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Pitting Corrosion of 410 Stainless Steel in HCl Solutions

Paul D. Krell

The University of Akron, pdk10@zips.uakron.edu

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PITTING CORROSION OF 410 STAINLESS STEEL IN HCl
SOLUTIONS

Honor's Project 4200:497

Sponsor: Dr. Hongbo Cong

By: Paul Krell

4/24/2017

Executive Summary

Problem Statement

AISI 410 stainless steel (SS) is a material commonly used in oil refining as the distillation column tray material. The distillation column is one of the first units in the refinery, so the crude oil still has various contaminants like HCl. The refining industry has good references for the corrosion rate of carbon steel, austenitic stainless steels, and nickel based alloys at the varying HCl concentrations and temperatures the material might experience as trays in crude unit distillation columns, but there is no good reference of martensitic stainless steels like 410^{[1],[2]}. To fill this knowledge gap, experiments were performed at several HCl concentrations and temperature combinations. The results of these experiments are summarized in Figure 1 below.

Results

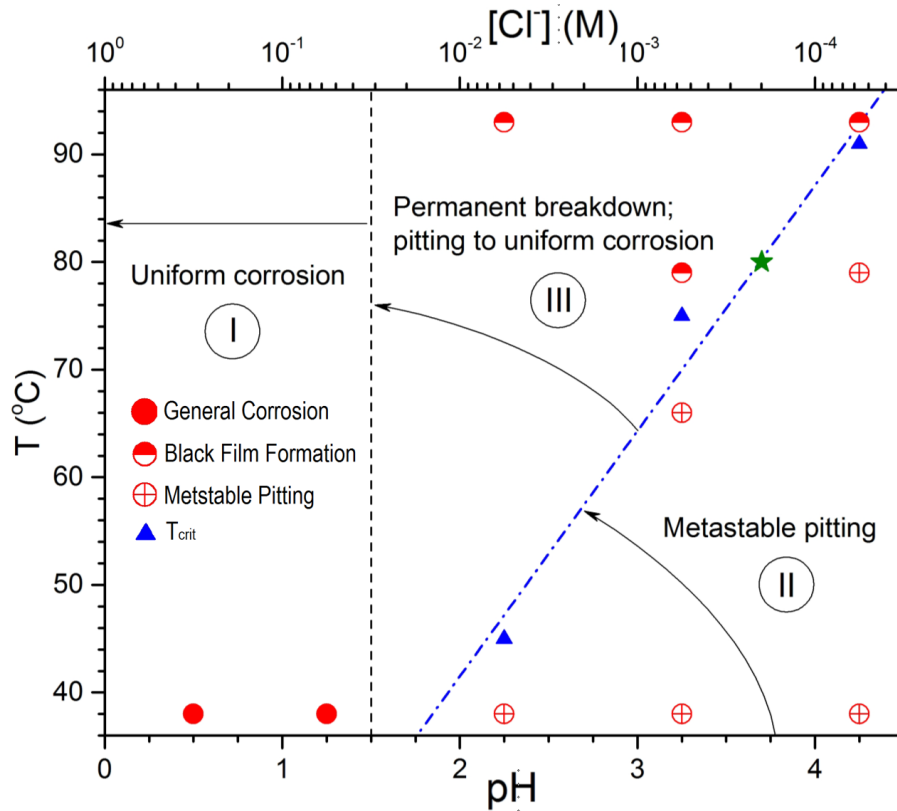


Figure 1: Summary of experimental results

Conclusions

The regions of the graph show the mode of corrosion. Region 1 is heavy uniform corrosion. Samples tested in region 1 had corrosion rates of at least one inch per year, so 410 SS should never be used in those environments. Region 2 is the environments that fall under the blue line. In these environments 410 SS experiences metastable pitting, with minor corrosion rates. 410 can be used in Region 2 environments. Region 3 is the environments that are above the blue line. In these environments 410 SS experiences active pitting due to permanent passive film breakdown. 410 should not be used in Region 3 environments.

Broader Implications

This project developed my academic research skills and prepared me for graduate studies. In addition experimental methods, I learned how to collect and use pertinent academic papers, organize a project, and critically analyze results to plan new experiments. This project also improved my presentation skills, which led to winning awards at the NACE student poster session and the University of Akron Industry Advisory Board poster competition.

These results can inform material selection so 410 SS is not used in environments which cause failure. Preventing failure in oil refineries prevents damage to life, the environment, and the economy, so improving material selection is an important task.

Future Work

To further refine the results of this project, the effect of the chloride anion (Cl^-) concentration should be studied at different pH levels. In the current project the solution was only HCl at different concentrations, so the proton cation (H^+) and Cl^- always varied together. It is known that Cl^- plays an important role in passive film breakdown, so separating its effect would be useful.

Introduction

410 SS is a commonly used material in the oil refining industry. As such, it is important to understand its corrosion properties so costly and dangerous failures can be avoided. There are two widely used corrosion references in oil refining, API 571 and API 581^{[1],[2]}. Both of them have corrosion rate tables for many corrosion mechanisms, including HCl corrosion. In HCl corrosion, there are corrosion rates for many materials at different temperatures and HCl concentrations, but there is no corrosion rate data for martensitic stainless steels like 410. This project is designed to supplement API 571 and API 581 and fill that gap. To make this project comparable, the temperatures and HCl concentrations tested were taken directly from those industry documents. Experimental methods include cyclic potentiodynamic polarization (CPP), potentiostatic hold with temperature ramp (temperature ramping), and exposure while monitoring OCP (exposure), coupled with sample analysis using SEM/EDX and 3D microscopy before and after experiments.

Background

Pitting and general corrosion of stainless steels is dependent on passive film breakdown. The pH at which the passive film breaks down in an environment is referred to as the critical pH. Previous work by Leckie found the critical pH of 410 SS to be 3.6 by anodic polarization, a technique similar to cyclic potentiodynamic polarization used in this project^[3]. In a study with constant pH, the chloride concentration was found to be a strong determining factor in the severity of pitting corrosion. In the study, the dependence of the pitting potential (E_{pit}) on $\log[\text{Cl}^-]$ was 130mV/dec^[4]. In a related study, Artens studied 410 SS in solutions at constant temperature and changed the chloride concentration. The Cl^- concentration at which pitting begins is called the critical chloride concentration. Artens found the critical chloride

concentration at 80°C to be 2×10^{-4} N [5]. While pitting relies on localized film breakdown, in some environments the passive film completely dissolves and general corrosion proceeds. In a study by Kelly, 410 was found to corrode at a rate of 0.47 in/year in pH1 HCl solution[6].

Experimental Methods

A 410 SS rod was used as the sample material. The exact composition of the rod is in Table 1. Passive films tend to be more vulnerable at sharp edges, so the samples were machined into rounded “bullet” samples. To avoid crevice corrosion the centers of the samples were tapped and held with a threaded rod, then hung so they were partially immersed. Samples were freshly grinded to 600 grit and cleaned before every experiment.

C	Si	Mn	Cr	Mo	Cu	Ni	Co	Al	P	S	N	Sn
0.129	0.29	0.43	12.24	0.12	0.05	0.42	0.021	0.02	0.02	0.001	0.027	0.003

Table 1: Composition of 410 samples

The experimental cell was cleaned and filled with 450 mL solution. Two graphite rods on opposite sides of the sample were used as counter electrodes, a Teflon tube was used as a gas connection, a K-type thermocouple and a heating mantle were used to control the temperature, and a condenser was used to prevent solution loss. A saturated calomel electrode (SCE) was used as the reference electrode, and was separated from the solution by a salt bridge and cooled to 10°C.

CPP experiments were performed according to ASTM G61. Prior to the experiment, the cell was deaerated with 99.9% argon gas for two hours, then the sample was inserted and the OCP was monitored for one hour. The initial potential used was -0.1 V vs. OCP, the potential was scanned upwards at a rate of 0.1667 mV/s up to 1 V vs SCE, and the potential was scanned

back down to -0.1 V vs OCP. Experiments were performed at 38, 52, 66, 79, and 93°C and at 0.50, 1.25, 2.25, 3.25, and 4.25 pH. The useful parameters out of these experiments are pitting potential (E_{pit}), repassivation potential (E_{rp}), and open circuit potential (OCP).

Temperature ramping experiments were performed in HCl solutions deaerated with 99.9% argon gas for two hours. Samples were polarized at 0.2, 0.3, and 0.4 V vs. SCE for 1 hour at room temperature, then continued to be polarized while ramping the temperature at a rate of 0.6°C/min up to 100°C. Other temperature ramping rates were studied, and the temperature ramping rate was found to have little effect. The useful parameter out of these experiments is critical temperature (T_{crit}), the temperature above which pitting begins.

Exposure experiments were performed for 65 hours in ambient HCl solutions. Environments studied were 38, 53, 79, and 93°C at 0.50, 1.25, 2.25, 3.25, and 4.25 pH. The useful data from these experiments were potential changes characteristic of metastable pitting and active pitting.

Data and Results

The 410 samples were analyzed using SEM/EDX. Material inclusions and their compositions are in Figure 2. Based on the amount of aluminum and oxygen in the inclusions, they are primarily made of Al_2O_3 or $\text{Al}_2\text{O}_3\text{-MgO}$. There are also sigma-phase particles in the material, which are rich in chromium (Figure 3).

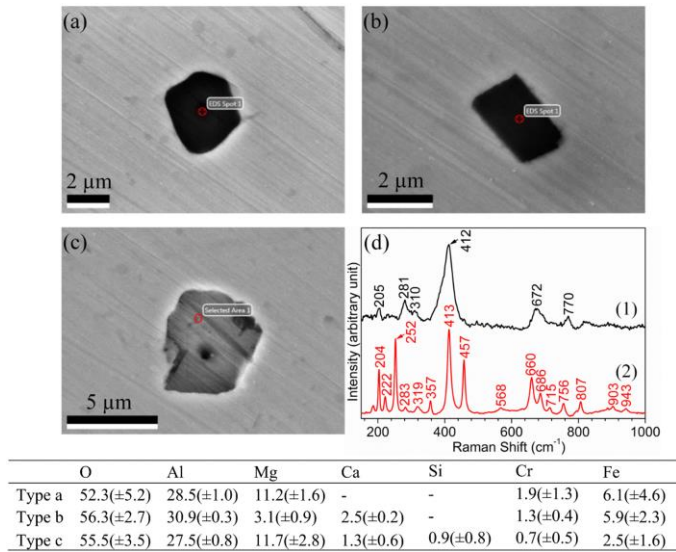


Figure 2: Material inclusions and their compositions

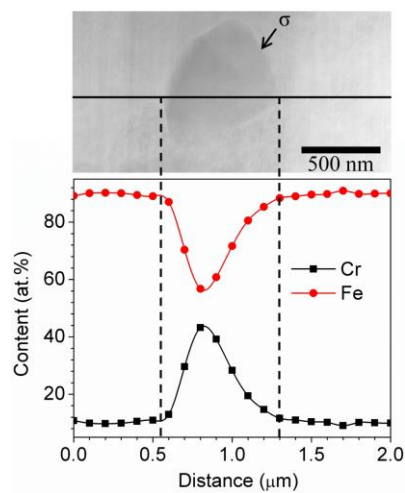


Figure 3: Chromium concentration around and across a sigma-phase particle

These material inclusion sites were also studied after exposure experiments. Figure 4 shows an inclusion site that has been analyzed after exposure to 3.25 pH solution at 38°C using SEM/EDX. The site preferentially corroded, leaving a pit of 4µm while the surrounding material had much less corrosion. A similar inclusion site did not experience preferential corrosion after exposure to 4.25 pH solution at 38°C (Figure 5).

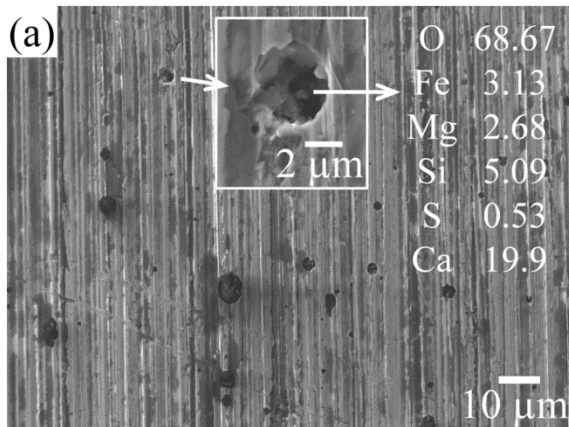


Figure 4: Inclusions site after exposure in pH 3.25 solution at 38°C

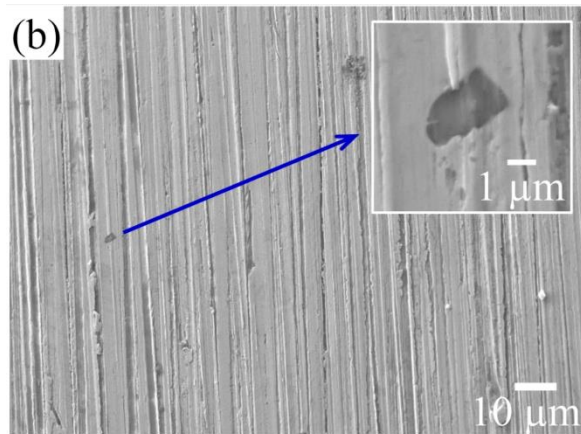


Figure 5: Inclusion site after exposure in pH 4.25 solution at 38°C

Many CPP experiments were performed to obtain E_{pit} , E_{rp} , and OCP values. An example of a CPP experiment that shows how those parameters were determined is Figure 6. Graphing CPP experiments together allows for fast visual comparison. In Figure 7 CPP experiments

performed at different temperature with the same pH are graphed. As temperature increases E_{pit} , E_{rp} , and OCP all decrease. Figure 7 also shows the samples after the experiments, with pits and discoloration becoming more dramatic at higher temperatures. Similarly, Figure 8 depicts CPP experiments performed at the same temperature using different pH solutions. As pH decreases E_{pit} , E_{rp} , and OCP decrease, and pitting and discoloration become more apparent.

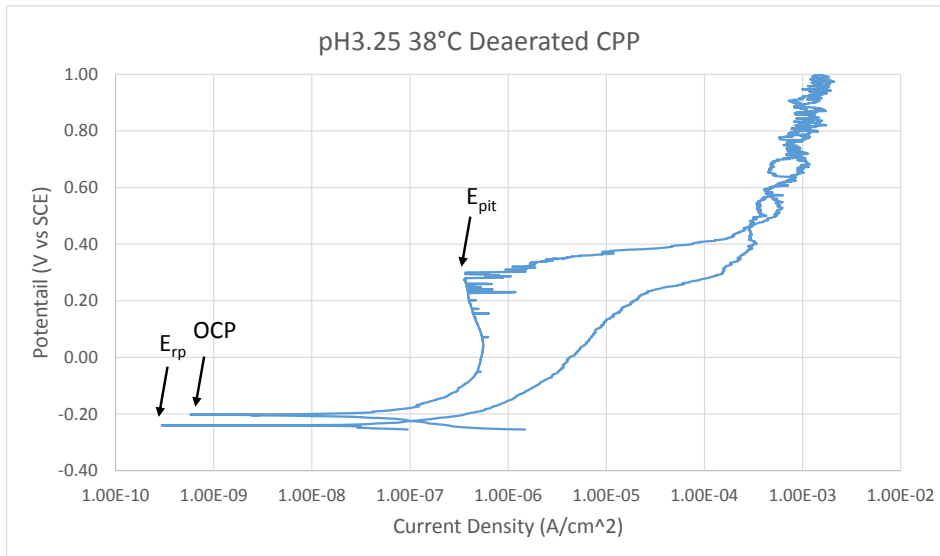


Figure 6: Example of an individual CPP experiment with important parameters identified

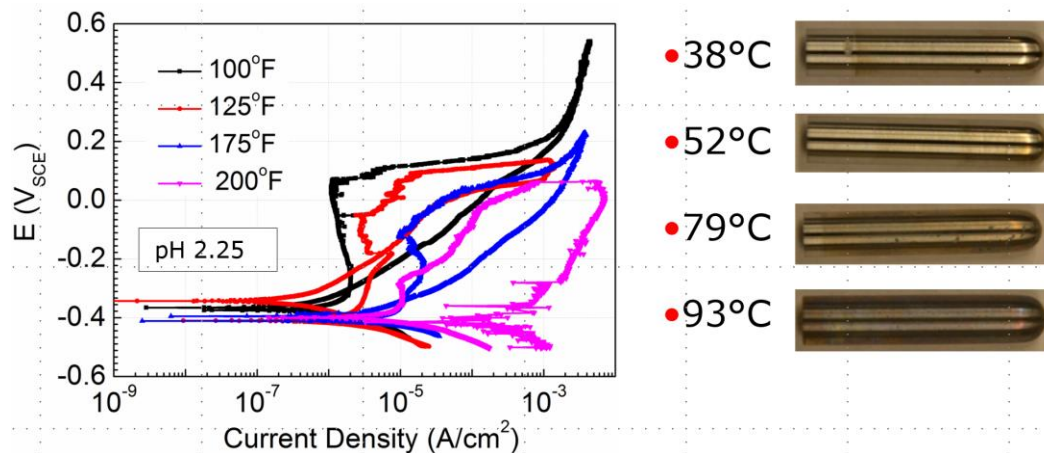


Figure 7: CPP experiments in pH 2.25 solution

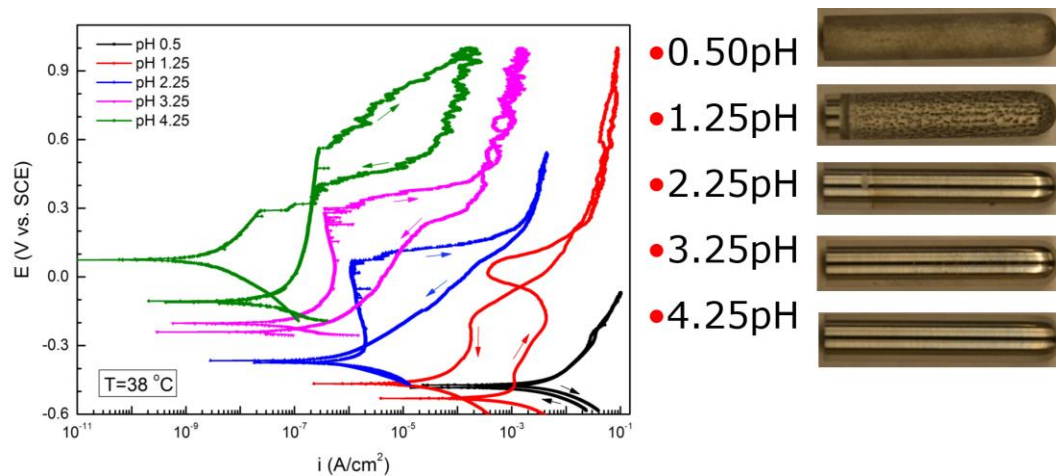


Figure 8: CPP experiments at 38°C

Temperature ramping experiments were performed to find T_{crit} in solutions of different pH. An example of a temperature ramping experiment is Figure 9. While the sample is held at a constant voltage, temperature is increased and the current is measured. When the current spikes up dramatically pitting has begun, and the temperature at which it occurred is T_{crit} . The results of the temperature ramping experiments are in Figure 10. T_{crit} has a strong linear fit with pH. Temperature ramping experiments were attempted at pH 1.25 but pitting began immediately, which means the critical temperature in pH 1.25 solution is below room temperature.

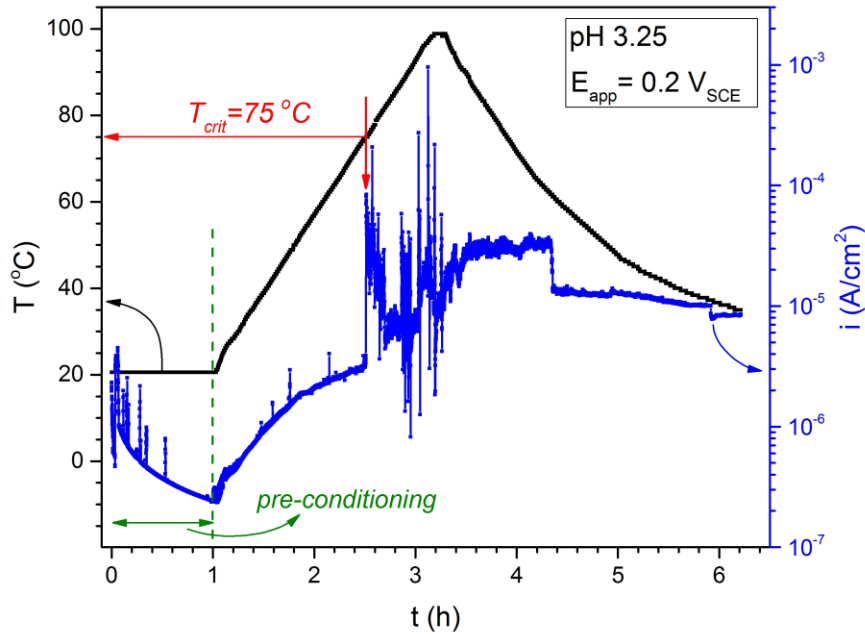


Figure 9: Example of a temperature ramping experiment

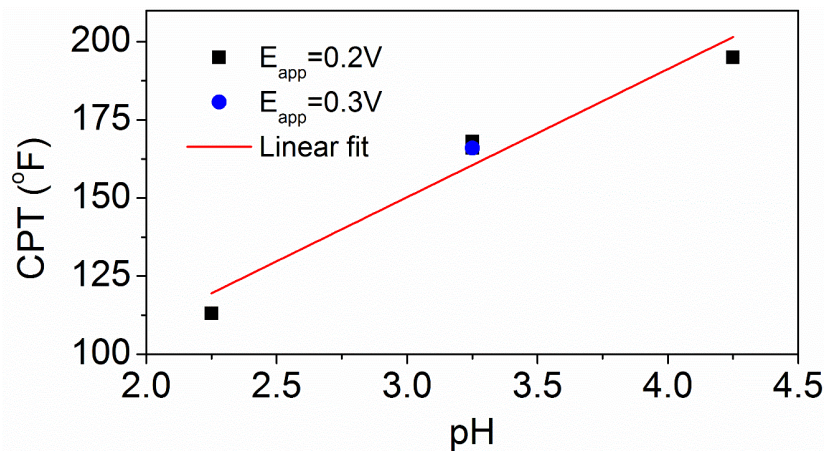


Figure 10: T_{crit} vs pH

Exposure experiments were performed to qualitatively measure the pitting behavior of 410 SS. Figure 11 depicts exposure experiments at 38°C using different pH solutions. In pH 3.25 and 4.25 solutions, there are “spikes” downward in potential that come back up. Those potential spikes indicate metastable pitting, in which pitting begins and then the passive film reforms. In pH 2.25 solution there is a “cliff” where potential falls and does not return. The cliff

indicates permanent passive film breakdown and active pitting. In pH 0.50 and 1.25 the potentials stay low the entire time, which indicates the passive film dissolves immediately and general corrosion begins. The general corrosion is apparent in the sample pictures.

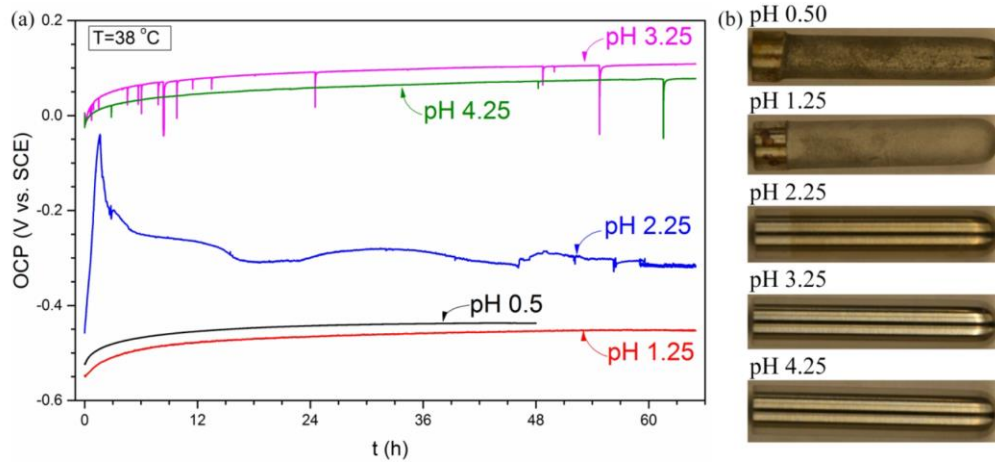


Figure 11: Exposure experiments at 38°C

Figure 12 depicts exposure experiments at 93°C. Every pH has a potential cliff, but 3.25 and 4.25 recover somewhat after 45 hours. This may be because of the black film formed is protective. The protection is not as strong as the passive film at lower temperatures, however, and corrosion is still proceeding.

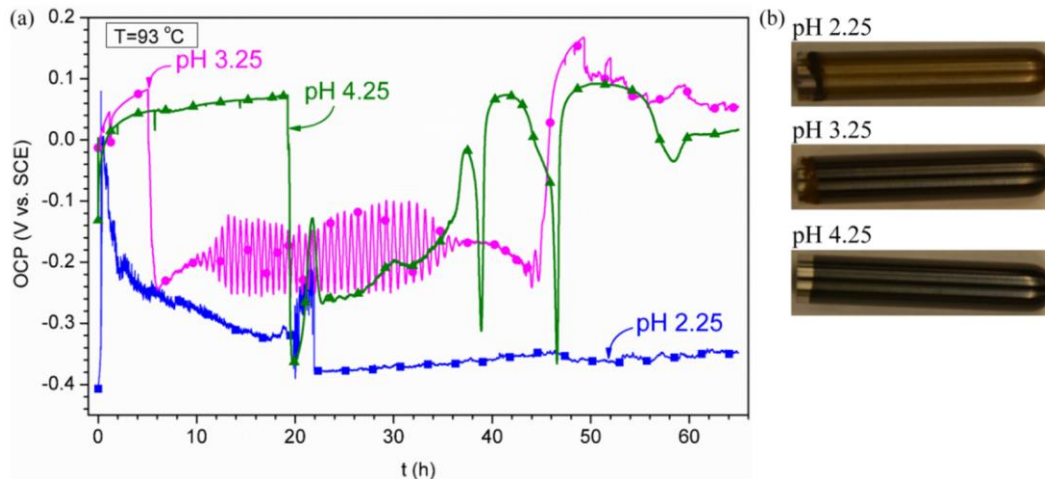


Figure 12: Exposure experiments at 93°C.

Figure 13 shows exposure experiments at pH 3.25 at different temperatures. At 38 and 66°C there are spikes that indicate metastable pitting. Starting at 79°C, there are cliffs that indicate active pitting and black film formation.

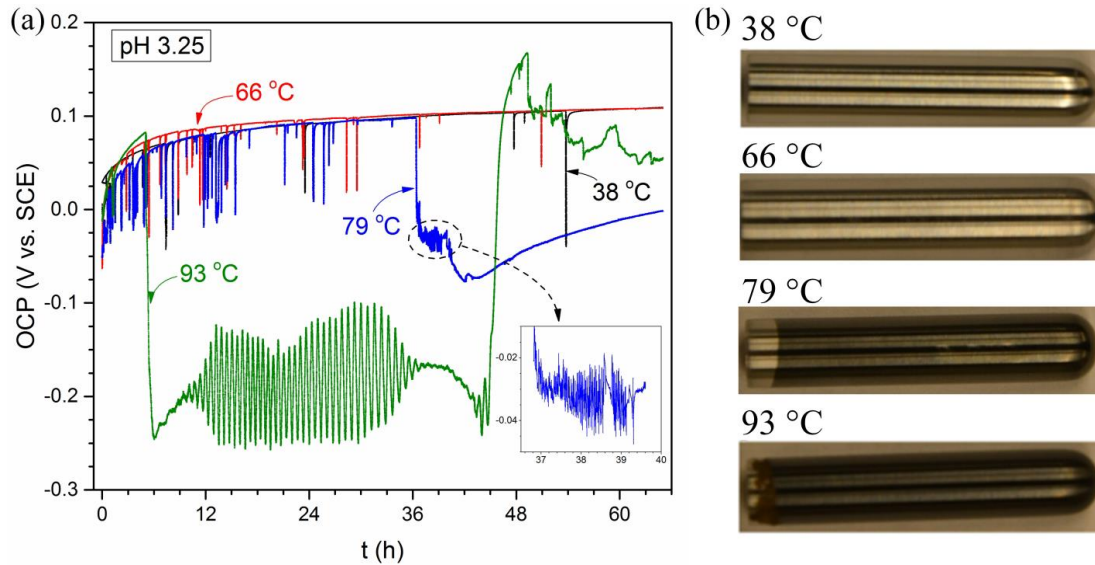


Figure 13: Exposure experiments at pH 3.25

Discussion/Analysis

Inclusion sites have different compositions from the bulk material, making them ideal sites for pit initiation. At 38°C, 410 SS in pH 3.25 solution experiences significant metastable pitting (Figure 11). After exposure, the inclusion sites were corroded away, making excellent pitting initiation sites (Figure 4). The pitting initiation sites were confirmed to be inclusion sites based on their concentrations of calcium and other elements that are dilute in the bulk material but concentrated in the pits. At 38°C in pH 4.25 solution, 410 SS experienced very little metastable pitting (Figure 11). After exposure, the corrosion-prone inclusions were found intact, confirming that 410 SS experiences little pitting in that environment.

The pitting behavior of 410 SS is most easily described by exposure experiments, where different patterns of potential drops indicate metastable pitting or active pitting. These results can be compared with CPP results to validate both methods and to make predictions based on CPP parameters. Figure 14 shows OCP, E_{pit} , and E_{rp} at 38°C in different pH solutions. At pH 4.25 OCP meets E_{rp} , and in the exposure experiment at this condition very little metastable pitting occurred. At pH 3.25 OCP is above E_{rp} and far from E_{pit} , and significantly more metastable pitting occurs. At pH 2.25 OCP approaches E_{pit} , and active pitting occurs. This analysis shows that quick CPP experiments can be used to supplement and validate long exposure experiments.

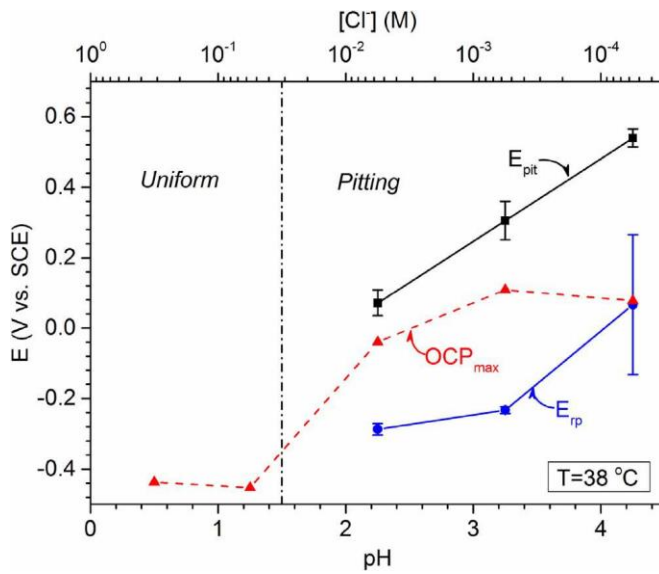


Figure 14: E_{pit} , E_{rp} , and OCP at 38°C

At pH 3.25 exposure experiments at 38 and 66°C experienced metastable pitting, while experiments at 79 and 93°C experienced active pitting (Figure 13). This can be explained by T_{crit} . At pH 3.25 T_{crit} is 75°C (Figure 9). Above T_{crit} 410 should experience active pitting, and below it should not. The exposure experiments follow this conclusion, making T_{crit} a powerful tool in material selection.

The results summarized in Figure 1 were put together using all of these methods. Every experiment carried out below T_{crit} only had metastable pitting, so T_{crit} was chosen to be the dividing line between active and metastable pitting. Points on the graph represent individual experimental results, which confirm this division.

These conclusions agree well with literature sources. Leckie found that the critical pH of 410 SS is 3.6, and in this project pitting rarely occurred above 3.25pH, and only at temperatures higher than Leckie studied. E_{pit} was found to have a strong dependence on chloride concentration (Figure 14), which agrees with the results of Pahlavan's study^[4]. General corrosion occurred below pH 1.25, which agrees with Kelly's conclusion that general corrosion occurs at pH 1. Artens found the critical chloride concentration for 410 SS at 80°C, to be 2×10^{-4} N. Critical chloride concentration is the concentration above which pitting occurs, similar to the definition of critical temperature. The critical chloride concentration at 80°C temperature falls on the T_{crit} line (Figure 1), lending credibility to T_{crit} 's prediction of pitting corrosion.

Literature Cited

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- [2] API Recommended Practice 581, Damage Mechanisms Affecting Fixed Equipment in the Refining Industry, American Petroleum Institute, Washington D.C., 2008.
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Appendices



Paul Krell
Experiment Summary