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ABSTRACT

The effects of fluoride on the corrosion behavior of Titanium Grade 7 (0.12-0.25% Pd) have been investigated. Up to 0.1 mol/L fluoride was added to the NaCl brines at 95°C, and three pH values of 4, 8, and 11 were selected for studying pH dependence of fluoride effects. It was observed that fluoride significantly altered the anodic polarization behavior, at all three pH values of 4, 8, and 11. Under acidic condition fluoride caused active corrosion. The corrosion of Titanium grade 7 was increased by three orders of magnitude when a 0.1 mol/L fluoride was added to the NaCl brines at pH 4, and the Pd ennoblement effect was not observed in acidic fluoride-containing environments. The effects of fluoride were reduced significantly when pH was increased to 8 and above.

INTRODUCTION

In the current Yucca Mountain high-level nuclear waste repository design, a drip shield structure made of Titanium Grade 7 will be constructed over the waste packages to prevent direct water seepage and rock fall onto the waste packages. Titanium Grade 7 (UNS R52400) is a titanium-based alloy with 0.12-0.25% Pd. The small addition of palladium is to ennoble the corrosion potential, thus improving the corrosion resistance of titanium in reducing environments. In most aqueous environments, Ti and Ti alloys demonstrate excellent corrosion resistance due to the protective oxide film that forms spontaneously and remains stable on the surface. However, Ti and Ti alloys are susceptible to corrosion in fluoride-containing environments due to the formation of complexes such as TiF_6^{2-} and TiF_6^{3-}, which are stable and soluble in electrolyte solutions.

The effects of fluoride on the corrosion of Ti and Ti alloys has been extensively studied by researchers for industrial and bio-medical applications.[1,2,3,4] However, there is relatively few publications available related to this subject in Titanium grade 7. Brossia and Cragnolino[5] reported no significant effects from [Cl^-], pH and temperature on the corrosion of Titanium grade 7 in waters without fluoride present. They also noted that the passive current densities measured during short-term potentiostatic testing were neither sustainable nor representative and that fluoride strongly altered the anodic polarization behavior of Ti grade 7, leading to significantly higher currents and, in some cases, corrosion attack under the crevice former.

The goal of this report is to study the effects of fluoride on the corrosion behavior of Ti grade 7 in NaCl brines containing fluoride subjected to various environmental variables, such as pH, [Cl^-], and temperature. Electrochemical polarization measurement techniques were used to characterize corrosion kinetics and susceptibility. The sustainability of fluoride influence was also studied.

EXPERIMENT PROCEDURES

The alloy used in this study was wrought mill annealed Ti Grade 7. Table 1 lists the chemical compositions.

Table 1. Composition of Ti Grade 7 (heat# P914) specimens

Elements	**C**	**Fe**	**N**	**O**	**H**	**Pd**	**Ti**
Concentration (wt%)	**0.02**	**0.07**	**0.01**	**0.11**	**0.001**	**0.12**	**Bal.**

The specimens used in electrochemical polarization measurements were metal discs measuring 15 mm in diameter and 3 mm in thickness. The disc specimens were placed in an ASTM G5 type flat specimen holder with an exposed surface area of approximately 0.75 cm^2. Specimens were wet ground with 600-grit SiC paper, and then ultrasonically cleaned in de-ionized water. A three-electrode cell with a capacity of 1 liter was used for all experiments. Approximately 900 mL of electrolyte were used in each test. A silver/silver chloride (Ag/AgCl, prefilled with 4 M KCl saturated with AgCl) reference electrode was used for measuring the potential of the working electrode. A solution bridge with a luggin probe was used to maintain an ionic conductive path between the working electrode and the reference electrode, while a cooling jacket was used to maintain the reference electrode at near room temperature. A platinum (Pt) rod or sheet was used as a counter electrode. To maintain the test solution at 95ºC, the electrochemical cell assembly was placed in a circulation temperature bath. An Allihn condenser was used to prevent solution loss through evaporation. The electrochemical polarization measurements were conducted through a commercial potentiostat and a frequency response analyzer integrated with a computer and the companion software.

The test solutions used in this study were NaCl brines at 1 mol/L (1 M) and 4 mol/L (4 M) concentrations. NaF was added into the NaCl brines to study the effects of fluoride, and fluoride concentration was controlled at 0, 0.001, 0.01 and 0.1 mol/L. The solution pH was adjusted prior to each test to pH values of 4, 8, and 11. Two temperatures, 60°C and 95°C were investigated. N_2 gas purging was used to de-aerate the test solutions. Gas purging began at least one-half hour before the specimens were placed into the solution.

Short-term electrochemical testing was first used to evaluate the effects of fluoride and other variables on corrosion behavior of Ti grade 7. In these tests, Ti grade 7 specimens were stabilized for 1 hour in the test solution, and then polarization resistance measurements and an anodic potentiodynamic polarization measurement were performed respectively. A potential scan rate of 600 mV per hour was used in all polarization measurements.

A longer-term type of testing was also used to evaluate the sustainability of corrosion resistance of Ti grade 7 as well as the effects of fluoride on the corrosion behavior of Ti grade 7 in NaCl brines. In these tests, Ti grade 7 specimens were exposed to the test solution for up to 1 week. Corrosion potential was monitored, and polarization resistance measurements were performed at various time increments during the exposure time line.

EXPERIMENT RESULTS

Anodic Polarization Behavior

Under a wide range pH range (4, 8 and 11), Ti grade 7 exhibited strong passivity in [F^-]-free NaCl brines. Figure 1 shows little change in the passive current density, although the threshold potential decreases as pH increases. The threshold potential is defined as the potential where the anodic current increases noticeably above the passive current, which appears to be related to the onset of oxygen evolution.

In contrast, with the addition of 0.1 M NaF into 1 M NaCl brines, the anodic polarization curves changed significantly for all pH values. Figure 2 shows the anodic polarization curves of Titanium grade 7 shifted to right due to the presence of 0.1 M NaF in the NaCl brines, at all three pH values (4, 8, and 11). At pH 4, the presence of 0.1 M [F^-] completely destroyed the passive behavior of Ti grade 7, as shown by the red curve. Based on the polarization behavior, the anodic dissolution of Ti grade 7 in acidic fluoride-containing brine needed slight over potential to reach a plateau value on the order of mA/cm^2 for anodic dissolution.

At neutral (pH 8) and alkaline (pH 11) conditions, the presence of fluoride also greatly diminished the passive range and noticeably increased anodic dissolution rates at the more anodic potentials. At pH 8, the passive region of Ti grade 7 was significantly narrowed (green curve). Although the anodic polarization curve shows increase in current density at the potentials above the threshold point (around –0.25 V Ag/AgCl), it should be noted that the current density was still relatively low, only in the range of several tens of μA/cm^2 or 10^{-5} μA/cm^2. At pH 11, Ti grade 7 did not exhibit the typical passivity, however, the anodic dissolution rate at and near the corrosion potential was close to the passive current observed in Figure 1. Based on the polarization behavior, no significant increase in corrosion rate of Ti grade 7 was expected in fluoride-containing brines at pH 8 and 11, unless an external anodic polarization was applied.

As shown in Figure 3, under acidic conditions (pH 4), the anodic polarization curves moved toward right (i.e. higher current densities) with increasing fluoride concentration,. The shift in the anodic polarization curve was even noticeable for the lowest fluoride addition, 0.001 M [F^-], being added in the test solution. Finally, a 250 mV drop in corrosion potential was observed when the fluoride concentration reached 0.01M and higher. This behavior shows that Ti grade 7 become more active in the presence of fluoride ions. Based on these results, it appears that, the benefit of Pd ennoblement was no longer effective when the fluoride concentration reached 0.01 M or higher.

Figure 4 and 5 show the anodic polarization curves of Ti grade 7 in fluoride-containing NaCl brines at pH 8 and 11, respectively. For both pH values (pH 8 and 11), there was only a very small shift in the anodic polarization curves when a 0.01 M fluoride was added to the NaCl solutions, but a much more prominent shift when the fluoride concentration was increased to 0.1 M.

Short-term corrosion rate

Prior to each potentiodynamic measurement, linear polarization resistance measurements were performed to determine the short-term corrosion rate. The corrosion rate, in micrometers per year, was calculated based on the polarization resistance (R_p) measurement results:

$$Corrosion\ Rate,\ in\ \mu m/yr = K_1 \cdot EW \cdot B/(R_p \cdot \rho)$$

where constant K_1= 3.27 μm·g/μA·cm·yr, EW is the equivalent weight of Titanium Grade 7 (11.98), ρ is the density of Titanium Grade 7 (4.51 g/cm^3), and B is the Stern-Gary constant 0.026 with the assumption of both anodic (β_a) and cathodic (β_c) Tafel constants of 0.12 V/decade. A unit of MΩ·cm^2 is used for R_p.

The short-term corrosion rate of Ti grade 7 in acidic (pH 4) NaCl brines increase exponentially with increase in fluoride concentration. Figure 6 shows the corrosion rate of Ti grade 7 could be increased three orders of magnitude when 0.1 M of NaF was added to NaCl brines. The corrosion rate increase was observed even with a fluoride concentration as low as 0.001 M. Except for a lower corrosion rate observed for 4 M NaCl + 0.1 M NaF at 95°C, all experimental data did not show strong effects from chloride concentration and temperature. The measured corrosion rate for Ti grade 7 in NaCl-only brines was approximately 1 μm/yr.

As shown in Figures 1 through 5, the presence of fluoride noticeably altered passive behavior in both neutral and alkaline NaCl brines whenever polarized to relatively high anodic potentials; however, the effect of fluoride on the short-term corrosion rate at pH 8 and pH 11 was minimal. Figure 7 shows the corrosion rate of Ti grade 7 at pH 8 and pH 11 to be nearly unchanged as the fluoride concentration in NaCl brines increased. This is indicative of the great resistance of Ti grade 7 even in fluoride-containing solutions as long as a neutral or alkaline pH is maintained and the alloy remains in the vicinity of its corrosion potential.

Long-term corrosion potential and corrosion rate

Based on the short-term corrosion results, fluoride was extremely detrimental to Ti grade 7 in acidic conditions, but had a relatively small or no effect in neutral or alkaline conditions. However, it was not clear whether this fluoride effect would remain for an extensive period of time. The longer-term tests were used to monitor the corrosion behavior of the Ti grade 7 in test solutions for up to one week and at the selected times, linear polarization resistance and electrochemical impedance were measured to determine the change in the corrosion rate. Since we were only interested in evaluating the change in the dissolution kinetics, 1/Rp was used to represent corrosion kinetics.

At pH 4, as shown in Figure 8, the active corrosion of Ti grade 7 caused by the presence of [F^-] in the test solution showed no signs of slowing down. For up to 1 week of exposure, the corrosion potential remained fairly stable, and even continued to move toward being more active. With the presence of 0.1M [F^-] in the solution, the corrosion potential of Ti grade 7 was decreased by nearly 800 mV, and the corrosion rate was increased by three orders of magnitude. The results clearly indicate that the presence of 0.12% Pd in Ti grade 7 did not ennoble the corrosion potential in acidic fluoride-containing environments.

At pH 8, as shown in Figure 9, Ti grade 7 showed adequate resistance against fluoride-influenced corrosion. With the presence of 0.1M [F^-] in the solution, the corrosion potential of Ti grade 7 was decreased by 300 mV in the early part of exposure. However, the corrosion potential was gradually trending upward. At the end of the week, the corrosion potential of Ti grade 7 in fluoride -containing solution was only about 100 mV lower than in the solution without fluoride. At the beginning of exposure, fluoride increased the corrosion rate of Ti grade 7 by nearly 2.5 times. At the end of week, this increase was maintained at approximately 2 times. In short, from the trends of corrosion potential and corrosion rate, Ti grade 7 appeared to maintain its corrosion resistance in fluoride -containing brines at the near-neutral pH value.

At pH 11, the fluoride influence was further diminished. Figure 10 shows that, after 3 days of exposure, both corrosion potential and corrosion rate of Ti grade 7 in the test solution with 0.1 M [F^-] showed little difference from those of the fluoride -free solution.

DISCUSSION

It is important to point out that the selection of the test environments does not reflect the realistic environments that might be present in the repository. Realistically, the repository environment is not expected to see high fluoride-containing brines with an acidic pH.

For the environmental conditions at the drip shield and waste packages, that are of low relative humidity, the waters that are in contact with the engineered barrier system components will be brines which can form either through seepage water evaporative concentration or through salt and/or dust deliquescence, and can be divided into three general types:[6]

- High calcium chloride
- High sulfate
- High carbonate.

All three brine types that are relevant to Yucca Mountain will contain relatively significant quantities of chloride and nitrate, whether derived from the evaporation of seepage water or deliquescence of salts in dust.

Calcium chloride brines can be neutral to acidic; however, the high calcium in this type of brine makes fluoride impossible to co-exist since CaF_2 is rather insoluble. The high sulfate brines have near-neutral pH values, and a small amount of magnesium, which would limit the concentration of fluoride in the brines. High carbonate brines generally are alkaline, even though the fluoride content in this type of brine can be relatively high. Therefore, one can conclude that in the Yucca Mountain repository environment, it is highly unlikely to have the type of brine with an acidic pH and high fluoride content.

Therefore, Ti grade 7 drip shield will be not likely to encounter serious fluoride enhanced corrosion in the Yucca Mountain repository due to lack of fluoride or lack of acidity in the brines that might be present.

CONCLUSIONS

Based on the work conducted to date, fluoride had a minimal effect on the corrosion of Titanium grade 7 in NaCl brines, as long as a neutral or alkaline pH is maintained. Considering the realistic brine chemistries might be present in the Yucca Mountain repository, the risk of serious fluoride-enhanced corrosion in Titanium grade 7 drip shield will be low due to lack of fluoride or lack of acidity in the brines that might be present.

Under acidic conditions fluoride can cause the active corrosion in Titanium grade 7, and the addition of Pd in Titanium grade 7 did not enhance the nobility of Ti in acidic fluoride-containing environments. The corrosion of Titanium grade 7 was increased by three orders of magnitude when a 0.1 mol/L fluoride was added to the NaCl brines at pH 4, and the Pd ennoblement effect was not observed in acidic fluoride-containing environments.

ACKNOWLEDGEMENTS

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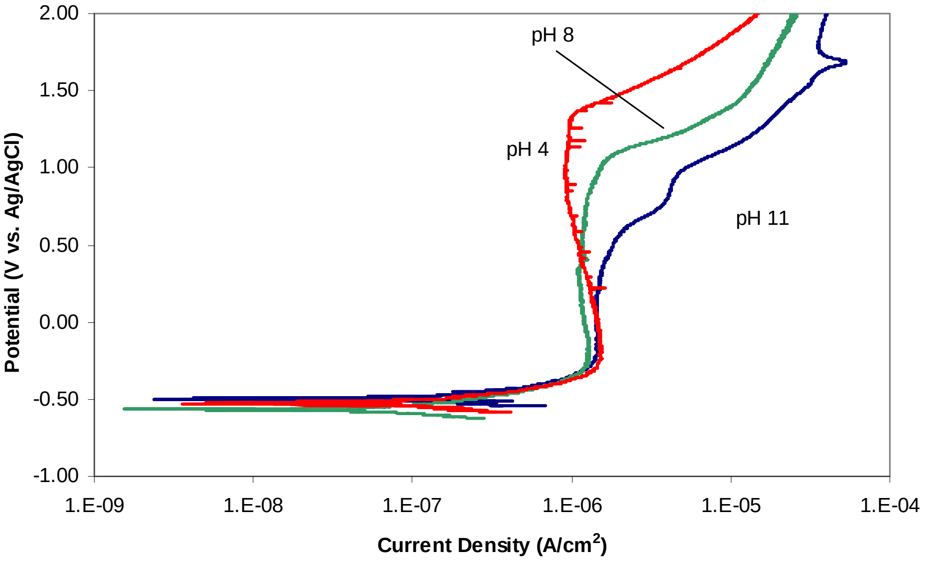

Figure 1. Anodic polarization behavior of Ti grade 7 in 1M NaCl solutions at 95°C. The test solutions were de-aerated with N_2.

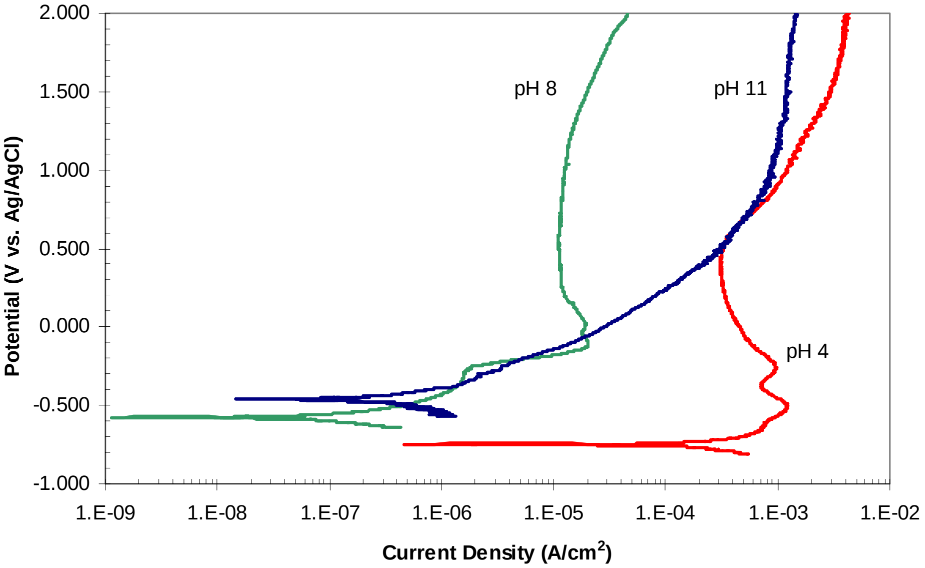

Figure 2. Anodic polarization behavior of Ti grade 7 in 1M NaCl + 0.1M NaF solutions at 95°C. The test solutions were de-aerated with N_2.

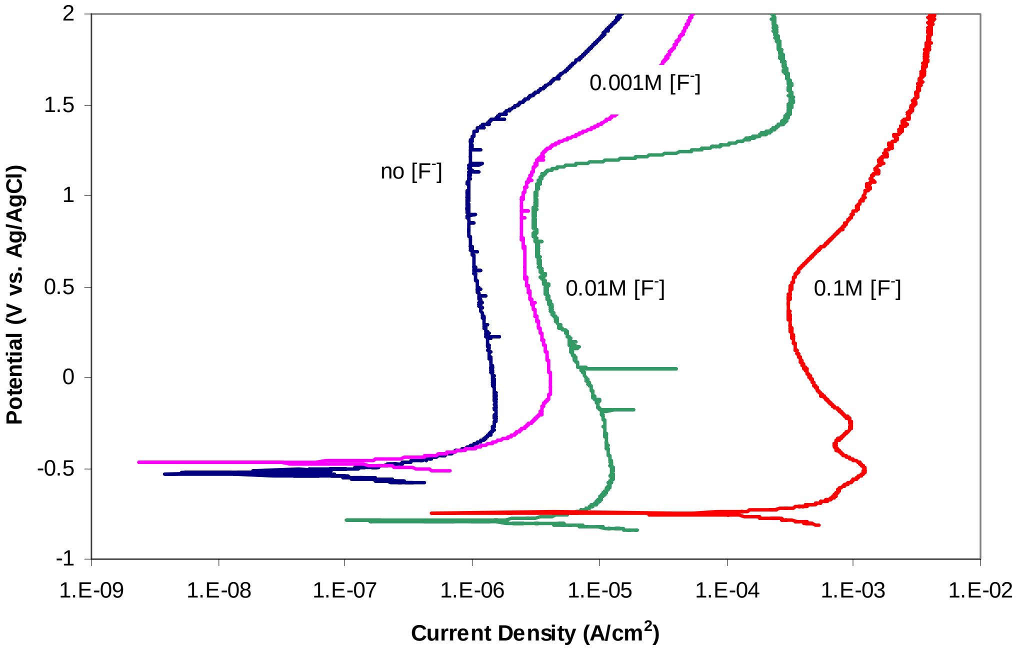

Figure 3. Anodic polarization curves shifted to right as increasing fluoride concentration in 1 M NaCl brines at pH 4, 95°C, and de-aerated with N_2.

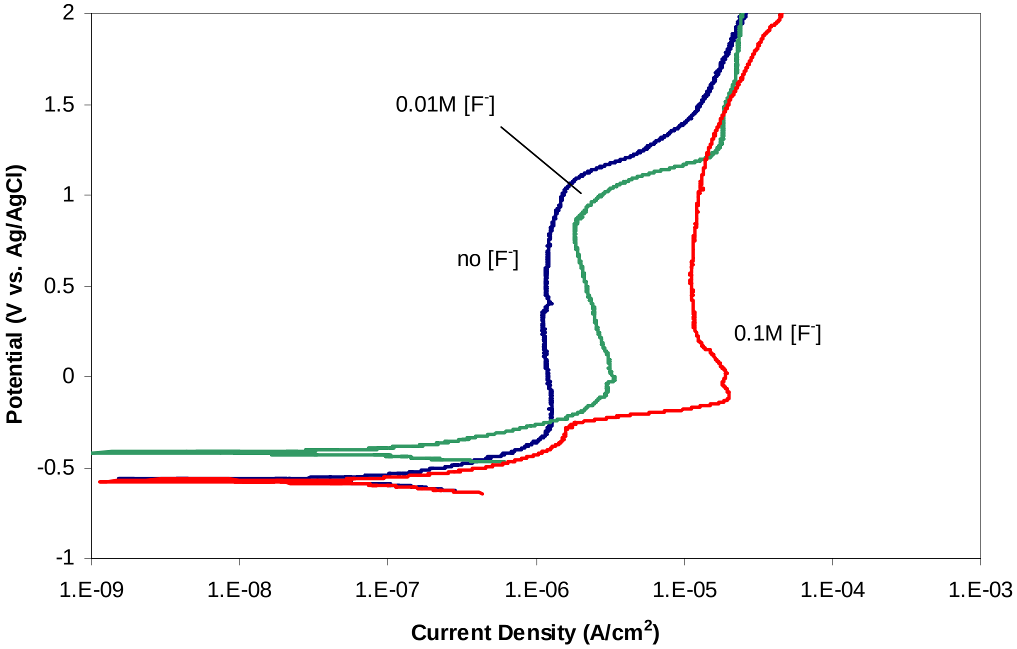

Figure 4. Anodic polarization curves shifted to right as increasing fluoride concentration in 1 M NaCl brines at pH 8, 95°C, and de-aerated with N_2.

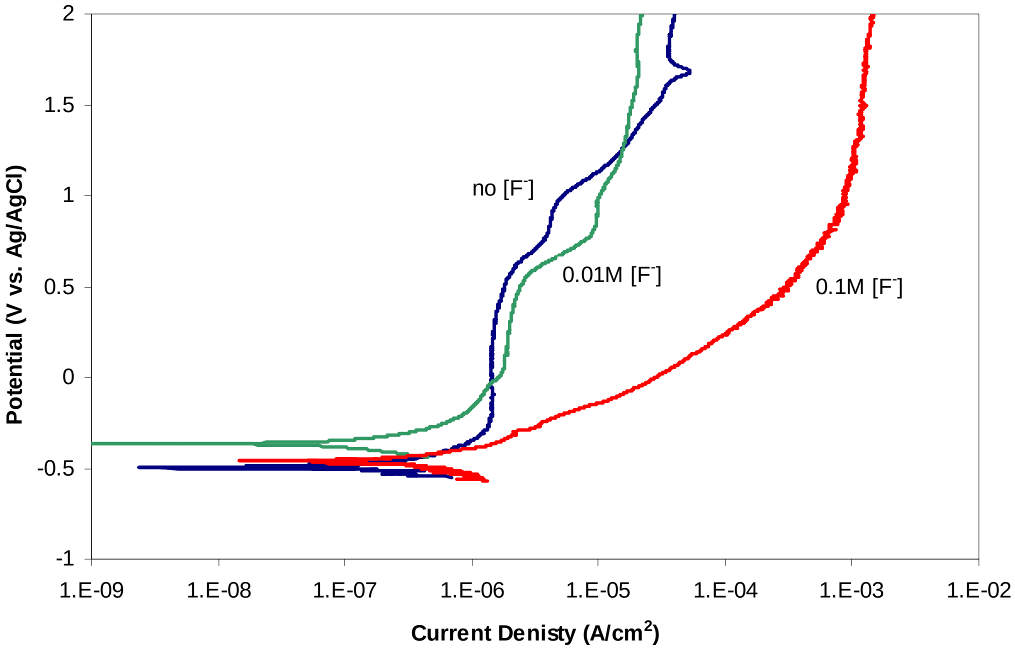

Figure 5. Anodic polarization curves shifted to right as increasing fluoride concentration in 1 M NaCl brines at pH 11, 95°C, and de-aerated with N_2.

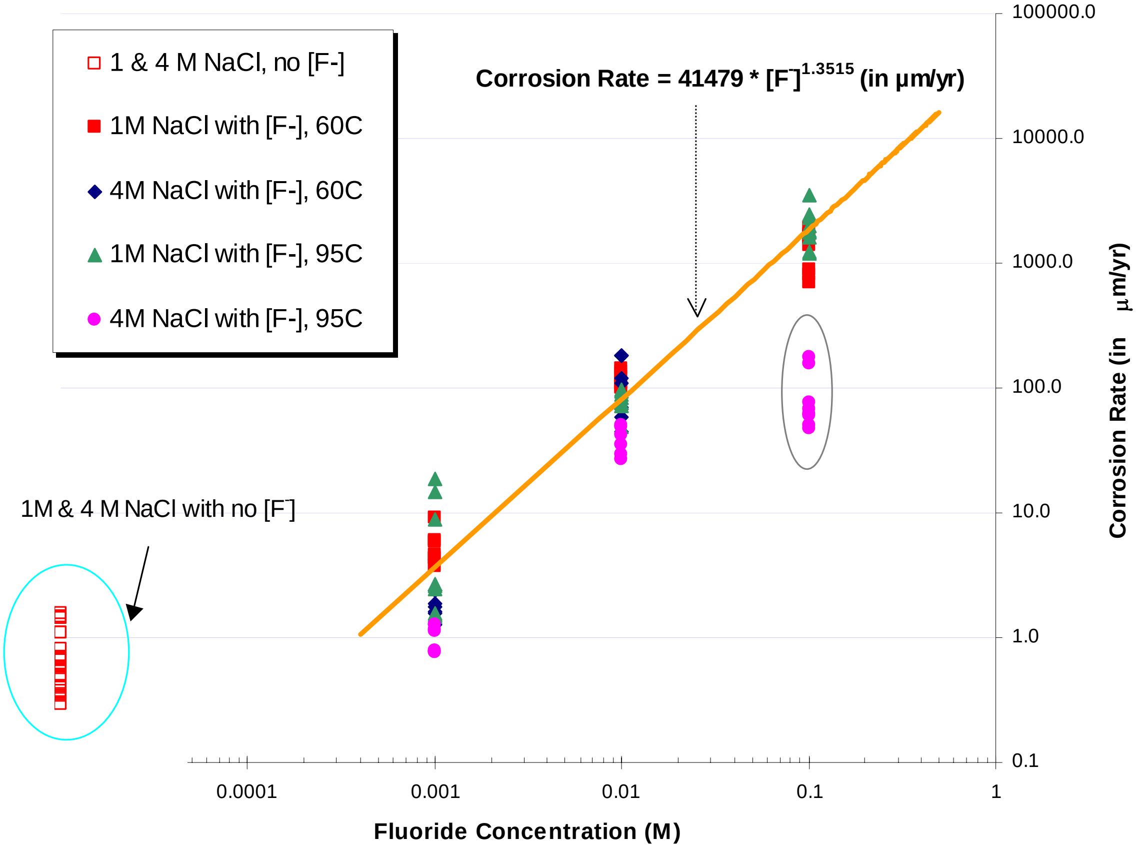

Figure 6. Fluoride effect on the corrosion rate of Ti grade 7 in acidic 1 M NaCl brines at pH 4, 95°C and de-aerated with N_2.

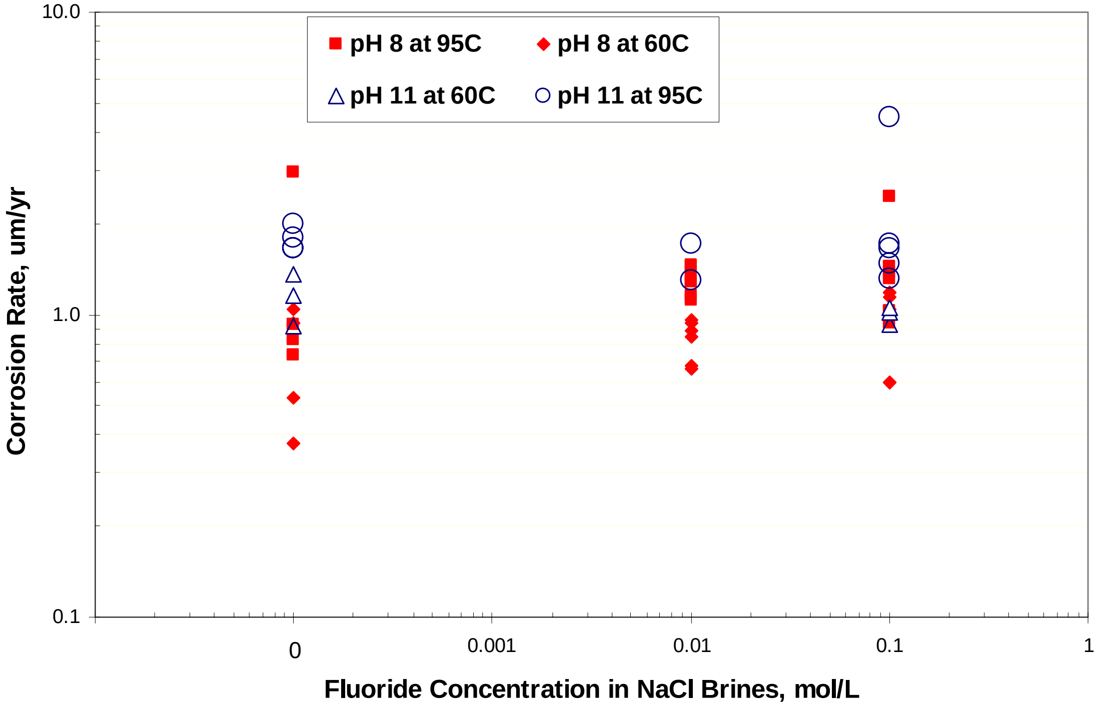

Figure 7. At pH 8 and 11, fluoride showed no significant effect on the corrosion rates of Ti grade 7. Tested in 1 M NaCl brines, at 95°C, and de-aerated with N_2.

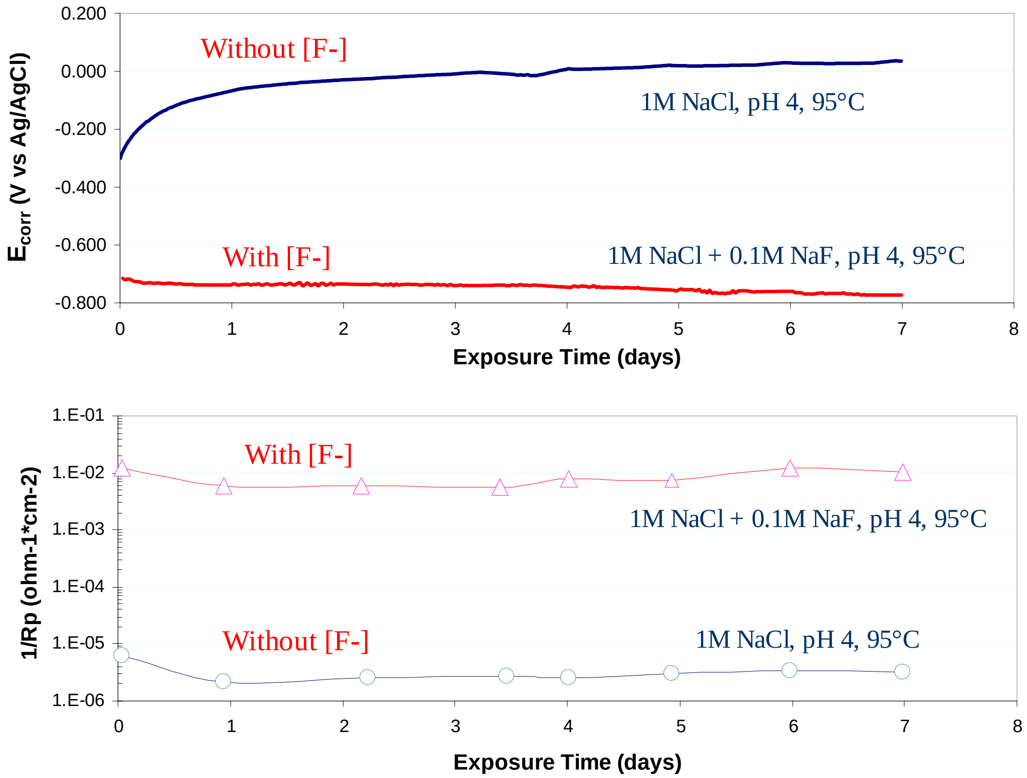

Figure 8. At pH 4, fluoride caused active corrosion rates on Ti grade 7. Test was conducted by exposing samples in 1 M NaCl brines, with and without fluoride, at 95°C and de-aerated with N_2.

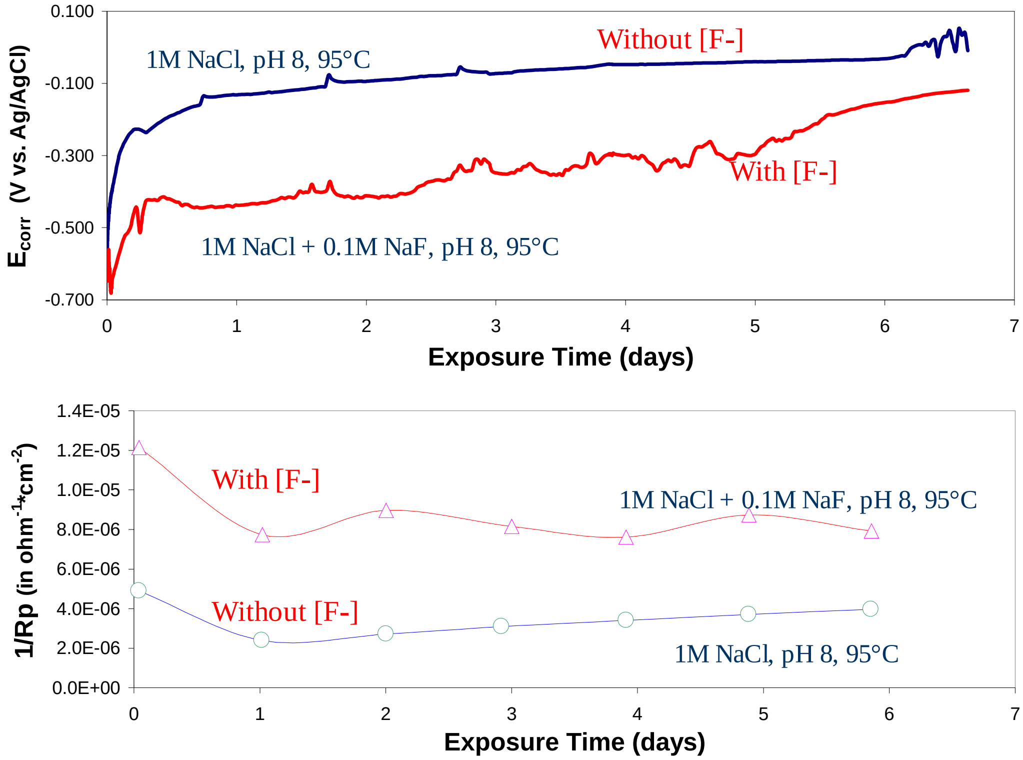

Figure 9. At pH 8, the fluoride effects on the corrosion potential and corrosion rate decreased significantly. Tests were in 1 M NaCl solution, with and without fluoride, at 95°C and de-aerated.

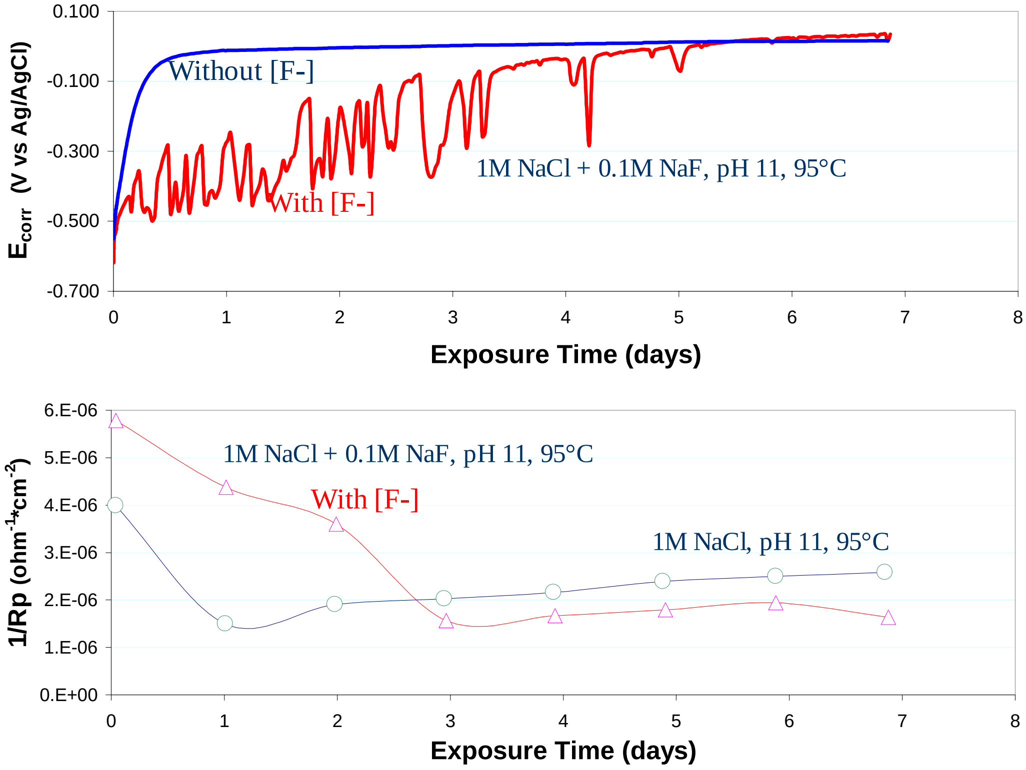

Figure 10. At pH 11, the fluoride effect on the corrosion potential and corrosion rate disappeared after 3 days. Tests were in 1 M NaCl solution, with and without fluoride, at pH 11, 95°C and de-aerated.