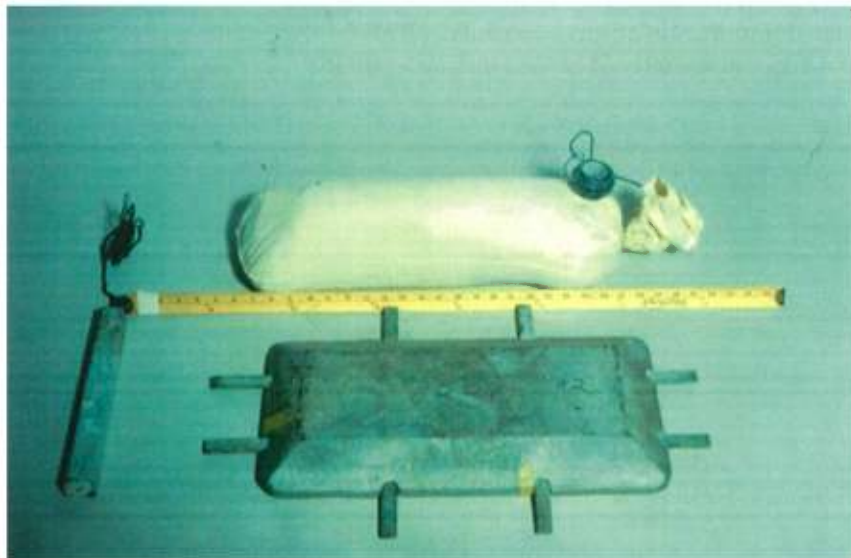


# RECLAMATION

*Managing Water in the West*

## Literature Review: Potentiodynamic Polarization Testing to Confirm the Suitability of Zinc Anodes in Natural Waters Specific to Reclamation

Research and Development Office  
Science and Technology Program  
Final Report 2014-6793IDNUMBER



By Roger Turcotte



U.S. Department of the Interior  
Bureau of Reclamation  
Research and Development Office  
Denver, Colorado

September 2014

## **Mission Statements**

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

*Photo on cover shows three styles of zinc anodes: a prepackaged anode at the top, a bare surface-mounting anode on the bottom, a bare rod anode to the left side, and a yard stick showing that each of these anodes is less than a yard long.*

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
T1. REPORT DATE Sept., 2014	T2. REPORT TYPE Research scoping		T3. DATES COVERED		
T4. TITLE AND SUBTITLE  Literature Review: Potentiodynamic Polarization Testing to Confirm the Suitability of Zinc Anodes in Natural Waters Specific to Reclamation			5a. CONTRACT NUMBER RY1541IR201416793		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 1541 (S&T)		
6. AUTHOR(S) Roger Turcotte, 303-445-2383			5d. PROJECT NUMBER 6793		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER 86-68180		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Roger Turcotte, Materials Eng. and Research Lab.			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Research and Development Office U.S. Department of the Interior, Bureau of Reclamation, PO Box 25007, Denver CO 80225-0007			10. SPONSOR/MONITOR'S ACRONYM(S) R&D: Research and Development Office BOR/USBR: Bureau of Reclamation DOI: Department of the Interior		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 6793		
12. DISTRIBUTION / AVAILABILITY STATEMENT Final report can be downloaded from Reclamation's website: <a href="https://www.usbr.gov/research/">https://www.usbr.gov/research/</a>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT ( <i>Maximum 200 words</i> ) In some fresh waters, zinc anodes can lose their ability to protect an immersed structure. The interplay of the chemical components of a fresh water is complex, so that determining by chemical analysis when zinc anodes can be used and when they will passivate is not straight forward; and field testing to ascertain passivation can take months. It is thought that potentiodynamic polarization might provide quick and simple way to test for this behavior.  In this scoping study, the literature was reviewed and contacts were made in an effort to uncover existing practices to test for passivation of zinc anodes. Information on practices involving potentiodynamic polarization was especially sought. While no one appears to be using this method for such a purpose, no indication was uncovered that the technique would not work.  Reclamation should try to develop a potentiodynamic polarization screening test of zinc anode material in fresh waters.					
15. SUBJECT TERMS Cathodic protection, galvanic anodes, sacrificial anode cathodic protection, zinc anodes					
16. SECURITY CLASSIFICATION OF: U			17. LIMITATION OF ABSTRACT  U	18. NUMBER OF PAGES  13	19a. NAME OF RESPONSIBLE PERSON Roger Turcotte
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER 303-445-2383

S Standard Form 298 (Rev. 8/98)  
P Prescribed by ANSI Std. Z39-18



# PEER REVIEW DOCUMENTATION

## Project and Document Information

Project Name: **Literature Review: Potentiodynamic Polarization Testing to Confirm the Suitability of Zinc Anodes in Natural Waters Specific to Reclamation**

WOID: X6793 Document Final Report

Document Author: Roger Turcotte Document date: 9/30/14

Peer Reviewer: William Kepler, Manager, MERL

## Review Certification

**Peer Reviewer:** I have reviewed the assigned items/sections(s) noted for the above document and believe them to be in accordance with the project requirements, standards of the profession, and Reclamation policy.

Reviewer  Date reviewed 9/20/14  
(Signature)



## **Executive Summary**

Although they develop only a small driving voltage, zinc galvanic anodes have some advantages over magnesium anodes. First, they generally don't cause cathodic disbondment of a coating even when directly mounted on the coated surface. Secondly, they are much more efficient than magnesium anodes, suffering much less autogenous corrosion. They are therefore useful when small amounts of current are needed, especially in low resistivity soil where they are buried in a sulfate rich backfill, or in sea water where chloride and sulfate levels are relatively high. Sulfates and chlorides tend to keep the zinc active.

In some fresh waters, where chloride and sulfate levels are low and deleterious components are higher, zinc anodes can passivate to less negative potentials, losing their ability to protect an immersed structure. The interplay of the chemical components in fresh water that can effect zinc passivation is complex, so that determining by chemical analysis when zinc anodes can be used and when they will passivate is not straight forward; and field testing to ascertain passivation can take months. It was thought that potentiodynamic polarization might provide quick and simple way to test for this tendency to polarize electro-positively.

In this scoping study, the literature was reviewed and corrosion experts who might have knowledge of research on zinc anode passivation were contacted in an effort to uncover existing practices to test for passivation of zinc anodes in a particular environment. Information on practices involving potentiodynamic polarization was especially sought. However, no one appears to be using this method for such a purpose. On the other hand, no indication was uncovered that the technique would not work.

As a follow-up to this study, it is suggested that Reclamation undertake development of potentiodynamic polarization testing of zinc anode material in fresh waters.





**Literature Review: Potentiodynamic Polarization Testing to Confirm the Suitability of Zinc Anodes in Natural Waters Specific to Reclamation**

# **Contents**

***Executive Summary* ..... *vii***  
***Main Report*..... *1***



## **Main Report**

Some metals when immersed in particular solutions react to form a surface film that will prevent any further significant corrosion. This mechanism, called passivation, is the method whereby stainless steels and many other alloys resist attack. While passivation is a desirable feature of engineering alloys, it is undesirable in galvanic anode materials; if galvanic anodes passivate, they can no longer protect a structure against corrosion. Hence, to prevent passivation, buried zinc galvanic anodes are surrounded by sulfate rich backfill to ensure that they stay active; however, surrounding zinc anodes with sulfates is not possible when they are used in immersion service, as the backfill would wash away. The environment itself must keep the anode active. The literature, as indicated in the following paragraphs, shows that passivation is impacted by various chemical constituents of an environment as well as by temperature.

The zinc anode material recommended for buried and fresh water applications is the ASTM B-418, Type II or high purity zinc. However, the NACE International CP-3 Manual (Cathodic Protection Technologist Course Manual) warns that waters high in such components as carbonates, bicarbonates, or nitrates can cause a noble shift in zinc potential, even at room temperature, and that higher temperatures accelerate this passivation effect.<sup>1</sup> That warning is based on earlier research, some of which will be mentioned below. As will be seen, the literature also indicates that sulfates and chlorides can help prevent passivation; however, there is little definitive information describing how much of which dissolved material is needed either to cause or to prevent passivation in natural waters.

In his 1979 Materials Performance magazine article, George Kurr refers to unpublished studies by Asarco Research indicating that when the amount of sulfates or chlorides exceeds the amount of bicarbonates, carbonates, nitrates, and phosphates, the potential of zinc will not be “seriously” affected regardless of temperature.<sup>2</sup> He follows up that statement by saying that bare zinc anodes should not be used until tests in solutions similar to the intended environment have shown compatibility. In addition, later articles cast doubt on a strict reliance on the stated balance of Kurr’s specified cations and anions. For instance, a recent paper presented at the NACE Corrosion 2010 Conference and Expo described experiments in Lake Maracaibo water in which various anode materials were tested; zinc anode materials were susceptible to passivation even though the water contained almost 1,500 ppm chloride ion, far in excess of carbonates and bicarbonates.<sup>3</sup> Other studies are also worth considering.

In a 1982 article published in Materials Performance magazine, Elwood Haney of Asarco Inc. adds borates, dichromates, tungstates, permanganate, and ferricyanates to the list of passivating anions, under certain conditions.<sup>4</sup> However, he indicates that these, along with phosphates, are less common in natural waters. He also

## Literature Review: Potentiodynamic Polarization Testing to Confirm the Suitability of Zinc Anodes in Natural Waters Specific to Reclamation

mentions that oxygen helps to ennoble the zinc, though it appears that oxygen concentration would need to be very low to keep zinc at its usual protective potential.

Haney also mentions that at least one study showed that calcium and silicates can help keep zinc anodes active.<sup>4</sup> He also found that sulfates were more effective than chlorides in keeping zinc active, though both were helpful in that respect. He indicates that increasing the concentration of inhibiting anions does not necessarily have an additive impact. Haney was able to show that the zinc electrochemical potential was adversely affected in a solution of 600 mg/L of  $\text{HCO}_3^-$  even at room temperature; thus elevated temperature is not necessary for ennoblement of the zinc, though elevated temperatures accelerate the effect.

In their "Handbook of Cathodic Corrosion Protection," von Beckmann et al. state that "the use of zinc anodes in fresh water is very limited because of their tendency to passivate."<sup>5</sup> These authors specifically warn that in waters low in salts and with low loading of the anode, less soluble basic salts such as basic zinc chloride are formed. They further indicate that waters containing phosphates can form the very insoluble  $\text{ZnNH}_4\text{PO}_4$ . However, these compounds will only precipitate in a narrow pH range around pH 7. Furthermore, weakly acidic, flowing, salt rich media can help solubilize surface films. They also state that at a temperature of 60°C, the structure of the surface film changes causing a shift to more positive potential in oxygen bearing fresh water; the result can be a potential reversal in which the rest potential of zinc becomes more positive than the potential of iron. Under such conditions, zinc would not protect, but would rather accelerate corrosion of iron or steel.

In a private communication, Frank Ansuini of EDI, Inc., supplied unpublished summary test results for zinc material his company had once contemplated using as zinc references cells in waters.<sup>6</sup> Zinc, either pure or as an anode alloy should have an uncoupled potential of -1100 mV with respects to a copper/copper sulfate reference cell. Since zinc is a solid, it should provide a rugged reference electrode if the potential is stable. The EDI test waters consisted of Parkman, Ohio well water, two surface waters, one being from Belmont, MA (MDC) and the other from Lincoln, RI (Providence Water Supply Board), and an artificial ASTM seawater mixture. The results showed that the potential of bare 99.99% zinc in the two surface waters shifted almost 300mV more cathodic (-800 mV<sub>(CSE)</sub>) in about 4 to 5 months. The same zinc material in the test well water stabilized at a potential about 125 mV more cathodic (-975 mV<sub>(CSE)</sub>) than the anticipated -1100 mV<sub>(CSE)</sub> in about 2 weeks. The pure zinc anode material in seawater stabilized at -1100 mV<sub>(CSE)</sub> in about 2 weeks. More detailed water chemistry information was not available.

In summary, therefore, the literature does not give specific guidance for determining when zinc anode material will passivate in natural waters. It only provides some general guidelines. Waters high in the more common constituent

carbonates, bicarbonates, and nitrates will tend to passivate zinc while waters high especially in sulfates, but also to some extent in chlorides, will tend to keep zinc active. However, less commonly, waters high in phosphates, borates, dichromates, tungstates, permanganate, and ferricyanates will also tend to passivate zinc, while waters high in calcium and silicates should help to keep the zinc active. Additionally, pH is sometimes essential for certain passive films to form. While not in itself causing passivation, elevated temperature can greatly accelerate the passivation process; 60°C was often mentioned in the literature as significantly accelerating the passivation process. Oxygen also helps to passivate zinc; but lowering oxygen sufficiently is not normally possible in natural waters.

As indicated above, the passivation process can occur over the course of weeks and even months. Testing by exposing zinc samples for months to determine passivation is often impractical. While the literature indicates that electrochemical methods have been used to study the general passivation behavior of zinc anodes, no indication was found that a specific screening test had been developed.

Potentiodynamic polarization is an electrochemical research method that passes current between a metal of interest and an inert electrode in a given solution to alter the electrochemical potential (V) of the test sample. The current passed and the potential held are recorded. This procedure progresses over the range of potentials of interest. Since current being passed correlates with the ongoing oxidation (corrosion) of the metal, passivation behavior, or lack thereof, of the metal can be displayed graphically; the display of a passivating situation shows up as a drastic drop in oxidation current once the potential is sufficiently noble. Since the literature does not indicate that a quick screening test employing potentiodynamic polarization has been developed, Reclamation could benefit by attempting to develop and prove out such a test in-house. That is the recommended next step in this research.

## References

1. "CP-3: Cathodic Protection Technologist Course Manual," Nace International, 2004.
2. Kurr, G.W.; "Zinc Anodes – Underground Uses for Cathodic Protection and Grounding," Materials Performance, National Association of Corrosion Engineers, April, 1979.
3. de Rincon, O.T., Salas, O., Sanchez, M., de Romero, M.F., Romero, G., Zamora, R., Palacios, C., Basile, J.C., and Suarez, J.; "Comparative Behavior of Sacrificial Anodes Based on Mg, Zn, and Al Alloys in Brackish Water," NACE Corrosion 2010 Conference and Expo, NACE International, 2010.

**Literature Review: Potentiodynamic Polarization Testing to Confirm the Suitability of Zinc Anodes in Natural Waters Specific to Reclamation**

4. Haney, E.G.; "The Zinc-Steel Potential Reversal in Cathodic Protection," Materials Performance, National Association of Corrosion Engineers, April, 1982.
5. von Baeckmann, W., Schwenk, W., and Prinz, W.; "Handbook of Cathodic Corrosion Protection," Gulf Professional Publishing, 1997.
6. Ansuini, F.; private communication.