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## **MIL-STD-889 and the Impacts on Corrosion Prevention**

**Rachel Black**

48110 SHAW ROAD, Bldg 2188  
NAS PATUXENT RIVER, MD 20670  
UNITED STATES OF AMERICA

[rachel.e.black2.civ@us.navy.mil](mailto:rachel.e.black2.civ@us.navy.mil)

**Rachel Cusic**

48110 SHAW ROAD, Bldg 2188  
NAS PATUXENT RIVER, MD 20670  
UNITED STATES OF AMERICA

[rachel.m.cusic.civ@us.navy.mil](mailto:rachel.m.cusic.civ@us.navy.mil)

### ***ABSTRACT***

*In determining galvanic compatibility, there are two components: the galvanic potential and galvanic current. Galvanic potential and galvanic current can be obtained by summing the polarization curves of the two materials and obtaining the intersection of the anodic and cathodic components.*

*While the potential can be used to show the propensity of materials to exchange electrons, the potential does not provide information about the rate the anodic material will corrode; therefore, two materials with greater difference in potential could have slow kinetics resulting in a slow corrosion reaction. Conversely, materials with little difference in potential could have a high corrosion density, and corrode rapidly when in contact.*

*Prior versions of MIL-STD-889 used galvanic potential to determine galvanic compatibility. While this provided a good first approximation of compatibility, it was not an accurate indicator of galvanic compatibility. In addition, novel materials would need to be classified in an existing category since there was no methodology for data reproduction.*

*The goal of the revision of the standard was to develop a method that utilizes the galvanic current and corrosion rate of the material pairing to determine galvanic compatibility. The new method provides clarity on data collection and processing so that any laboratory can complete the method for materials of interest.*

**Keywords:** Specialists' meeting, galvanic corrosion, conductive materials, materials protection.

## **1.0 INTRODUCTION**

### **1.1 Summary**

For over 50 years, galvanic compatibility among dissimilar conductive materials has been assessed using the difference of the conductive materials' open-circuit potentials (OCP) – the convention has been such that the closer the OCP between any two metals, the more compatible when coupled galvanically. The widespread use of this methodology stems from the ease of generating OCP data, as well as the straightforward comparison and calculation of the differences in OCP. Although at a first approximation this methodology can generally provide approximated information, the fact that it does not factor in the electrochemical kinetics of the conductive materials in a given environment means that inaccurate compatibility decisions are often made.

For instance, when using the difference in potential to assess the galvanic compatibility of a titanium alloy with an aluminium alloy versus a stainless steel alloy with an aluminium alloy, the analyst would determine that the stainless steel with the aluminium alloy would be more favourable. While according to the potential, this would appear to be true, when looking at the kinetics (I.e. galvanic current), the analyst would find that the stainless steel would cause the aluminum to corrode at a faster rate than the titanium paired with the aluminium. This is one example where a design decision based on potential would cause corrosion to occur at a faster rate than if you base the decision on the galvanic current.

Here we describe our approach to determine galvanic compatibility using the galvanic corrosion rate as the figure of merit. For a detailed methodology, refer to Appendix B of MIL-STD-889. The “best practices” methodology outlined in the standard ensures that data is generated in a repeatable and validated manner across laboratories and users. The methodology was validated using a round-robin approach among members of industry, government, and academia. The analysis of the data using a deconvolution approach is described, in which individual components of anodic and cathodic reactions are obtained. Finally, deconvoluted data was used to obtain estimated galvanic currents between metals. Using Faraday’s law, the corrosion rate for the anodic member of the couple is then determined, and thresholds are established for compatibility.

## **1.2 Background**

Galvanic corrosion is defined in NACE/ASTM-G193-20a as the “accelerated corrosion of a metal because of an electrical contact with a more noble metal or non-metallic conductor in a corrosive environment.” When two dissimilar metals are in contact in the presence of an electrolyte, electrons will flow from the active (anode) to the noble (cathode) metal in the couple. Which metal is the anode or the cathode depends on the relative position of their open circuit potentials (OCP) with respect to each other. That is, the anode will always have a lower OCP (towards the negative direction) than the cathode. In this arrangement, the oxidation reaction occurs on the anode and the reduction reaction occurs on the cathode – the oxidation reaction generally manifesting itself as metal dissolution and pitting, and the reduction reaction usually generates hydrogen or hydroxyl ions. The relative value of a metal’s OCP will depend on several conditions, such as the electrolyte composition and concentration, electrolyte film thickness, pH, temperature, and the surface condition of the metal.

For decades, galvanic compatibility during design, development, and maintenance has been determined using the difference between the OCP of any two metals to be coupled. The OCP of various metals are commonly tabulated from noble (positive potentials) to active (negative potentials). Although there is no strict threshold or value that determines which two metals are galvanically compatible, the goal is to minimize their OCP difference as much as possible (see Figure 1). For example, some Army specifications call for a galvanic difference of 100 mV or less between two dissimilar metals in order to call them compatible while Naval Aviation specifications call for a difference in OCP of 250 mV or less.

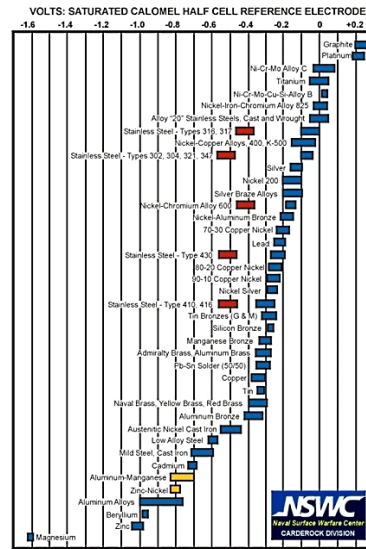


Figure 1: Galvanic series of representative metals.

Although at a first approximation this approach of minimizing the potential difference between two dissimilar metals would seem appropriate, in reality it does not guarantee that the galvanic interaction between the metals will be minimized. Since the OCP is a thermodynamic quantity, it does not offer any information about the kinetics (e.g., current, corrosion rate, etc.) of the galvanic couple. The electrochemical kinetics of a given metal are what determines the extent of the galvanic current in the galvanic couple. An illustration of a polarization curve is shown in Figure 2.

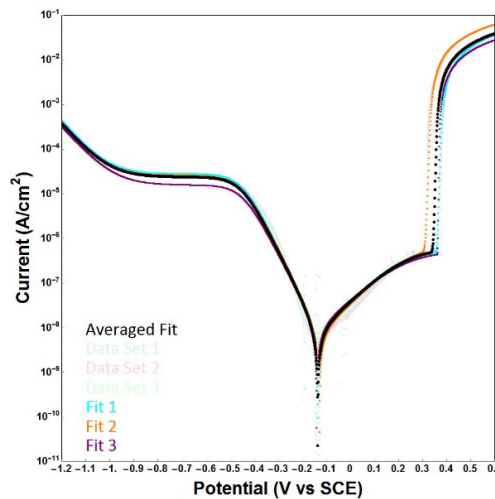
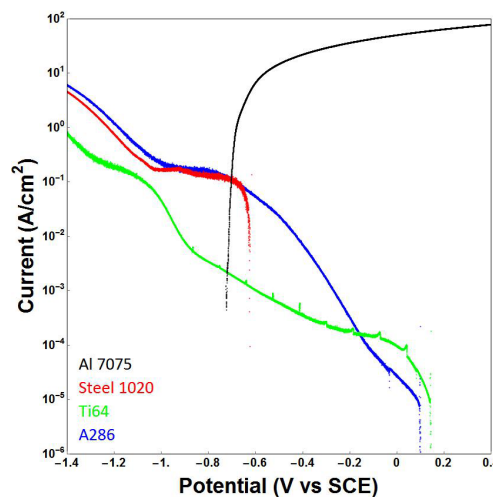


Figure 2: Potentiodynamic scans for steel 13-8Mo PH in artificial seawater.

To generate a full potentiodynamic scan, two separate scans, one in the anodic direction and one in the cathodic direction, are completed. The scans are then plotted together to form the full potentiodynamic scan. The potential where the two curves converge is called the  $E_{\text{corr}}$ , or corrosion potential, and the current where the two curves converge is called the  $i_{\text{corr}}$ , or corrosion current. To calculate the  $i_{\text{corr}}$ , the intersection point of the anodic and cathodic Tafel slopes closest to OCP are used. Using Faraday’s Law, the  $i_{\text{corr}}$  can then be used to determine the corrosion rate of the material.

In traditional mixed metal theory, the cathodic potentiodynamic scan from one material along with the anodic potentiodynamic scan from a second material are overlaid and the intersection point of the two curves is used to determine the galvanic potential and galvanic current. The galvanic current can then be used in Faraday’s law to calculate the galvanic corrosion rate of the anodic member of the couple. While this method worked well for materials where the intersection point did not occur at the OCP, for materials where the intersection point occurred at OCP, erroneous galvanic current values were calculated. To combat this, the anodic potentiodynamic scan values for each material and the cathodic potentiodynamic scan values for each material were summed to generate a galvanic potentiodynamic scan. The galvanic current and galvanic potential were then determined similarly to an individual potentiodynamic scan. More information on this can be found in the discussion section.

In Figure 3, the voltage-current (i.e., potentiodynamic scan) behavior of Al7075, A286 stainless steel, 1020 steel, and Ti6Al4V are presented.



**Figure 3: Potentiodynamic cathodic scans for steel 1020, A286, and Ti6Al4V, and anodic scan for Al7075.**

Relative to Al7075, both Ti6Al4V and A286 have more noble OCP values, whereas the OCP of 1020 steel is fairly close to the OCP value of Al7075. Notice that if we were to follow the approach of OCP values to determine galvanic compatibility, we would recommend A286 over Ti6AL4V since the latter has a higher OCP. However, if we look where each material meets with Al7075 – which would give their galvanic current interaction – Ti6Al4V gives approximately three orders of magnitude lower galvanic current than A286. That is, if we were to couple Ti6Al4V to Al7075, the latter would corrode at a rate one thousand times less than if it were coupled to A286. Conversely, we would recommend coupling 1020 steel to Al7075 since their OCP difference is small. Nonetheless, 1020 steel gives the same galvanic current as A286 even though they are separated by almost 0.7 V. Thus, Figure 3 is a clear illustration of the disadvantages of using galvanic potential to determine galvanic compatibility.

As illustrated above, the metric for determining galvanic compatibility should be galvanic current. In order to change this method, accurate and validated data is required, as well as a proper data analysis methodology.

## 1.2 Purpose

The technical revision of MIL-STD-889 shifted the methodology for assessing galvanic compatibility from a galvanic potential driven approach to a galvanic current driven approach. The revision also provides a method that utilizes galvanic current and corrosion rate to determine galvanic compatibility of any two conductive materials. The revision provides guidance on the data processing and mixed metal theory, which assists in comprehending the data. The report provides additional background and information on the revision, illustrates the reasoning behind this change, and the impacts of this change moving forward.

## 2.0 DISCUSSION

### 2.1 Data Acquisition

MIL-STD-889 was initially released in 1969 to define and classify dissimilar metals and provide requirements for protecting incompatible materials. The first technical revision was conducted in 1976 and included the galvanic series based on Army Missile Command Report RS-TR-67-11, “Practical Galvanic Series.” While this revision incorporated an improved understanding of galvanic corrosion, there were three main downsides to the standard. (1) The standard did not accurately reflect the kinetics involved in the galvanic interaction between two materials. (2) Materials were grouped together based on their main alloying element, which does not provide insight into compatibility between different alloys. (3) There was no method for reproducing the data and existing methods for generating polarization curves were too vague to generate reproducible data. Because of these reasons, a technical revision based on both potential and kinetics was sought after. To prepare for the technical revision, a modernization of the standard was completed in 2016, which updated the terminology and references.

Prior to collecting polarization data, a reproducible method was required. This was to ensure that data collected using the standard could be accurately compared regardless of where the data was collected. As such, the “Best Practices for Polarization Data Acquisition: Data Collection Guide for MIL-STD-889 Technical Revision” was written. This document, which is provided in Appendix B of MIL-STD-889, the method section of this report, and modified for AMPP- TM21510, underwent testing with partners from six facilities. At the conclusion of the testing, the data was analyzed using ASTM E691. Figure 4 shows the summary of the round robin testing.

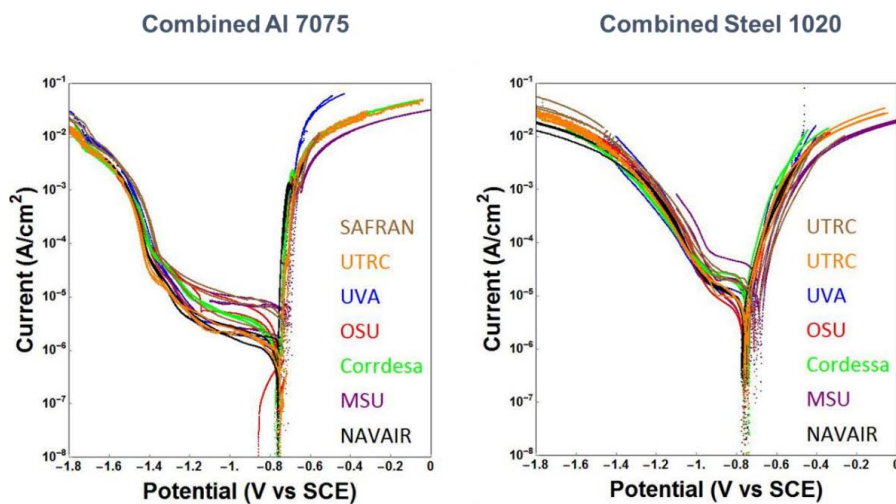


Figure 4: Summary of round robin test data.

Within this dataset, two laboratories were identified as outliers. After consulting with those laboratories, it was determined that there was a slight deviation from the best practices document. All other laboratories followed the procedure and generated data within statistical acceptability of the average dataset. This deviation illustrates how a lack of specificity in the procedure leads to inaccurate data and how following the methodology ensures the appropriate precautions are taken for maximum data reproducibility.

In addition to the experimental procedure, the Best Practices document states for each material, three anodic and three cathodic scans shall be completed. The data is collected in triplicate due to the slightly variable results caused from the differences in the material surfaces. In addition, each set of potentiodynamic data (a paired cathodic and anodic potentiodynamic scan) shall be deconvoluted by three analysts. After an outlier analysis is performed, the average of the remaining potentiodynamic scans are completed.

The methodology can be found in Appendix B of MIL-STD-889.

## **2.1 Data Analysis**

An integral component in the reproducibility of MIL-STD-889 results is the analysis and production of an average of each triplicated dataset. The procedure to produce this result in a natural and representative way is non-trivial and will thus be addressed below.

### **2.1.1 Averaging and Deconvolution**

Crucial to any data analysis process is appropriate post-processing of the input. Of particular concern when dealing with polarization curves is the generation of full polarization curves from separate anodic and cathodic scans. The inherent sensitivity of electrochemistry to sample preparation and environmental conditions makes the selection of anodic and cathodic pairs non-trivial. Fortunately, open circuit potential (OCP) is a clear and consistent indicator of reproducibility in electrochemical experiments. As no voltage has been applied to the system at OCP, the material has not been perturbed from its resting electrochemical state. It is the only in situ point of comparison between anodic and cathodic scans. Ensuring agreement between OCPs is essential to ensuring the anodic and cathodic portions represent the same material and environmental conditions. A significant difference in these conditions can have wide ranging (though diminishing) impacts across the entirety of the anodic or cathodic curve. Allow a tolerance of (+/- 50 mV) in OCP between curves and produce additional samples if there is insufficient agreement between your data.

Once individual polarization curves are produced from the raw data. The results of the repeated experiments for each material must be naturally averaged. This process is fraught with pitfalls. Polarization curves have regions which change drastically in both current and potential across different regions, discrediting common averaging techniques.

Averaging of current across potential is not effective, as experiments are often offset from one another by unique starting OCPs. This leads to a significant mismatch in those regions of the polarization curve which shift with OCP. Similar arguments can be made for the inverse case. While there are many ways that this can be performed, two methods will be described here, averaging across the implicit time component and deconvolution.

The first technique to naturally averaging polarization curves is by averaging across the implicit time component of polarization curves. Polarization curves vary potential at a constant rate over time. Thus averaging with respect to distance from OCP matches data over time implicitly. When this is combined with an average of the initial OCP values an averaged polarization curve is generated. While theoretically sound, this method has practical limitations. While some reactions shift with OCP, others do not. This leads to comparable mismatches to the above methodology. This method also limits the scope of viable averaged results to the smallest dataset collected.

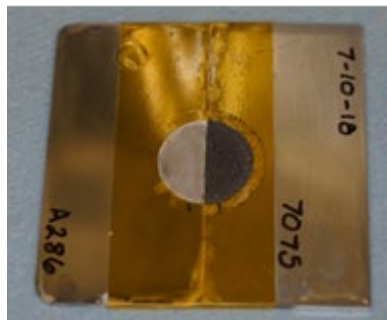
The second methodology is deconvolution, which is a more robust and naturalistic average and the methodology used in MIL-STD-889. It relies on fundamental properties of polarization curves. Each polarization curve is a simple summation of the individual current contributions of each electrochemical reaction at a given potential. These reactions defer in their constituents, but they fall into limited classes of exponential functions. These functions (and their numerical approximations) are defined in “An Iterative Method for Fitting Complex Electrode Polarization Curves” by K.S. Yeum and O.F. Devereux, *Corrosion*, Vol. 45, pp. 478-487 (1989).<sup>1</sup>

Common to all these functions is a term which define the slope of current by potential for each reaction and a current intercept point. Combined, these constants fix the position of each electrochemical reaction in place. More complicated reactions have terms that define a maximum current limit on the reaction due to diffusion limitations, surface passivation, or other restricting values. This allows individual reactions to hold a constant current after reaching the limiting potential, which is observed in experimental observations.

The deconvolution process consists of choosing a number of functions which match the position, slope, and current limits found in each polarization curve and summing them to form a full polarization curve. To test the effectiveness of these functions when compared to the polarization curve, a minimization function is used. The features are then visually checked to see if they match experimental results. Once the fitting function has been minimized across all experimental results for a material, the constants across these common functions are averaged and used to fit the experiments. This allows the slope, current limits, and potential at which these reactions start to naturally be aggregated across the different results.

### 2.1.2 Mixed Potential Theory

In traditional mixed potential theory, the intersection point of two potentiodynamic curves is determined to be when the galvanic current and the galvanic potential in a 1:1 anode to cathode ratio. This method was originally developed by Wagner and Traud and also states that the rate of the faradaic process is independent of other simultaneously occurring faradaic processes at the electrode.<sup>2</sup> To verify this method, we collected potentiodynamic data on A17075 and A286, then overlaid the polarization curves and determined the intersection point. We also collected potentiodynamic data on a sample where the materials of interest were joined and masked in a 1:1 anode to cathode ratio. An example of the sample is shown in Figure 5.



**Figure 5: Example of one of the joined samples.**

The final verification was a galvanic test using a zero resistance ammeter (ZRA) test.

As shown in Figure 6, the intersection point of the individual polarization curves is almost identical to the intersection point of the joint sample and the results of the ZRA, providing verification that using mixed potential theory is a valid approach; however, upon collection and analysis of more data, there were some instances of inconsistent findings.

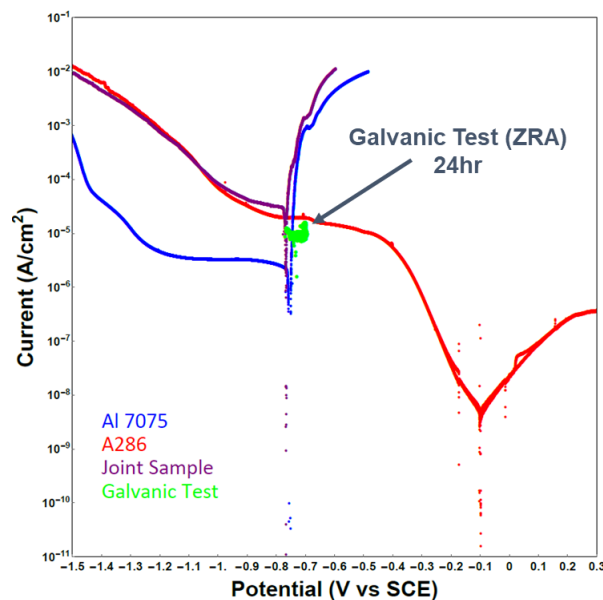


Figure 6: Galvanic potentiodynamic scan, zero resistance ammeter test, and individual material potentiodynamic scan overlaid on a single plot.

While Figure 6 details an example where mixed potential theory works well, we found this method only produced accurate results in instances where the intersection point of the two materials did not occur on the steep slope around OCP. For materials where the intersection point occurred on the steep slope around OCP, mixed potential theory tends to produce values for the galvanic corrosion current that are artificially high or low.

### 2.1.3 Mixed Potential Theory: Summation Method

To find a solution to this, we revisited mixed potential theory as outlined by Wagner and Traud. Their study indicated that the reactions are only dependent on the electrode potential and thus the polarization curves for independent cathodic and anodic processes can be added to predict the overall rates and potentials.<sup>2</sup> As such, rather than determining the intersection point of two materials polarization curves, the entirety of the potentiodynamic data could be summed and the galvanic current and galvanic potential could be determined using the same methodology used to determine the  $i_{CORR}$  and  $E_{CORR}$  of an individual polarization curve.

To verify this method, we collected potentiodynamic data on material pairings where the intersection occurred on the steep slope near OCP and materials where the intersection did not occur on the steep slope near OCP. By doing this, we could ensure that the erroneous data could be improved while not changing data on materials with correct information. Figure 7 and Figure 8 are an example of the testing that was completed.



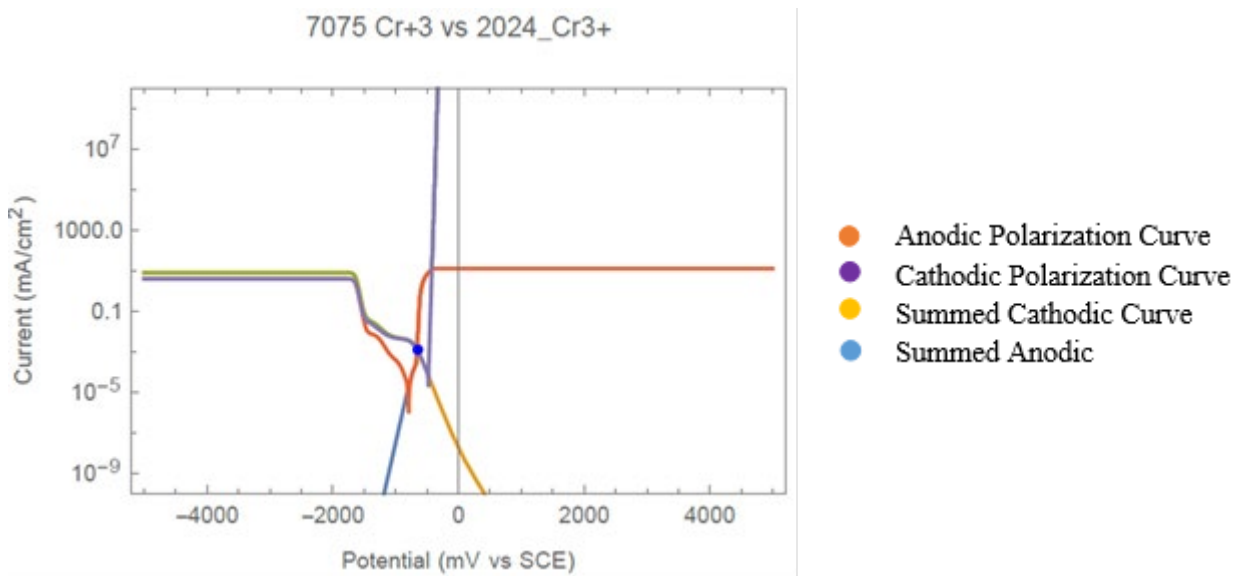


Figure 7: Validation of summation method of two materials with further OCPs.

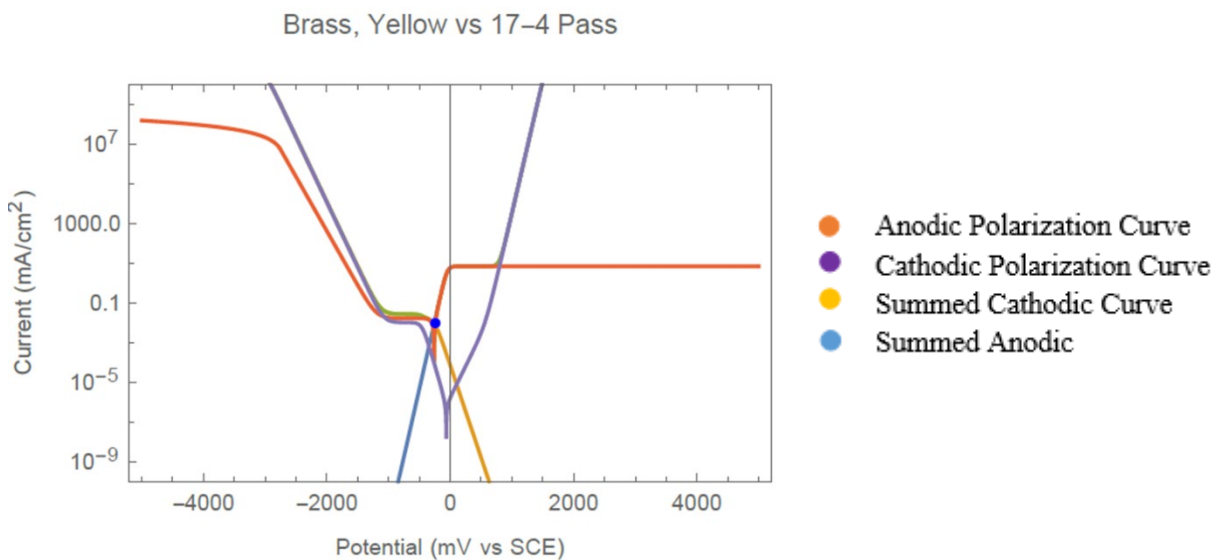


Figure 8: Validation of summation method utilizing materials with OCPs near one another.

After the method was validated, all the data was reanalyzed utilizing the summation method. The galvanic current for various pairings were checked for accuracy. This included comparing galvanic currents for materials that have OCP's that both intersect away from and on the steep slope at OCP. The results of the summation method improved the data for materials that intersect around OCP while maintaining the integrity of the data of materials that intersect away from OCP.

### 2.1.3 Generation of Compatibility Tables

After finalizing a method for the data analysis, the compatibility tables were generated. Initially, the  $i_{corr}$  for commercially pure aluminum was used to determine a starting threshold for compatibility. The corrosion current by which commercially pure aluminum corrodes at was experimentally determined to be 0.1

mil/year, which is roughly  $1 \times 10^{-10}$  mA/cm<sup>2</sup>. While this was an initial estimate, the corrosion current compatibility threshold that commercially pure aluminum corrodes needed to apply to other materials as well. To do this, galvanic compatibility thresholds were analyzed in half magnitude (power of 10) steps. This was completed to understand where the galvanic compatibility becomes non-linear indicating the least amount of change in galvanic compatibility among the material set. We determined that threshold to be  $1 \times 10^{-11}$  mA/cm<sup>2</sup>.

In practicality, galvanic current is not able to be easily applied in aircraft design; however, the corrosion rate is. Eqn (1) was used to calculate the galvanic corrosion rate (CR) of the anodic member of the couple.

$$CR = 1.2415 \times 10^{12} \left( \frac{iM\rho}{zF} \right) \quad (1)$$

where CR represents corrosion rate (mil/yr), *i* represents current density (A/m<sup>2</sup>), *M* is molar mass (kg/mol),  $\rho$  is density, *z* is the valence of the electron, and *F* is Faraday's constant (C/mol). The constant in front of the equation is to convert from m/s to mil/yr

The following assumptions were made:

- 1) The valence of the main element represent the valence of the material.
- 2) If there was no density for a specific alloy, the density of the primary element was used. kg/m<sup>3</sup>.

This equation is a modification on Faraday's law. ASTM G102 can also be used to determine the corrosion rate from the current density.

By converting the compatibility tables from galvanic corrosion currents to galvanic corrosion rate, the information in the table can directly be used to make design decisions.

A disadvantage of the compatibility table in MIL-STD-889C was that the table only told the Cognizant Engineering Authority if the galvanic pairing was compatible or incompatible. The table did not provide information on the level of incompatibility, which is important in design decisions. As such, materials determined to be incompatible were grouped based on the rate of corrosion. The groups were created starting at 0.01 mil/year and progressed in power of 10 intervals, with an additional group between 1 to 10 mil/year. This additional group was created based on the number of pairing within this range and the desire for an increased awareness within this range.

### **2.3 Path Forward**

While the new version of the MIL standard became active upon release, it can take time for users to implement the standard in their systems. This is because legacy systems are not required to use the newest versions of the standards as they are released. To minimize future corrosion concerns, it is strongly recommended that legacy platforms implement MIL-STD-889D for repair and maintenance. In addition, due to the specificity of the data within MIL-STD-889, it is unlikely that every material of interest can be captured in the compatibility table. While the purpose of Appendix B is to provide those interested in other materials the procedure for collecting those materials, efforts to make additional data available is desired.

In addition, there is interest for data to be collected in various environments such as a thin film environment. Additional research into methods for accurate and consistent data collection must be completed prior to inclusion of this data in MIL-STD-889.

### **3.0 CONCLUSION**

While using galvanic potential alone is a sufficient first approximation for galvanic compatibility, the possibility for inaccurately assessing incompatible materials decisions is still possible. Potentiodynamic scans provide information on both the potential ( $E_{\text{corr}}$ ) and the kinetics ( $i_{\text{corr}}$ ) of the material. The  $E_{\text{corr}}$  and  $i_{\text{corr}}$  give a comprehensive, electrochemical assessment of the material, enabling informed material compatibility decisions.

As a result of shifting the determination of galvanic compatibility from electrochemical potential to the galvanic corrosion rate, greater resolution into how incompatible two materials are can be communicated to the Cognizant Engineering Authority. This information will allow the cognizant engineering authority to make material selection and finishing specifications decisions based on the corrosion rate allowable in a specific application. Additionally, the newly developed method for generating polarization curves will allow for various laboratories to generate polarization data, further broadening the usability of MIL-STD-889.

### **4.0 REFERENCES**

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