

LA-UR-17-21185 (Accepted Manuscript)

The Corrosion Behavior of Technetium Metal Exposed to Aqueous Sulfate and Chloride Solutions

Kolman, David Gary
Goff, George Scott
Cisneros, Michael Ruben
Boland, Kevin Sean
Jarvinen, Gordon
Poineau, Frederic
Czerwinski, Kenneth

Provided by the author(s) and the Los Alamos National Laboratory (2017-08-01).

To be published in: Journal of The Electrochemical Society

DOI to publisher's version: 10.1149/2.1561706jes

Permalink to record: <http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-17-21185>

Disclaimer:

Approved for public release. Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

The Corrosion Behavior of Technetium Metal Exposed to Aqueous Sulfate and Chloride Solutions

David G. Kolman¹, George Goff¹, Michael Cisneros¹, Kevin Boland¹, Gordon Jarvinen¹,
Frederic Poineau², Ken Czerwinski²

1 - Los Alamos National Laboratory
Los Alamos, NM 87544

2- University of Nevada Las Vegas
4505 S. Maryland Pkwy.
Las Vegas, NV 89154

Abstract

Metal waste forms are being studied as possible disposal forms for technetium and other fission products from spent nuclear fuel. As an initial step in assessing the viability of waste forms, technetium corrosion and passivity behavior was assessed across a broad pH spectrum (pH -1 to pH 13). Measurements indicate that the open circuit potential falls into the region of Tc^{+7} stability, more noble than the region of presumed passivity. Potentiodynamic polarization tests indicate that the Tc samples are not passive. Both electrochemical results and visual inspection suggest the presence of a nonprotective film. The corrosion rate is relatively independent of pH and low, as measured by linear polarization resistance. No evidence of passivity was observed in the Tc^{+4} region of the potential-pH diagram following in-situ abrasion, suggesting that Tc does not passivate, regardless of potential.

Introduction

Potential waste forms from proposed spent nuclear fuel reprocessing strategies are being developed in the U.S. Department of Energy Fuel Cycle Research and Development Program. Technetium is a fission product of particular concern for repository disposal because of its high fission yield, long half-life (2.1×10^5 years), and high solubility and mobility in groundwater as pertechnetate. Proposed flow sheets for metal waste forms involve the separation of technetium from other components in the spent fuel followed by alloying of technetium with other elements to be disposed in a repository. The alloying of technetium is desirable to reduce the melting point of the technetium waste form and potentially improve its corrosion resistance.

In recent years, a variety of studies have been performed on various technetium alloy waste forms.^{1,2,3} Alloy waste forms have involved alloying technetium with Zircaloy and / or stainless steel components^{4,5,6}. Alloying has been successful in producing lower-melting materials; however the alloy products are composed of multiple phases having complex microstructures. Because the technetium release from these alloys is dominated by the least corrosion-resistant phase, understanding the corrosion response of these alloys involves the interplay of the metallurgy and corrosion behavior of the component phases. As an initial step, the corrosion and passivity of pure Tc must be understood.

There has been limited research regarding the electrochemical response of pure technetium metal. Published potential pH - diagrams for Tc - water systems suggest that Tc is an active metal with a narrow region of presumed passivity.^{7,8,9,10} Technetium is presumed passive in the Tc^{+4} state as TcO_2 . At more noble potentials, Tc is presumed to actively corrode in the Tc^{+7} state as pertechnetate. Cartledge examined the corrosion behavior of technetium exposed to 1 N H_2SO_4 .¹¹ It was concluded that the presence of hydrogen in solution in the metal inhibited passivity. A black film, surmised to be hydrous $Tc(OH)_4$, was observed. Spitsyn also found that Tc was not passive in strong acid.¹² More recently, Ferrier et al. examined the dissolution behavior of Tc metal exposed to strong HNO_3 and HCl .¹³ They found that chemical dissolution rates were higher in HNO_3 but that the electrochemical reactions rates were similar. There was no apparent presence of TcO_2 . The formation of TcO_2 from first principles has also been studied.¹⁴ Johnson et al. examined the release rate of Tc from a complex alloy containing small amounts of Tc and found that the Tc release rate was low.¹⁵ Spitsyn found that exposure of technetium metal to seawater resulted in minimal Tc corrosion and no biofouling.¹⁶

There is somewhat more work in the literature regarding the electrochemistry of Tc in solution, including the effect of TcO_4^- ions on corrosion of iron. Much the electrochemistry focusses on the Tc^{+4} to Tc^{+7} transition.^{8,9,17,18} There is some discrepancy regarding the potential for the transition due to the sluggishness of the reaction.^{8,17} Cartledge found that TcO_4^- ions were inhibitive for steels.^{19,20,21,22} It was hypothesized that competitive adsorption of TcO_4^- plays a role in the inhibition.

There are no published studies of technetium metal corrosion in solutions other than strong acids. Because technetium waste forms may potentially be exposed to some type of groundwater, the corrosion behavior of technetium exposed to aqueous solutions of more neutral pH is of interest. Moreover, although the lack of passivity has been observed, no investigations of passive film formation have been performed. The goal of this study is to examine the electrochemical behavior of technetium across a wide range of pH in order to determine corrosion and film formation mechanisms.

Experimental Procedure

⁹⁹Tc is a β -emitter. Therefore, all tests were performed within the confines of a radioactive material hood at Los Alamos National Laboratory.

Technetium metal was produced by thermal decomposition of ammonium pertechnetate to TcO_2 (450°C, 1 hr, Ar) followed by reduction of the TcO_2 to Tc (700°C (24 h) - 900°C (4 h), Ar - 5% H_2). Chemical analysis (ICP-MS) of the Tc metal indicated that the Tc metal did not contain an appreciable amount of impurities (< 10 ppm).

Specimens were mounted in epoxy and polished to a 500 grit finish with SiC paper. The polished samples were ultrasonically cleaned in ethanol for five minutes. Crevice corrosion between the metal and the epoxy mount was not apparent following testing. The exposed metal surface area varied between 0.027 and 0.14 cm^2 depending on the individual sample.

Solutions were composed of reagent-grade chemicals and distilled, deionized, 18 M Ω water. Acidic solutions were composed of sulfuric acid, neutral solutions were composed of borate buffer (0.033M $\text{Na}_2\text{B}_4\text{O}_7$ plus 0.30M H_3BO_3) and alkaline solutions were composed of sodium hydroxide. Na_2SO_4 solutions were composed of 0.3mM Na_2SO_4 pH adjusted with H_2SO_4 . Approximately 50 ml of solution was used for each test. Solutions were room temperature—self-heating of the technetium (< 0.3 g) from radioactive decay was considered negligible. Solutions were not actively aerated nor deaerated. A commercially available, computer-controlled potentiostat and frequency response analyzer were used to perform the electrochemical measurements. The electrochemical cell was a 100-mL, five-neck flask incorporating a saturated Ag / AgCl reference electrode and a platinized-niobium mesh counter electrode. Data are plotted vs. NHE. For concentrated acid solutions (> 0.1M), solution pH was calculated considering the effect of activity coefficients. For all other solutions, the stated pH is a measured pH.

Prior to polarization, working electrodes were immersed in solution for four hours and the open circuit potential (OCP) monitored. Potentiodynamic polarization tests used a scan rate of 0.1 mV/s. Scans were performed from 30 mV cathodic of open circuit for anodic polarization and 30 mV anodic of open circuit for cathodic polarization tests. Linear polarization resistance was acquired from the open circuit region of the polarization scans (~ -30 mV to +30 mV). Impedance data fitting was performed with complex nonlinear least squares circuit fitting software. Open circuit and potentiodynamic polarization tests were replicated at least twice to assess the reproducibility of the results, with as many as 9 replicate tests performed.

Individual impedance spectra were acquired every 100 mV with a potentiodynamic ramp (0.1 mV/s) and 4 h hold preceding each test. A 10-mV rms AC voltage signal was applied at frequencies between 100 kHz and 10 mHz using potentiostatic control.

Results and Discussion

The regions of corrosion or passivity in potential - pH diagrams are inferred from the solubility of the predominant corrosion reaction products. In the case of technetium, the stable oxidation states for all but a narrow acidic region are +4 (TcO_2) and +7 (TcO_4^-). The region of TcO_2 stability is presumed to be a passive region based upon TcO_2 solubility.⁷

The thermodynamic values used as inputs to the Tc potential - pH diagrams are not as well established as most other elements. A thorough examination of the known data¹⁷ concluded that the data of Cartledge were likely the most accurate. These are the thermodynamic data referenced here. Discrepancies in thermodynamic data values arise from the potential drift and general sluggishness of the reaction⁸ and great care is necessary to obtain accurate data.

Open circuit potential (OCP) traces (not shown) show that technetium generally approaches steady state at 4 h. Longer duration open circuit measurements have shown little change in the open circuit potential beyond 4 h. For instance, the open circuit potential of Tc exposed to pH 3.2 H₂SO₄ was found to be 0.406V_{NHE} at 4 hours and 0.379V_{NHE} at 91 hours. The difference between these two values is within the scatter of the 4 h measurements. Therefore, a 4 h stabilization period was used to assess the OCP prior to polarization tests.

The 4-h open circuit potential measurements for Tc exposed to solutions of various pH are shown in Figure 1. The OCP values are superimposed on the potential - pH diagram. Regardless of pH, OCP values fall near or above the Tc⁺⁴ to Tc⁺⁷ transition. Even though OCPs are generally stable at four hours, there is significant scatter in the OCP data. Regression of the open circuit potential data indicates that open circuit potential should fall into the +7 region for essentially any solution - only solutions of pH less than -0.8 would be predicted spontaneously corrode in the +4 region. The measured OCP values are consistent with those found by Ferrier et al.¹³

Above the Tc⁺⁴ to Tc⁺⁷ transition, Tc is not predicted to spontaneously passivate and previous work^{12,13} has failed to observe Tc passivity. Regardless of environment, Tc does not appear to spontaneously passivate based on the representative anodic polarization data of Figure 2. Given that the OCP lies above the Tc⁺⁴ to Tc⁺⁷ transition, passivity would not be predicted, so these tests alone cannot reach a conclusion as to whether Tc might passivate in the +4 region.

A thick black film was observed on surfaces following polarization. The film was not very adherent and could be wiped away easily. Attempts to analyze the film composition and structure using diffraction and Raman spectroscopy were unsuccessful.

Anodic Tafel slopes acquired from polarization curve fitting are plotted as a function of pH in Figure 3. The significant variability between tests (and the large values to a lesser extent) suggests that anodic dissolution is not controlled by Tafel kinetics. The lack of passivity, thick surface film and anodic Tafel slope variability suggest that the dissolution of Tc metal is anodically mass transport controlled. The large variability does not appear to be an experimental artifact given that replicate cathodic tests (not shown) do not reveal the wide variability observed upon anodic polarization.

Linear polarization resistance measurements as a function of pH are shown in Figure 4. Polarization data were acquired from the linear region of the polarization curves around open circuit. Although there is some scatter, the polarization resistance appears to be largely invariant with pH. An invariant corrosion current density is consistent with that shown by Ferrier¹³ et al over the -0.5 to 2.5 pH range. Over this pH range, it appears that corrosion is oxygen reduction rate limited so an invariant corrosion rate would be expected. The polarization resistance is

relatively high ($\sim 100\text{k}\Omega\text{-cm}^2$), therefore the corrosion rate is relatively small. Even though polarization resistance is invariant with pH, Ferrier et al did show a significant increase in corrosion current in more concentrated acids than those used here (6M HNO_3). In our laboratory, a test exposing Tc to 3M HNO_3 resulted in a polarization resistance of $11\Omega\text{-cm}^2$, approximately 4 orders of magnitude less than that in H_2SO_4 . Therefore, nitrate appears to be far more aggressive than sulfate at low pH.

Electrochemical impedance spectroscopy (EIS) was used to probe the surface of Tc exposed to various solutions. Spectra for Tc exposed to borate buffer are shown in Figure 5. Open circuit for the test was $0.33V_{\text{NHE}}$ so the three spectra were taken 30 mV below, 70 mV above and 170 mV above OCP. The spectra acquired closest to open circuit revealed the presence of two time constants. Polarization away from OCP resulted in a change to the spectrum - one time constant appears at high frequency with the appearance of inductive looping at low frequency. The appearance of two time constants is consistent with the presence of the surface film. The appearance of two time constants near open circuit is not always present in every solution, however inductive looping is always observed at potentials well above open circuit (Figure 6). Cartledge observed TcO_4^- ion inhibition of steel²¹ which was attributed to weak, reversible adsorption of TcO_4^- on the steel surface. It is unclear whether the observed inductive looping at low frequency here is attributable to adsorption of TcO_4^- but the spectra appear consistent with an adsorbed-intermediate impedance response.^{23,24}

At the most noble open circuit potentials ($\text{pH} < 1$), the cathodic reaction appears to be limited by oxygen reduction (Figure 7) given the limiting current observed. Approximately 250 mV below open circuit a second cathodic reaction is observed. This second reaction is likely attributable to one of the many sulfur compound reduction reactions.⁷ The cathodic reaction on Tc exposed to $\text{pH} 3.2 \text{H}_2\text{SO}_4$ appears to be dominated by the same reaction as the more acidic solutions, judging by the similar cathodic Tafel slope.

It was unclear whether Tc could passivate in the +4 region because the mixed potential placed the potential in the +7 region, regardless of pH. In order to investigate whether Tc might passivate in the +4 region, in-situ abrasion tests were performed. The sample was potentiostated in the immune region ($-0.3V_{\text{NHE}}$) while exposed to $\text{pH} 3.2 \text{H}_2\text{SO}_4$ and abraded in-situ under potentiostatic control. Abrasion involved the use of SiC paper affixed to the end of a laboratory scoopula. Immediately following abrasion, anodic polarization was initiated. A comparison of the polarization data following abrasion to conventionally-acquired data (Figure 8) indicates little difference other than a slightly higher current. The higher current is likely attributable to the removal of the air formed film as well as the lack of a 4 h OCP where a film might grow. Most notably, there is no change in the polarization curve when the 0 to +4 transition is crossed. Although inferential, this suggests that a passive film does not form in the +4 region.

The impedance response following in-situ abrasion is shown in Figure 9. In this test, the sample was abraded in situ in the immune region while exposed to $\text{pH} 3.2 \text{H}_2\text{SO}_4$, held potentiostatically for 4 h, and EIS performed. The sample was then potentiodynamically ramped 100 mV more electropositive, held for 4 h, and EIS performed. The sequence was repeated

through the immune and +4 regions into the +7 region. The potentials used for the three tests shown, $-0.193 V_{\text{NHE}}$, $+0.107 V_{\text{NHE}}$ and $+0.407 V_{\text{NHE}}$ correlate the regions of immunity (Tc), passivity (Tc^{+4}) and transpassivity (Tc^{+7}) respectively. All three of the tests shown reveal similar one time constant behavior. Moreover, no obvious breaks in the impedance fit parameters are observed at the electrochemical transitions (Figure 10). This suggests that no significant changes to the surface occur upon polarization.

Given the disparity in some of the published thermodynamic data and the lack of observed passivity, an experimental check of the 0 to +4 transition was performed. Samples were held potentiostatically in pH 3.2 H_2SO_4 , and serially abraded using in the manner described above. The potential was then stepped 100 mV and serially abraded. The process was repeated over a 1V range. The results are shown in Figure 11. Tests below $0.1V_{\text{NHE}}$ reveal cathodic current spikes upon abrasion. Therefore, at these potentials, the Tc does not appear to oxidize. At $0.107 V_{\text{NHE}}$, the current is cathodic until the surface is abraded. Following abrasion, small anodic spikes are seen. Results indicate that the 0 to +4 transition occurs between $0.007 V_{\text{NHE}}$ and $0.107 V_{\text{NHE}}$ which agrees with the published data.

Conclusions

The polarization and impedance response of pure Tc metal exposed solutions of various pH was measured. The open circuit potential of Tc metal was found to generally reside in the +7 region of the potential - pH diagram. Technetium was found to actively dissolve upon anodic polarization although corrosion rates were found to be low. The corrosion rate was also found to be largely invariant with pH in sulfate solutions. Variable anodic Tafel constants, multiple time constants in the impedance spectrum and the presence of a black film suggest that Tc dissolution is anodically mass transport controlled. No evidence of passivity was observed in the +4 region of the potential - pH diagram following in-situ abrasion. Results from this study may be used as an input for release rate modelling of waste forms exposed to groundwater of similar pH. The results also provide a basis for understanding the corrosion behavior of more complex waste forms containing Tc.

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under Contract DE-AC02-06CH11357. Funding for this research was provided by an NEUP grant from the U.S. Department of Energy, Office of Nuclear Energy, through INL/BEA, LLC, 00129169, agreement No. DE-AC07-05ID14517.

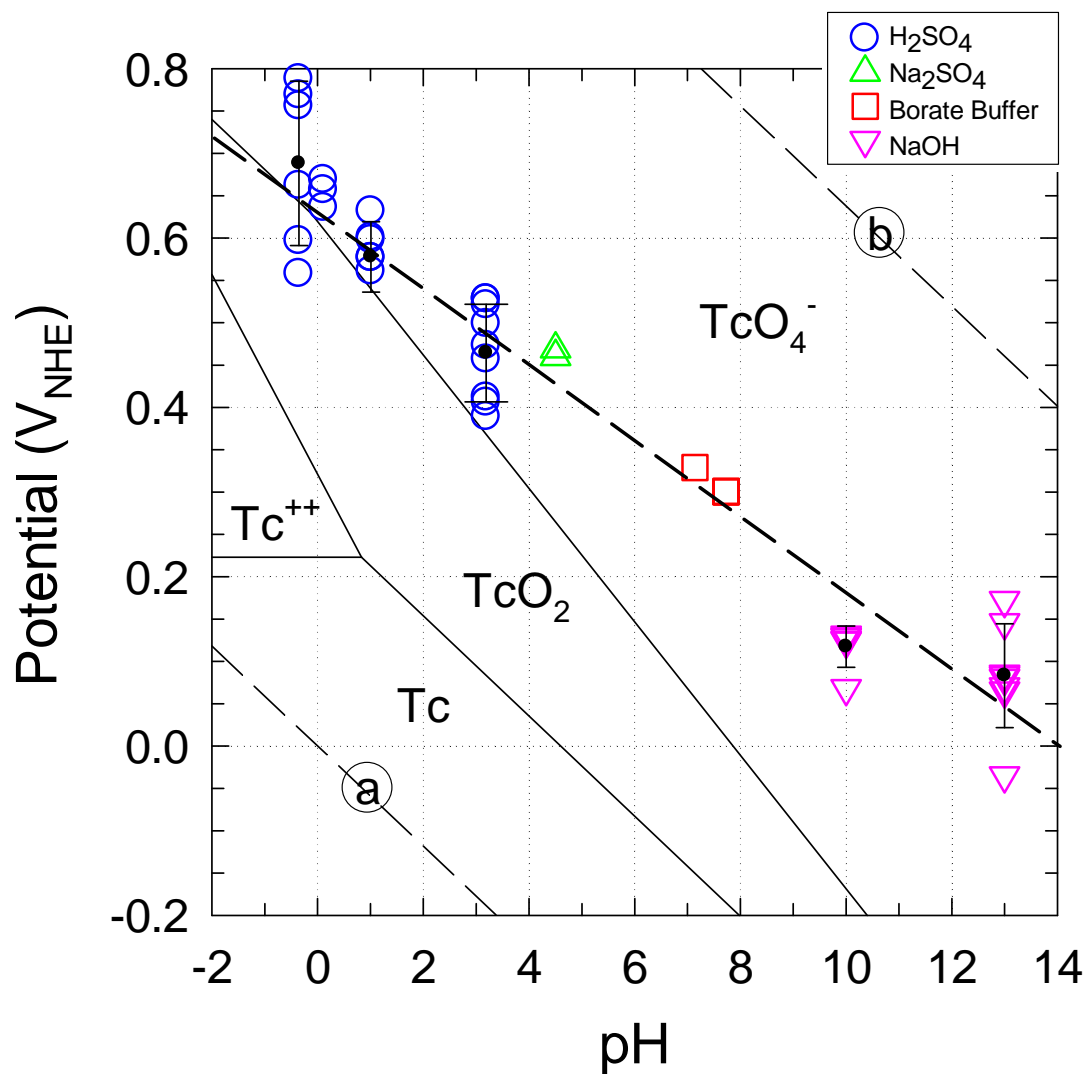


Figure 1. Replicate open circuit values (following 4h of immersion) superimposed on the potential - pH diagram ($[\text{Tc}] = 10^{-6} \text{ M}$).⁸ Means and standard deviations are shown for replicate tests where more than 3 replicate tests were performed. The heavy dashed line is a linear regression of the open circuit values. a and b are the hydrogen and oxygen evolution lines, respectively.

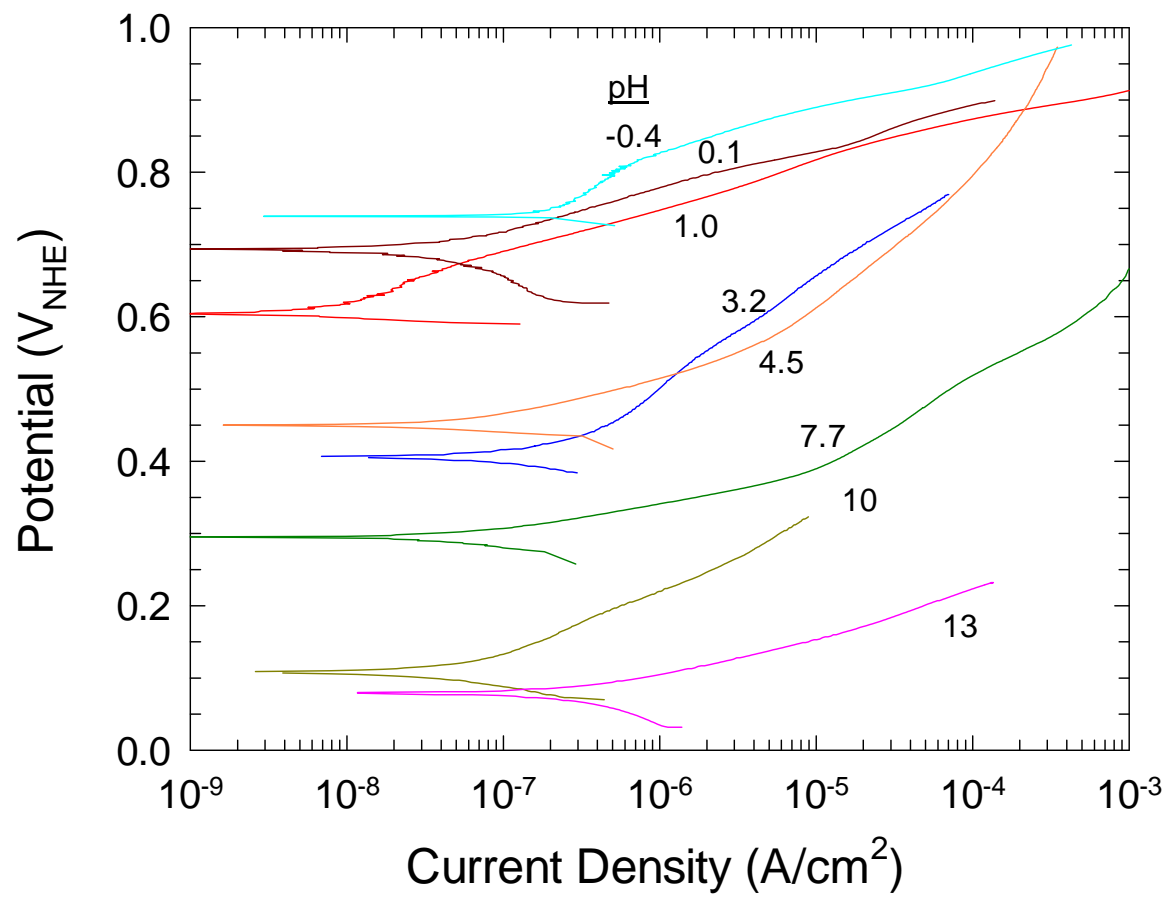


Figure 2. Representative potentiodynamic polarization curves for Tc exposed to solutions of various pH.

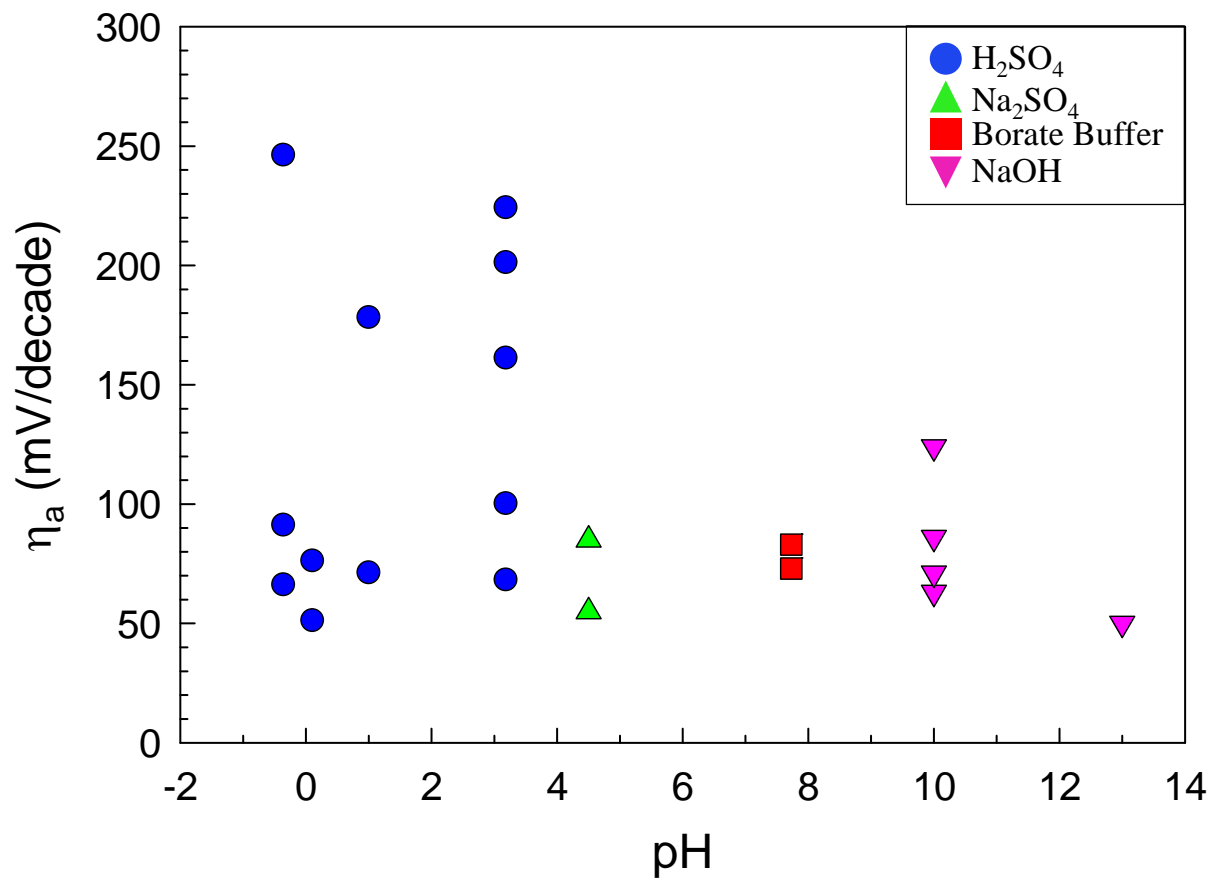


Figure 3. Anodic Tafel slopes as a function of pH.

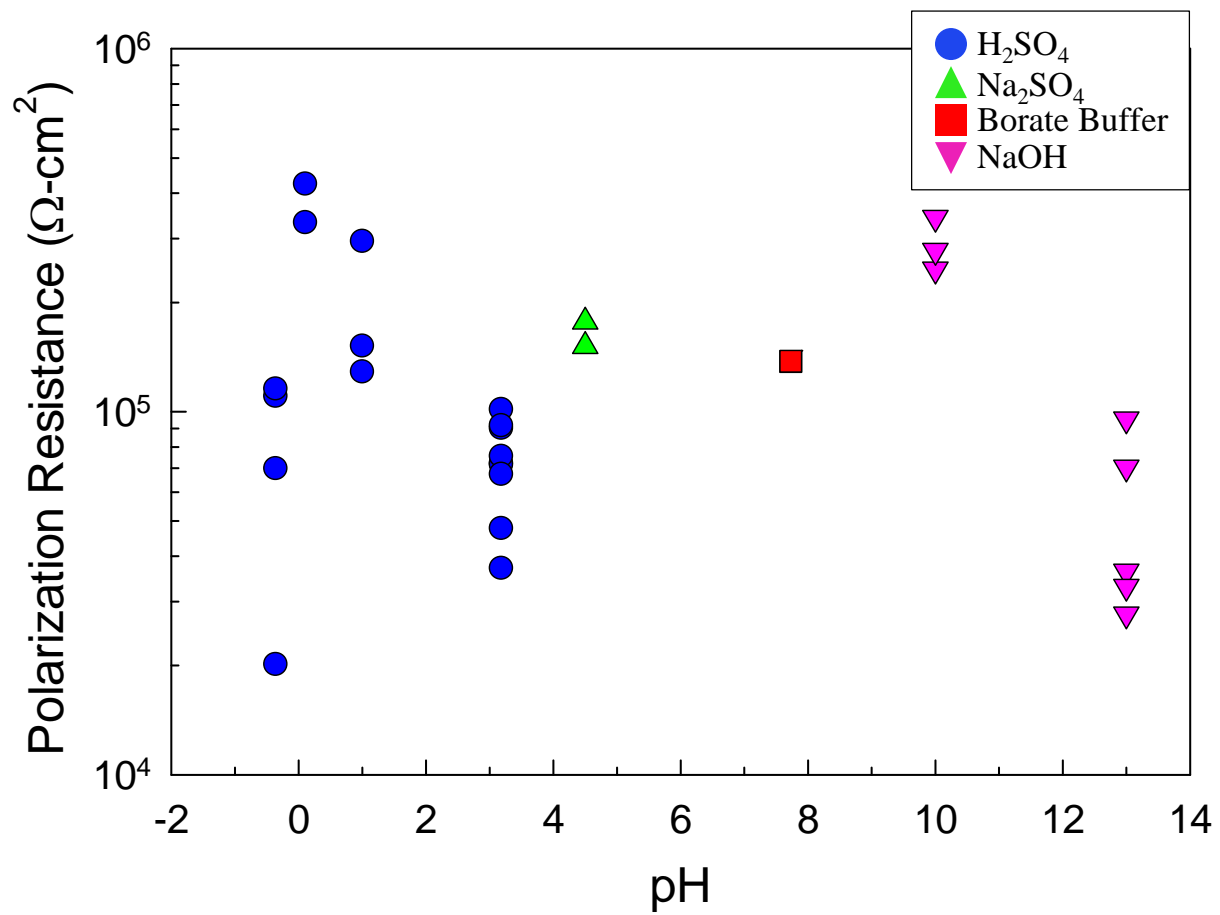


Figure 4. Linear polarization resistance of Tc as a function of pH.

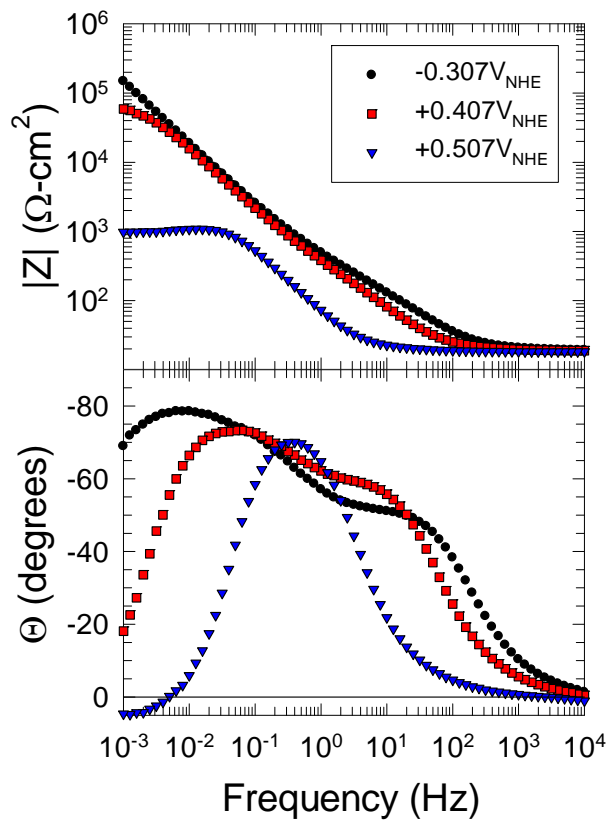


Figure 5. Impedance spectra from Tc exposed to borate buffer solution.

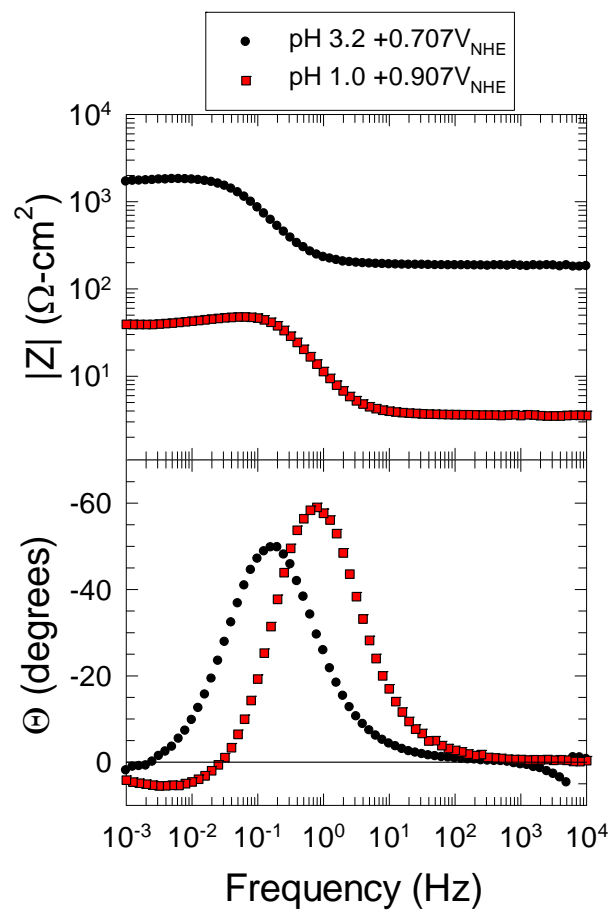


Figure 6. Impedance spectra from Tc exposed to H_2SO_4 .

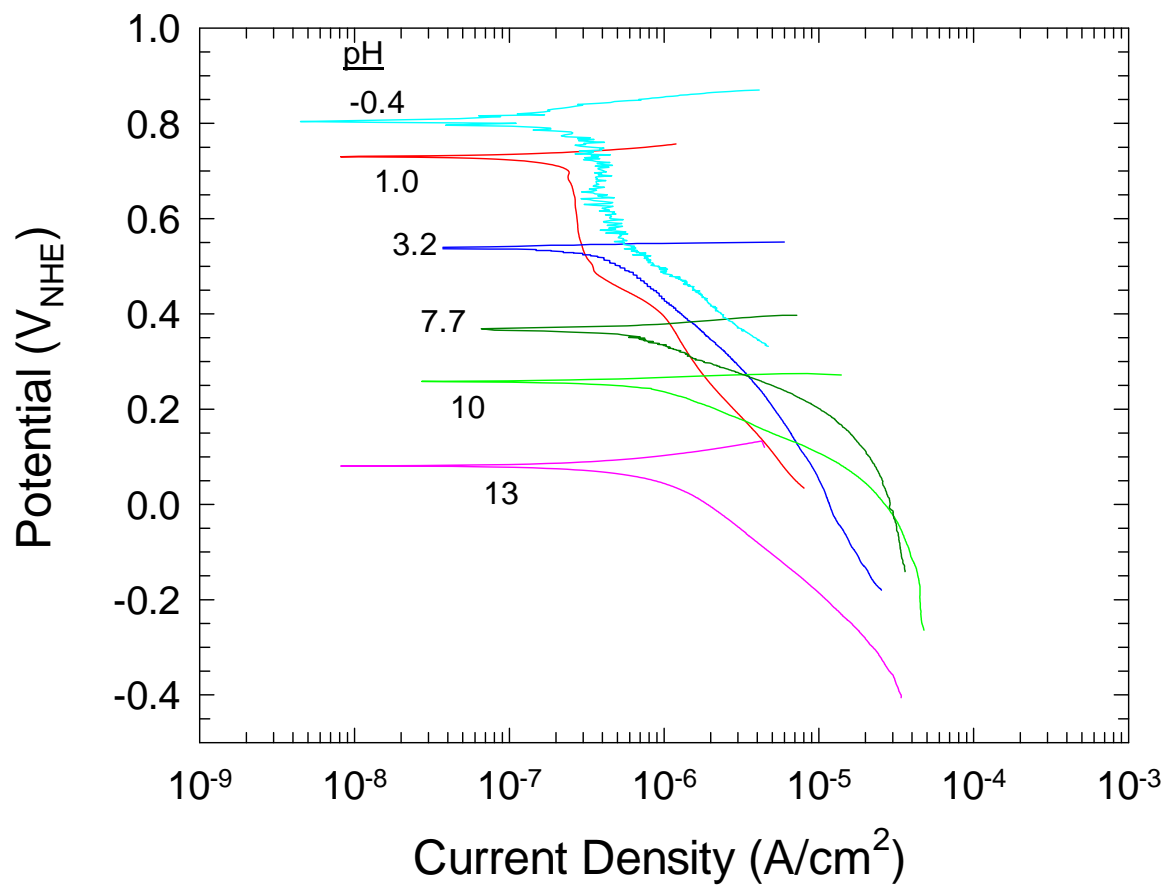


Figure 7. Representative potentiodynamic polarization curves for Tc exposed to solutions of various pH.

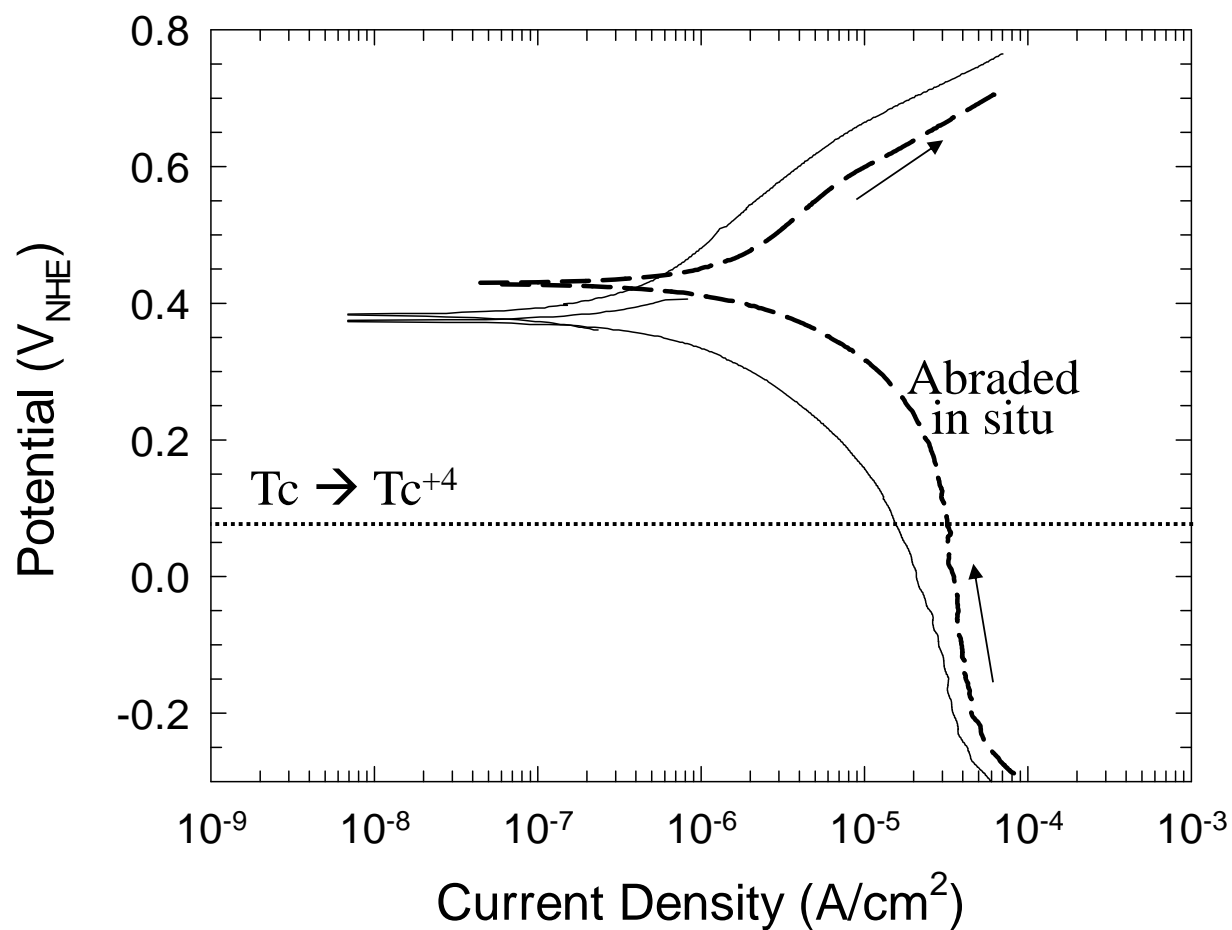


Figure 8. Anodic and cathodic polarization data for Tc exposed to pH 3.2 H₂SO₄. The heavy dashed line is a polarization scan following in-situ abrasion at $-0.3V_{\text{NHE}}$.

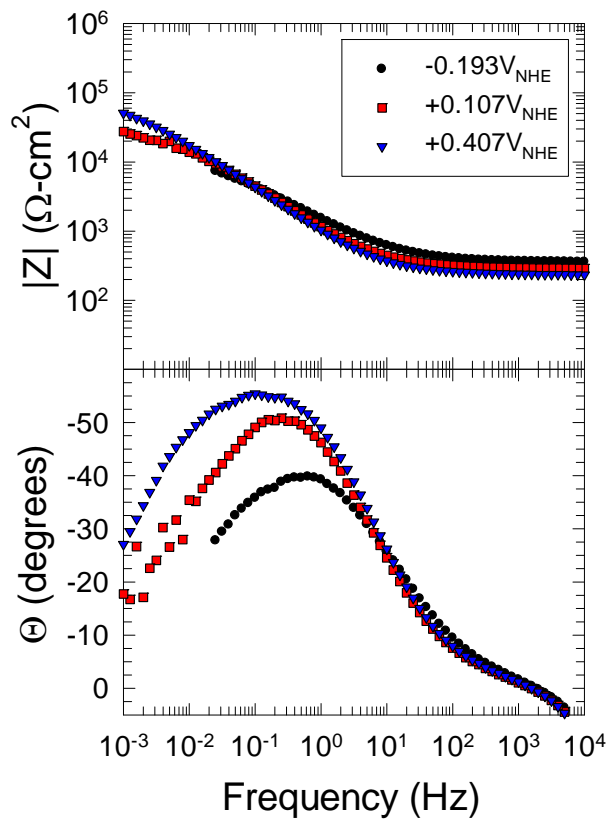


Figure 9. Impedance spectra of Tc exposed to pH 3.2 H_2SO_4 following in-situ abrasion. Representative tests from the immune ($-0.193\text{V}_{\text{NHE}}$), +4 ($0.107\text{V}_{\text{NHE}}$) and +7 ($0.407\text{V}_{\text{NHE}}$) regions are shown.

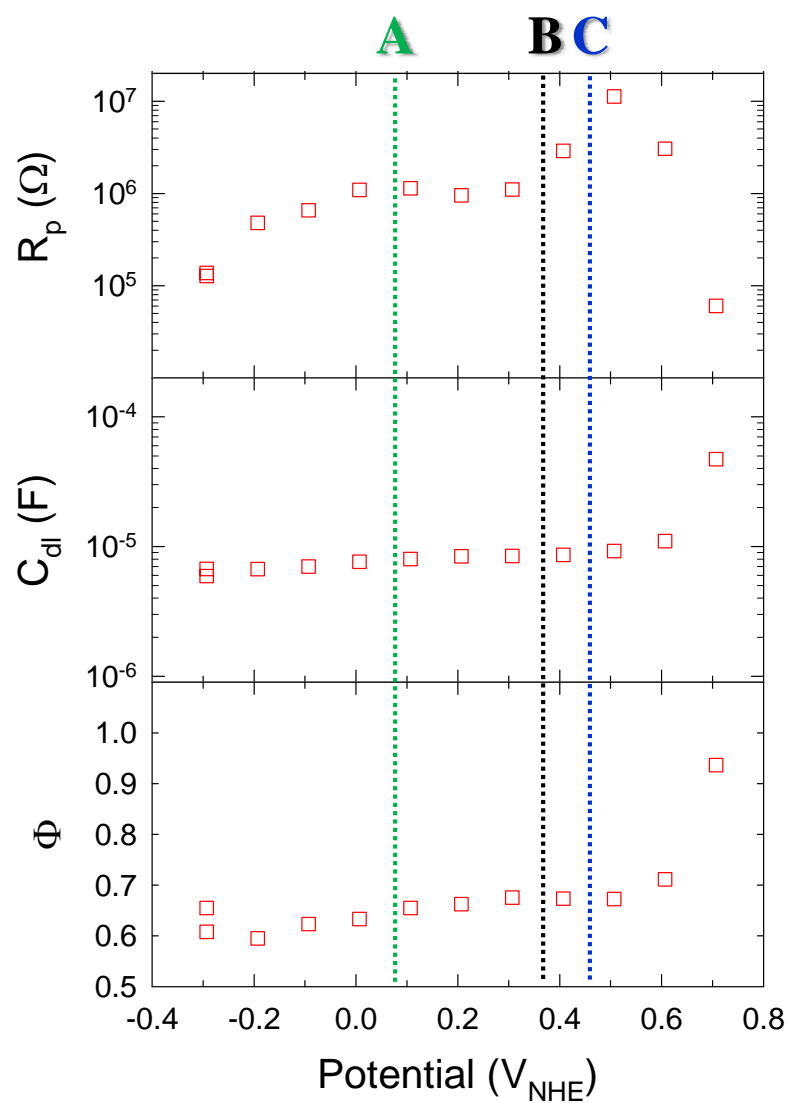


Figure 10. Fit data from impedance spectra (Tc, pH 3.2 H₂SO₄) following in-situ abrasion. Replicate tests at -0.3V_{NHE} were performed. Vertical lines are the A) published Tc to Tc⁺⁴ transition^{7,8}; B) published Tc⁺⁴ to Tc⁺⁷ transition^{7,8}; and C) open circuit potential.

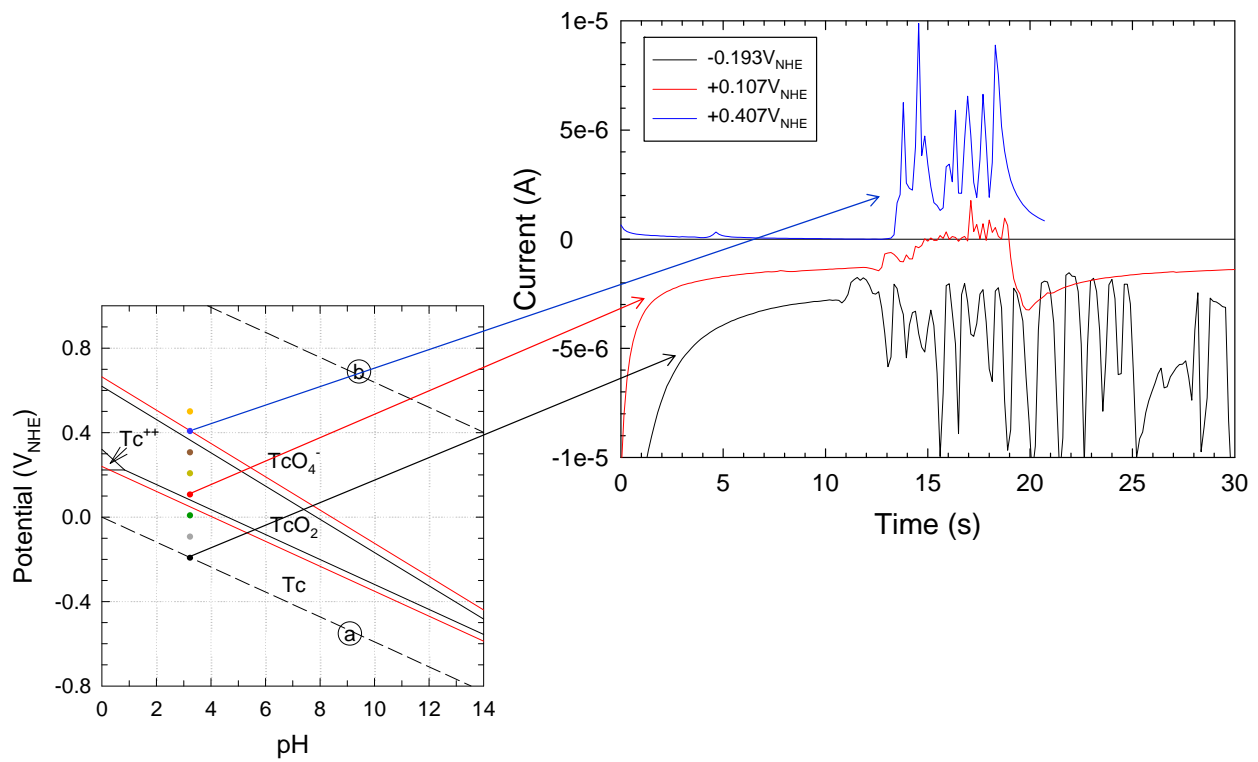


Figure 11. Bottom left - Potentials at which abrasion tests were performed, superimposed on the potential - pH diagram. Top right - Selected potentiostatic abrasion tests on Tc exposed to pH 3.2 H_2SO_4 .

References

- 1) W.L. Ebert, "Alloy Waste Form Testing Strategy Roadmap", Argonne National Laboratory, FCRD-SWF-2013-000226, July 22, 2013
- 2) "Separations and Waste Forms FY 2011 Accomplishments Report", Idaho National Laboratory Report INL/EXT-11-24155, December 2011.
- 3) J.V. Crum, D. Strachan, A. Rohatgi, M. Zumhoff, *J. Nuc. Materials*, **441**, 103 (2013).
- 4) J. Chen, R. Asmussen, D. Zagidulin, J. Noel and D. Shoesmith, *Corrosion Science*, **66**, 142 (2013).
- 5) R. Asmussen and D. Shoesmith, *Corrosion*, **70**, 177 (2014).
- 6) N. Das, G. Abraham, P. Sengupta, A. Arya, V. Kain and G.K. Dey, *J. Nuclear Materials*, **467**, 489 (2015).
- 7) Marcel Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", National Association of Corrosion Engineers, 1974.
- 8) G.H. Cartledge and W.T. Smith, *J. Phys. Chem.*, **59**, 1111 (1955)
- 9) J.W. Cobble, W.T. Smith and G.E. Boyd, *J. Am. Chem. Soc.*, **75**, 5777 (1953).
- 10) B.J. Lewis, W.T. Thompson, F. Akbari, C. Morrison, and A. Husain, *J. Nuc. Materials*, **340**, 69, 2005.
- 11) G.H. Cartledge, *J. Electrochem. Soc.*, **118**, 1752 (1971).
- 12) V.I. Spitsyn, M.M. Kurtepov, and R.A. Baru, *Doklady Akademii Nauk SSSR*, **229**, 673 (1976).
- 13) M. Ferrier, F. Poineau, G.D. Jarvinen, and K.R. Czerwinski, *J. Radioanalytical and Nuclear Chem.*, **298**, 1809 (2013)
- 14) C.D. Taylor, *J. Phys. Chem. C*, **118**, 10017 (2014).
- 15) S. G. Johnson, D. D. Keiser, M. Noy, T. O'Holloran and S. M. Frank, "22nd Symposium on Scientific Basis for Nuclear Waste Management", D.J. Wronkiewicz, and J.H. Lee eds., Materials Research Society, Vol. 556, pp. 953-960, 1999.
- 16) V.I. Spitsyn, P.V. Strekalov and O.A. Balakhovskii, *Protection of Metals*, **17**, 522 (1981).
- 17) J.A. Rard, M.H. Rand, G. Anderegg, and H. Wanner, "Chemical Thermodynamics of Technetium, Volume 3", M.C. Amaia Sandino and Erik Östholms eds., Elsevier, Amsterdam (1999).
- 18) G.H. Cartledge, *J. Electrochem. Soc.*, **118**, 232 (1971).
- 19) G.H. Cartledge, *J. Phys. Chem.*, **59**, 979 (1955).
- 20) G.H. Cartledge, *J. Phys. Chem.*, **60**, 28 (1956).
- 21) G.H. Cartledge, *Corrosion*, **11**, 335t (1955).
- 22) G.H. Cartledge, *Corrosion*, **29**, 361 (1973).
- 23) D.C. Silverman, *Corrosion*, **45**, 824 (1989)
- 24) M. Keddam, *Corrosion* **62**, 1056 (2006).