as those reported.⁴¹

Comparison of Behavior of Titanium in Tap and Distilled Water

Figure 10 compares the breakdown voltage and pitting potential for titanium samples in distilled and tap water containing various amounts of NaCl. At NaCl contents greater than 0.1 percent, passive films broke down at about the same voltages in both tap and distilled water solutions; however, at lower concentrations, breakdown voltages in tap water were substantially higher. This effect may be due to the presence of inhibitors in the tap water which improved titanium's breakdown characteristics. It should be noted that these observations reflect previously observed reproducibility of results. At 0.01 percent NaCl, the breakdown voltage of titanium in tap water was 13.7 V (SCE) higher than in distilled water. Pitting potentials at chloride contents of 0.01 percent and above 0.5 percent were about the same in both distilled and tap water; at intermediate NaCl contents, the pitting potential in distilled water was slightly lower than in tap water. (This observation also reflects the previously

observed accuracy of the results.) These results show that although inhibitors in tap water substantially improve breakdown voltages at low chloride concentrations, they do not significantly improve the pitting potentials. Furthermore, the voltage drops across the solution that lowered the measured potential were more pronounced in distilled water than in tap water, particularly at low chloride contents. This observation, together with recognition of the previously observed reproducibility of pitting potentials, suggests that there is little, if any, difference between the pitting potentials of titanium in the distilled and tap water solutions used in this investigation.

Figure 11 illustrates the dependence of titanium's pitting potentials on NaCl content of distilled and tap water plotted on linear axes. This plot shows that the repassivation potential increases very rapidly with decreasing chloride content only at very low NaCl concentrations; also, at low chloride concentrations, small fluctuations in solution chloride content can greatly change both the breakdown voltage and pitting potential.

The breakdown voltage begins to increase appreciably at NaCl concentrations below about 0.25 percent, while pitting potentials improve greatly at NaCl concentrations below 0.5 percent in tap water and at 0.25 percent in distilled water.

Visual Observations

Samples changed color during potentiodynamic scans; colors such as green, blue, purple, and brown were observed. However, there appeared to be no correlation between color and the onset of passive film breakdown. Breakdown was characterized by pit formation under stagnant bubbles either at the surface of the sample nearest the platinum electrode or at the bottom of the sample. As current increased, several pits formed, and gas evolved at the platinum electrode. After long periods of corrosion, the most severe pitting occurred at the corners of the samples, and precipitates of corrosion products were observed in the solution. Some samples which were exposed for longer periods of time (more than 2 to 3 hours) showed very severe pitting and rounding off of corners. These observations showed that titanium substrates can be damaged extensively in only a few hours if the film breaks down. Therefore, it is obvious that to maintain the integrity of coated titanium anodes, conditions where the film is unstable, even for a short period of time, should be avoided.

⁴¹R. Baboian, "Platinum Consumption in Cathodic Protection Anodes," *Materials Performance*, Vol 16, No. 3 (March 1977), pp 20-22; M. A. Warne and P. C. S. Haywood, "Platinized Titanium Anodes for Use in Cathodic Protection," *Materials Performance*, Vol 15, No. 3 (March 1976), pp 39-42.

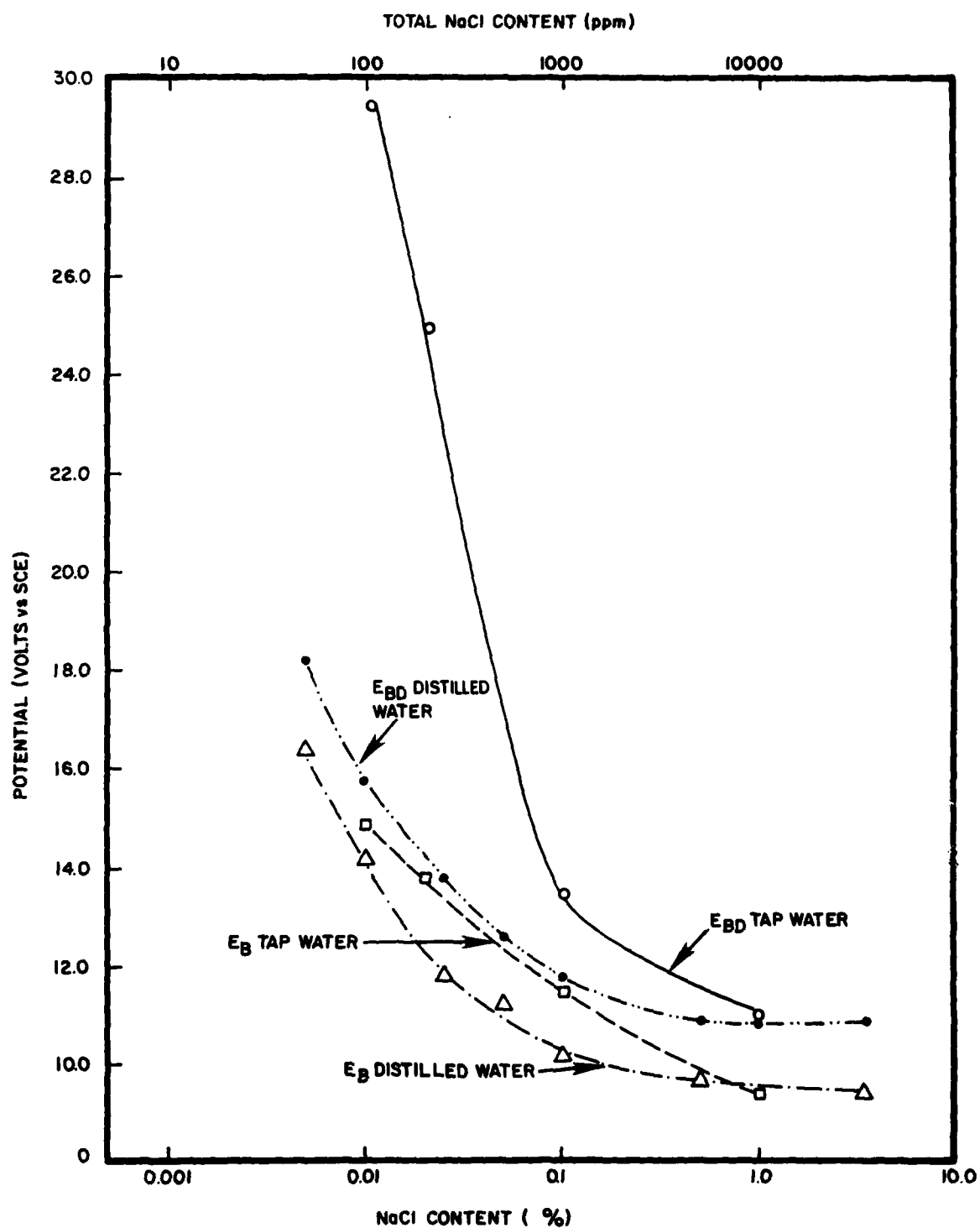


Figure 10. Comparison of the breakdown voltages (E_{BD}) and pitting potentials (E_B) of titanium in distilled and tap water.

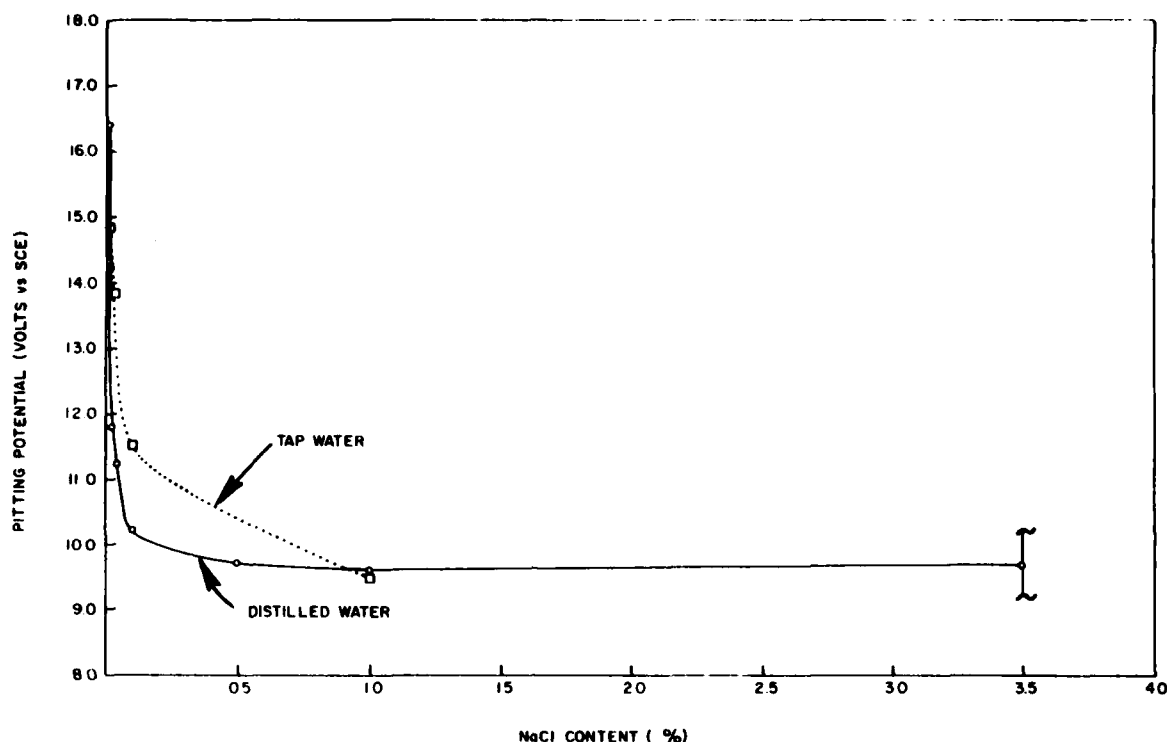


Figure 11. The dependence of titanium's pitting potential on NaCl content of distilled and tap water.

Application to Titanium Anodes

The pitting potential is the maximum voltage (versus a reference) which will insure that titanium will not pit, regardless of surface condition (i.e., passive or already pitted); this potential should not be exceeded when using impressed current anodes. In typical fresh river waters such as the Ohio River, the chloride content is only about 30 ppm (0.003 percent), as shown in Table 6. Both breakdown voltages and pitting potentials of titanium are expected to be much higher than the 9.17 V (SCE) (worst case) observed in the highest chloride-containing distilled and tap water solutions. Titanium can be used as a substrate material for platinum or ceramic-coated anodes for impressed current cathodic protection systems where voltages do not exceed 9.17 V (SCE). Furthermore, the presence of other ions in river waters is expected to increase the breakdown voltage, making pitting less likely. Thus, titanium substrates may be used for impressed current cathodic protection systems using platinum or ceramic coatings.

5 SUMMARY OF RESULTS

The following text summarizes the major results of this investigation.

The breakdown voltage and pitting potential of titanium in solutions of 3.5 percent NaCl in tap water were 10.90 ± 0.80 and 9.66 ± 0.49 V (SCE), respectively.

Breakdown voltages varied from 18.2 to 10.90 ± 0.80 V (SCE), and pitting potential varied from 16.4 to 9.66 ± 0.49 V (SCE) for distilled water solutions containing from 0.005 to 3.5 percent NaCl. The breakdown voltage of titanium immersed in tap water containing less than 0.005 percent NaCl could not be measured because the potentiostat could not apply sufficient voltages to break down the sample.

For tap water solutions containing from 0.01 to 1 percent NaCl, breakdown voltages varied from 29.5 to 11.0 V (SCE), and pitting potentials varied from 14.8 to 9.5 V (SCE). Relatively small improvements in the

Table 6
Typical Analysis of Major River Waters

River	Location City, State	Date Month/Day/Year	[SO ₄] mg/L	[Cl] mg/L	Dissolved Solids mg/L	Hardness as CaCO ₃ mg/L	Specific Conductance μmohs	pH
Alabama	Claiborne, AL	9/19/78	8.2	7.4	71	43	133	7.7
Arkansas	Little Rock, AK	9/1/77	35	86	...	...	545	8.1
Arkansas	Coolidge, KS	9/26/78	2500	220	4420	1700	4450	8.1
Arkansas	Hutchinson, KS	9/6/78	180	920	1990	...	3400	8.2
Black Warrior	Northport, AL	9/25/78	51	5.7	114	64	190	6.5
Columbia	Dalles, OR	7/26/77	11	2.7	81	...	144	8.0
Illinois	Pekin, IL	8/23/78	96	60	28	...	700	8.6
Mississippi	St. Paul, MN	9/26/77	25	12	201	170	343	8.2
Mississippi	Alton, IL	9/13/77	36	12	226	170	400	8.2
Mississippi	Vicksburg, MS	9/7/77	54	26	223	140	420	7.7
Missouri	Pierce, SD	9/15/78	200	9.5	...	210	700	8.8
Missouri	St. Joseph, MO	9/14/77	97	9.7	282	260	420	7.7
Monongahela	Braddock, PA	3/13/78	200	24	341	180	555	6.6
Ohio	Greenup, KY	9/20/78	110	17	290	150	455	7.4
Ohio	Markland, KY	9/15/78	90	28	268	160	645	7.9
Red	Alexandria, LA	9/8/78	160	230	707	260	1260	8.0
Snake	Burbank, WA	9/6/78	17	8.0	113	66	174	8.1
Tennessee	Pickwick, TN	9/21/78	14	8.0	90	65	160	6.5
Tennessee	Paducah, KY	4/11/78	14	5.9	92	83	170	7.8
Tombigbee	Gainesville, AL	9/13/78	8.5	11	81	52	155	7.7
Tombigbee	Coffeeville, AL	9/20/78	39	20	132	22	253	7.9

pitting potential were observed in low NaCl content tap water solutions, although breakdown voltages improved substantially. Breakdown voltages of samples immersed in tap water solutions containing up to 0.005 percent NaCl exceeded 80 V (SCE).

IR drops in high resistivity solutions could be as high as 1 to 2 V, but these voltage drops did not affect result trends.

The breakdown voltage and pitting potential of titanium in 3.5 percent NaCl in distilled water were insensitive to scan rate (for applied voltage scan rates from 1.8 to 5.6 V/hr) and to previous surface pitting.

General characteristics of potentiodynamic scans for titanium in both distilled and tap water solutions were found to be reproducible. Characteristic current maxima were observed at approximately 1.7 and 9.4 V (SCE).

At low chloride concentrations, breakdown voltages improved substantially in tap water (relative to distilled water). However, pitting potentials appeared to be the same in both solutions.

Breakdown voltages in both solutions were substantially improved at only NaCl concentrations below

0.25 percent. Pitting potentials were substantially improved below 0.5 percent NaCl in tap water and below 0.25 percent NaCl in distilled water.

At low NaCl concentrations (below 0.1 percent), both pitting potentials and breakdown voltages increase rapidly with decreasing NaCl content. This behavior suggests that at these NaCl concentrations, a small increase in NaCl content can substantially reduce both the pitting potential and breakdown voltage.

Pitting began at a face of the sample (away from corners) and, even after a few hours, severe pitting which caused rounding of the corners of the samples had occurred. Samples changed color during potentiodynamic scans but color could not be associated with the onset of breakdown. The breakdown of passive films formed on titanium appeared to result from an electrochemical reaction rather than dielectric breakdown, and crevice corrosion of samples was not observed.

6 CONCLUSIONS AND RECOMMENDATIONS

The pitting potential and breakdown potential of titanium (99 percent pure) increases with decreasing NaCl content in both distilled and tap water (Chapter 4).

The pitting potential of titanium (99 percent pure) in distilled water solutions containing 3.5 percent NaCl was 9.66 ± 0.49 V, and the breakdown potential was 10.90 ± 0.80 V with respect to a Saturated Calomel Electrode (SCE). In tap water, pitting potentials as low as 9.5 V (SCE) and breakdown voltages as low as 11.0 V (SCE) were observed.

Pitting of titanium caused extensive damage to samples after a few hours. As a result, it is recommended that conditions where titanium anodes may pit be avoided, even for short periods of time. Operation of anodes below the pitting potential insures that pitting

will not occur, regardless of whether the surface is passive or pitted.

The chloride content of freshwater rivers is usually very low; for example, the Ohio River contains only 0.003 percent chloride, and both breakdown voltages and pitting potentials will be much higher than those observed in waters containing higher chloride concentrations.

It is recommended that impressed current anodes using titanium substrates be used to protect hydraulic structures and that the operating potential of such anodes not exceed 9.17 V (SCE) (the worst case pitting potential).

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