

The Effect of Silicon on the Electrochemical Corrosion Resistance of Carbon Steel

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Resistance of Carbon Steel

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CAL POLY STATE UNIVERSITY
Materials Engineering Department

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Prof. Trevor Harding
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Abstract

The purpose of this study was to investigate how the silicon (Si) content of carbon steels affects their electrochemical corrosion resistance. Tests were conducted using concentrated HCl and carbonated water on three carbon steels with different levels of silicon: 0.02, 0.19, and 0.94 weight percent. Like H_2S , the prime concern of Chevron, HCl and CO_2 are corrosive components in oil refinery. Electrochemical properties were measured using a potentiodynamic test outlined in Standard ASTM G59-97: Test Method for Conducting Potentiodynamic Polarization Resistance Measurements. Previous studies have determined that adding silicon to steel increases the corrosion resistance; however, results show that corrosion rates appear to increase with higher silicon content within HCl.

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1.0 Introduction

Steel has been an integral part of technological and industrial development since antiquity, with the earliest known example of steel production dating back 4000 years.¹ Since that time, steel production techniques and materials have continually evolved. Steel was not seen in its modern form until the 18th century, which brought advances in using the coal derivative coke instead of the previously more common component charcoal.²

Modern steel is an alloy composed of iron and up to 2 weight percent carbon, often with other alloying elements (e.g. Si, Mn, Cu) that can have a significant impact on the properties and microstructures of the material. In 2010, the world annual production of crude steel reached about 1.4 billion tonnes used in a multitude of applications. Most steels are produced using one of two methods: integration of raw materials (e.g. iron ore, limestone, coke) in a blast furnace or basic oxygen furnace or recycling of scrap metal through an electric arc furnace.³

Carbon steel is the most commonly used material in the refining and petroleum industry; in fact, up to 80% of the components are comprised of carbon steel. This material is widely used because it is inexpensive, readily available, easily fabricated, and can be heat-treated after welding. It is used in particular for large pipelines, heat exchangers and pressure vessels in refining. Low alloys (C-Cr-Mo) may also be used for furnace tubes, piping, heat exchanger shells, and separator drums because they tend to have adequate strength retention and

resistance to sulfidic corrosion. In more corrosive environments, such as high-temperature sulfidic and naphthenic acid, stainless steels are used.⁴

1.1 Corrosion

Corrosion is the chemical reaction of a material with its environment that causes degradation of the material. The reaction can be classified in multiple ways including by the nature of the corrodent of which there are two categories, wet and dry.⁵ In this classification scheme, wet corrosion refers to the corrosion of a material in an aqueous environment with an electrolyte, and dry corrosion refers to the corrosion of a material in a gaseous environment, typically at high temperatures. Appearance of the corroded metal (uniform or localized) is another way to classify corrosion. Uniform corrosion occurs when the corrosion reaction takes place over the entire surface of a material while localized corrosion occurs at specific locations.⁶

Corrosion can also be classified by the mechanism of corrosion, which normally falls under the categories of electrochemical and direct chemical. The most common corrosion mechanism is electrochemical, taking place when two or more electrochemical reactions occur, including at least one oxidation reaction and one reduction reaction. To be classified as electrochemical corrosion, there are four main requirements that the reaction must satisfy. There must be an anode and a cathode to provide sites for oxidation and reduction, respectively. There must also be paths for electrons to flow from the anode to cathode, and a path for the

movement of ions from cathode to anode. If any one of these four components is removed, corrosion stops.⁵

Depending on the environment, metals will exhibit one of three responses to an electrochemical reaction: immune, active, or passive. Materials that are thermodynamically stable within an environment are immune and will not corrode. Active metals undergo the corrosion reaction within certain environment and form corrosion products. In passive behavior, corrosion initially occurs but the reaction product is insoluble, acting as a protective film. This coating significantly lowers the rate of corrosion but if broken, the metal reverts to active behavior. In order to determine how a metal will act, the thermodynamics and kinetics of the system need to be analyzed. Thermodynamics states that a reaction will occur spontaneously if it lowers the free energy of the system. Potential-pH diagrams, or Pourbaix diagrams (Figure 1), utilize the thermodynamics in order to predict the behavior of a pure metal at 25 °C given the pH and potential of an electrolytic solution.

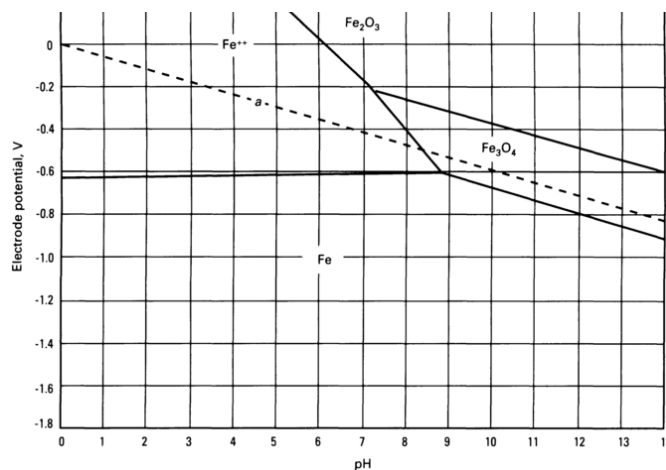


Figure 1: Pourbaix diagram for iron in water.⁷

Steels are primarily composed of Fe; therefore, the potential-pH diagram of Fe is used to predict the behavior of this material. The three main regions of the diagram correspond to the three types of corrosion behavior: immunity, passivation, and active corrosion. The region labeled "Fe" corresponds to immune behavior; the iron's expected chemical state is solid, metallic iron. The region labeled Fe_2O_3 corresponds to passive behavior, with the printed chemical formula describing the protective oxide layer that forms. Finally, the region labeled " Fe^{2+} " corresponds to active behavior, showing that solid iron is being converted to its ionic form.

1.2 Forms of Corrosion Damage

Metals or alloys can exhibit a variety of corrosive behaviors. Several forms of corrosion relevant to the petrochemical industry are pitting corrosion and hydrogen damage.

Every engineering metal or alloy is susceptible to pitting corrosion depending on the environment. This highly localized form of corrosion features sharply-defined holes, which may be small or large and can form closely together or are isolated. Pitting corrosion can be difficult to detect because material failure can occur with small weight loss as early as a few months to as long as several years. Causes of pitting include: biological organisms, breaking of the protective oxide coating via a mechanical or chemical process, and a local loss of passivity. In steels, Fe

can form shallow pits when immersed in soil or deep pits within a seawater environment.⁵

Hydrogen damage covers multiple types of corrosion all due to a reaction between a metal substrate and hydrogen with residual or applied stresses on the system. Multiple hydrogen processes, including sulfide stress cracking and hydrogen embrittlement, can affect steels exposed to sour environments such as H₂S. Internal pressures of hydrogen form stresses present in hydrogen induced cracking (HIC) while steels undergoing hydrogen stress cracking and sulfide stress cracking (SSC) utilize applied stresses.^{6, 8, 9}

After absorbing enough hydrogen, many high-strength steels (typically quenched and tempered or precipitation-hardened) may lose tensile ductility, causing material failure. This form of corrosion, hydrogen embrittlement, requires a small amount of hydrogen present (0.1 to 10 ppm) to initiate, which can originate from gaseous hydrogen and thermal processing. Hydrogen stress cracking is considered a form of hydrogen embrittlement, observable in a temperature range from -100 C to 100 C. The internal diffusion of hydrogen to stress concentration starts an internal crack, initiating corrosion. Sulfide stress cracking is considered to be a form of hydrogen stress cracking in the presence of water and H₂S. HIC can corrode steel pipelines in three steps: hydrogen atoms first form on the substrate surface, diffuse into the steel, then the build-up in voids and fissures

forming blisters. Internal pressure increases eventually causing cracks that connect the blisters.^{6, 8, 9}

1.3 Prevention

Corrosion can be prevented using one or more of the following methods: alloy additions and four others, including coatings and inhibitors. Si has been found to have various effects when added to steels. For example, most steels contain a small percentage of silicon as it makes it harder and stiffer by hardening the ferritic phase. It also alters the electrical and thermal properties by increasing resistivity. The addition of Si in steel removes oxygen, as it is an important deoxidizer. At high temperatures, silicon can increase oxidation resistance of steel.¹⁰

Serajzadeh and Taheri studied the effects of Si on the flow behavior of steel.¹¹ The authors found that an increase in the Si content increased the strength of austenite while decreasing the rate of dynamic recovery and recrystallization as well as the diffusion rate of C. It was concluded that these factors led to an increase in flow stress and consequently, higher activation energy for silicon steel than of the self-diffusion energy for austenite.

Another study measured the effect of silicon coatings on the corrosion rates of various steels by measuring the mass lost within each test environment. It was concluded that the corrosion resistance of the steel containing higher silicon

contents increases with siliconizing time along with the carbon content of the steel.¹²

Although limited data is available on the effects of Si on the corrosion resistance of steels, it is known that if enough Si is added to steel, the stress corrosion resistance of the material can increase. In one experiment, five 4340 steel samples each containing different levels of Si (0.09 wt. % to 2.15 wt. %) were placed under tensile stress, then NaCl solutions were dropped onto the samples. It was observed that stress corrosion crack velocity decreased in the samples containing higher amounts of Si although the threshold stress intensity parameter did not increase.¹³

Because of these limited results, it may be beneficial to explore C-based steels that contain Si.

1.4 Testing

There are multiple electrochemical methods of corrosion testing, all of which are based on the mixed-potential theory. This theory provides information about corrosion and can help to determine the corrosion rate or the corrosion behavior of the metal (active, passive or immune).¹⁴

An elementary electrochemical cell (Figure 2) is composed of two half-cells. The anodic site, where the metal is located, is linked to the cathodic site by a metallic

path. Net oxidation reaction occurs at the anode while net reduction takes place at the cathode. The corrosion rate is equal to the anodic and cathodic rates. During these reactions, there is a transfer of electrons and ions at the surface of the anode and cathode and therefore a change in electrical potential. This constitutes the electrochemical cell where electrons flow from the anode to the cathode.¹⁴

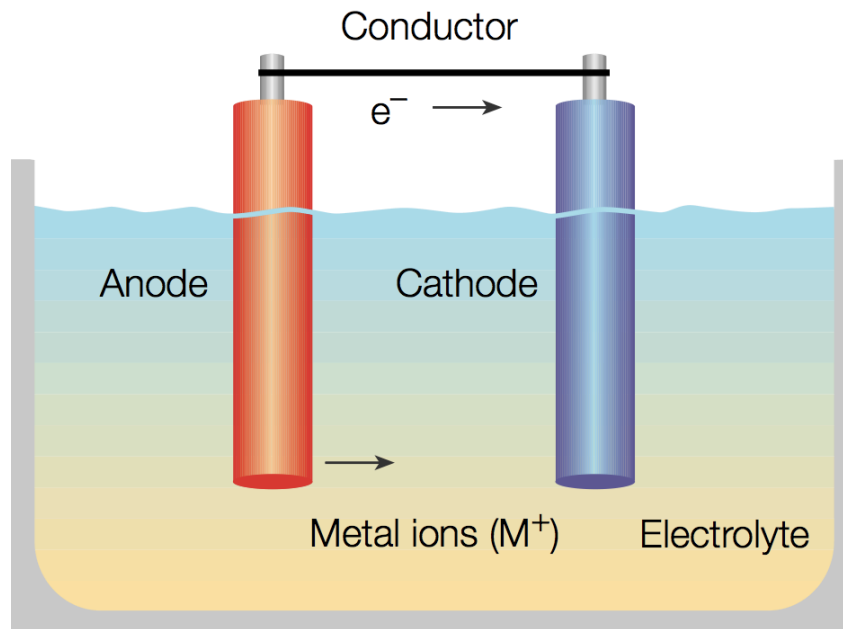


Figure 2: Diagram of an electrochemical cell.¹⁵

Electrochemical corrosion is often tested using a potentiostat. A metal sample, along with two different electrodes, is immersed within an electrolyte solution (Figure 3). The potentiostat allows the user to adjust the potential of the sample and measure the current between the working (sample) and the reference electrode. Anodic and cathodic reactions take place at the working electrode where the corroding metal is placed. The reference electrode has a constant electrochemical potential while the counter electrode conducts the current from

the working electrode leaving the solution. For a potentiostatic experiment, potential is constant and current is measured as a function of time. In a potentiodynamic experiment, potential varies and current is now a function of potential. Conversely, current can be controlled instead of the potential for a galvanostatic or galvanodynamic experiment.¹⁴

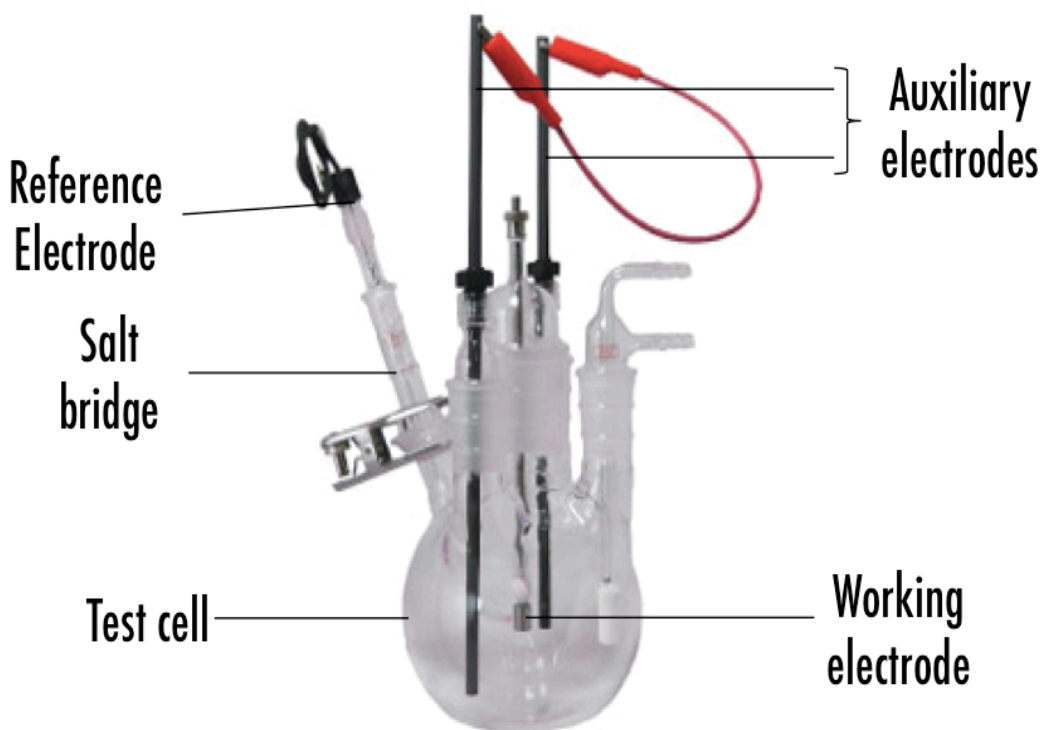


Figure 3: A schematic potentiostat highlighting the different components.¹⁶

Employees of Chevron were interested in the corrosion behavior of carbon steel in H_2S at high temperatures. It was suspected that changing the Si alloy content in carbon steel affects the electrochemical corrosion resistance of the material. The corrosion resistance of multiple steels was to be measured using ASTM G59-97: Standard Test Method for Conducting Potentiodynamic Polarization

Resistance Measurements. Similar to and containing references of ASTM G5-94, this test describes how to take polarization resistance measurements of working electrodes of various samples.^{17, 18}

2.0 Experimental Procedure

Instead of hydrogen sulfide (H_2S), a dangerous chemical, corrosion properties were to be tested in hydrochloric acid (HCl) and aqueous carbon dioxide (CO_2). These two solutions are acidic gases known to cause corrosion problems in the petrochemical industry. CO_2 is corrosive, especially if hydrated (such as aqueous CO_2); however, corrosion can be prevented using an aqueous CO_2 solution with a pH value greater than 6. The solution chosen, carbonated water, contained a pH of 7.2 (Appendix B). On the contrary, HCl is a strong acid and can be found in refineries (in chlorine salts dissolved in water or suspended solids). A molarity of 12 M, the highest concentration at which HCl is thermodynamically stable, was chosen for testing.¹⁹ The electrochemical properties of three steels, ASTM A516-GR70, A106M, and C1020 (Appendix A) were measured using potentiodynamic tests, outlined in Standard ASTM G59-97: Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements. Six different tests were run, with each sample tested in each solution, three times for consistency.

2.1 Test Cell Preparation

900 mL of the desired solution was placed in the polarization cell. Both auxiliary electrodes were rinsed with distilled water and placed into the glass adapters,

which were fit into the 24/40 joints of the cell. The salt-bridge probe and purge tube were placed in the test cell as well, and after closing the center with a glass stopper, the salt bridge was filled with test solution. Tests were conducted at room temperature (between 21.8 and 22.0 °C).

2.2 Sample Preparation

Less than one hour before each test, a reference electrode was wet ground using 240 and 600 grit SiC paper, rinsed with distilled water and ethanol then dried.

The reference electrode was weighed and total surface area that would be exposed to the solution was calculated using dimensions specified to the nearest 0.01 mm. Finally, the sample was mounted onto the electrode holder and placed within the corrosion cell. Adjustments were made to the salt bridge so that the tip was about 2 mm or 2 times the tip diameter (whichever was larger) from the working electrode.¹⁸ Each electrode was connected to the potentiostat (Parstat 2273) via the cell connector: the working electrode lead and sense electrode lead to the working electrode, the counter electrode lead to one auxiliary electrode, reference electrode lead to the reference electrode (saturated KCl was used), and ground cable to a metal surface. An alligator-alligator test lead was used to connect the two auxiliary electrodes together. Tests were run using a potentiodynamic linear sweep at a rate of 0.1660 mV/s.

2.3 Calculations

Density

The density of each steel was calculated as follows: samples that were not used were weight and measured to calculate the density of each sample. These values were then averaged to obtain the average densities (Table I).

Equivalent weight

The equivalent weight of an element is its atomic weight divided by its valence. For an alloy, it is equal to the sum of the equivalent weight of the element greater than 1 weight %.²⁰ Equivalent weight of each sample was determined (Table I).

Table I: Calculated density and equivalent weight of samples

	C1020	A516	A106
Density (g/cm ³)	7.996	8.205	8.344
EW	27.67	27.65	27.28

Corrosion rate

Theoretical corrosion rates were calculated using Equation (1)²⁰:

$$CR = K \times \frac{i_{\text{corr}}}{\rho} \times EW \quad (1)$$

Where K is a constant, i_{corr} is the corrosion current density from Tafel plots ($\mu\text{A}/\text{cm}^2$), ρ is the density of the working electrode (g/cm^3), and EW is the equivalent weight of the working electrode.

3.0 Results

Tafel plots provided the corrosion potential (E_{corr}) and i_{corr} of each test. From this information, the corrosion rates of each test were determined and averaged among those samples in carbonated water (Figure 4a) and those in HCl (Figure 4b).

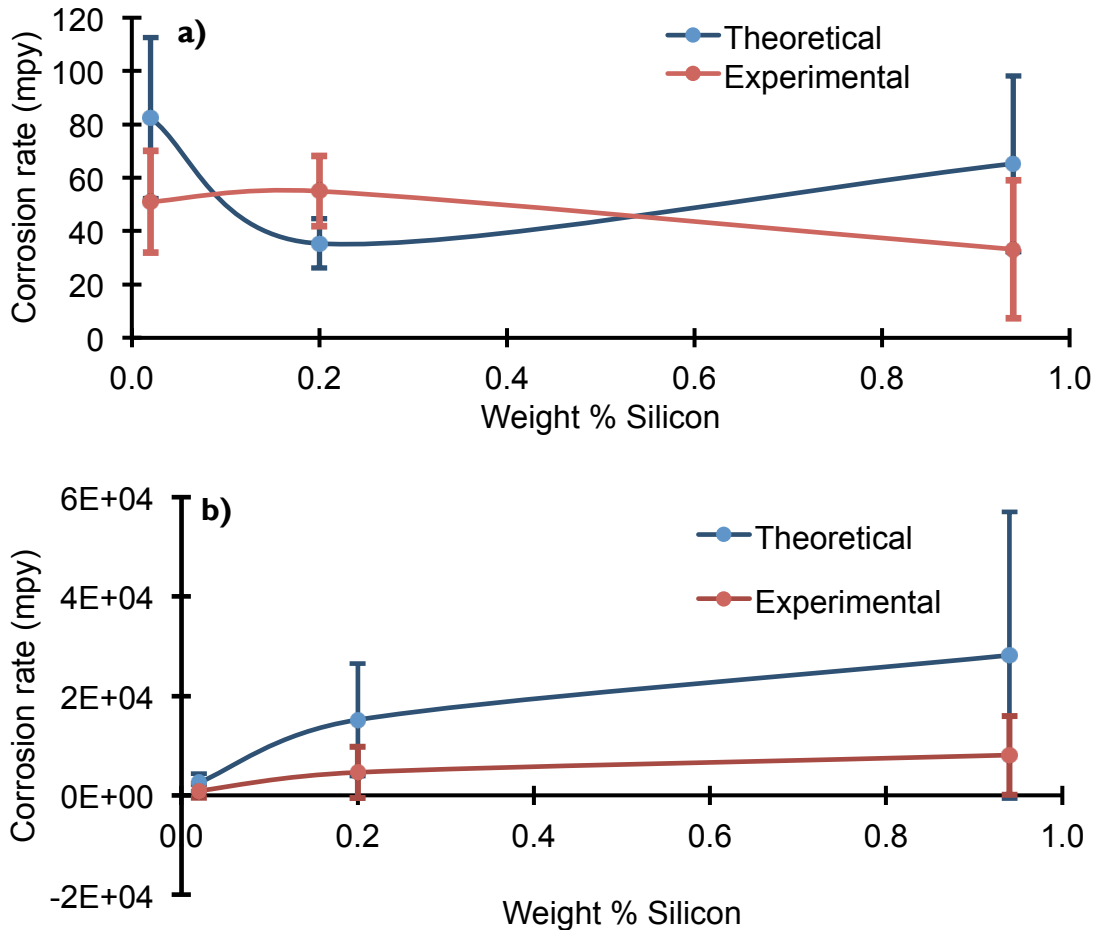


Figure 4: Corrosion rates of steels immersed within a) carbonated water and b) 12M HCl for an hour. Note the difference in magnitude of corrosion rates between the two solutions.

Weights of samples were measured before and after potentiodynamic tests then averaged (Figure 5). It is important to note that weight loss was much more dramatic in HCl than in carbonated water.

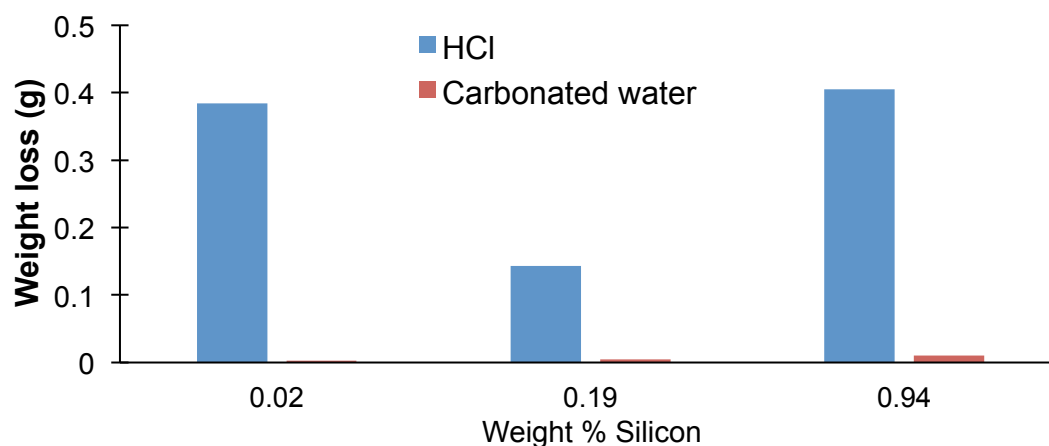


Figure 5: Average weight loss of samples due to corrosion.

Additionally, micrographs of each sample were taken with a scanning electron microscope (SEM) (Figure 6).

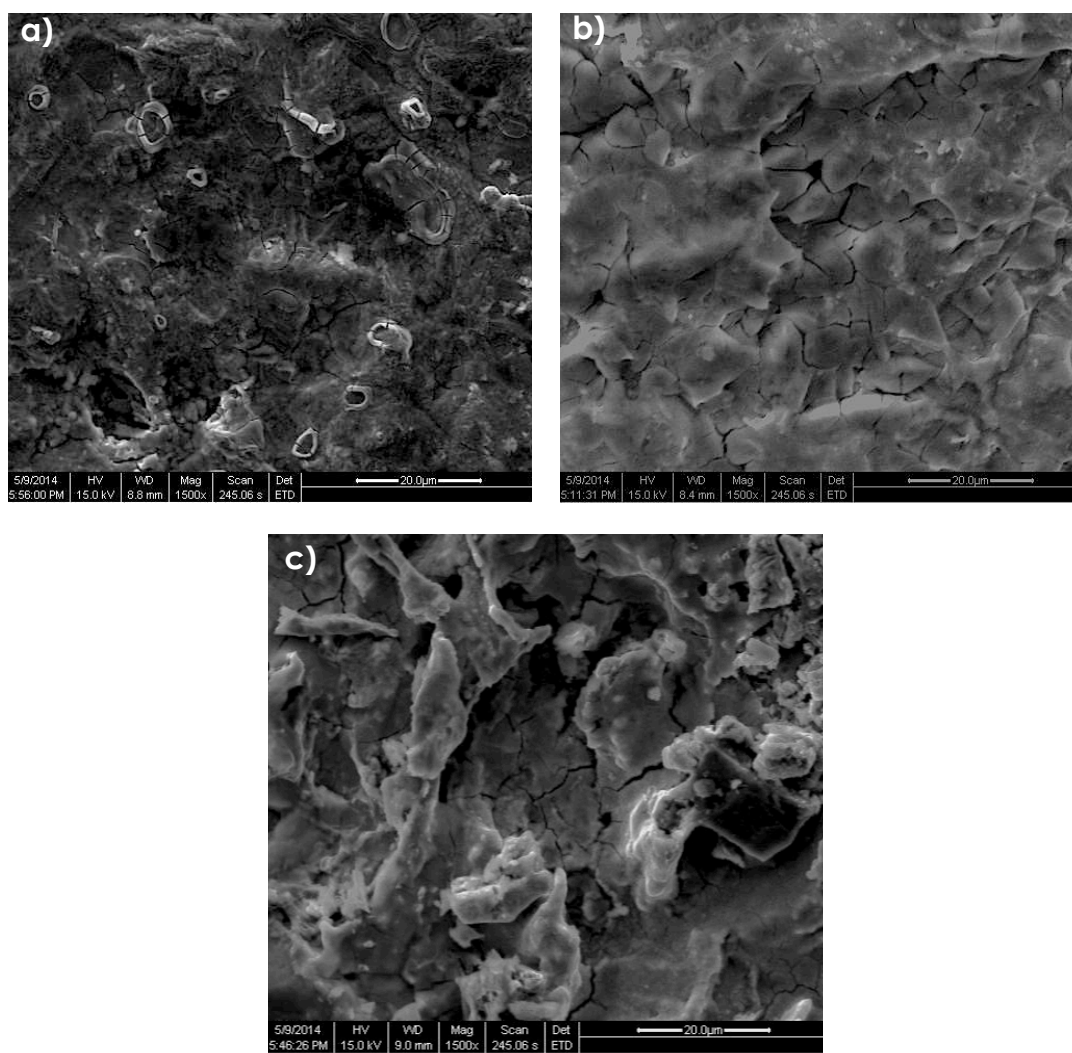


Figure 6: SEM images of a) A106 at 1500x, b) A516-GR70 at 1500x, and c) C1020 at 1500x, all after being immersed in 12M HCl for an hour.

4.0 Discussion

Results show that corrosion rates within carbonated water did not have a specific trend based on Si content due to inconsistencies between theoretical and experimental data. It was indicated that steel samples containing higher Si contents had higher corrosion rates in HCl, supported by theoretical values. Unfortunately, each level of Si in both solutions had high standard deviations, sometimes larger than the averaged value.

Average weight loss of samples within HCl shows a decrease with increasing Si content to the 0.19 level then increases at the 0.94 level. This contradicts the corrosion rate trend; however, it is important to note that both corrosion rate and weight loss were much more significant in HCl than in carbonated water. Samples containing higher Si content had higher weight loss when immersed in carbonated water, which was unexpected based on the results from corrosion rates.

The small holes in Figure 6a, found over the entire surface, indicate the sample went through pitting corrosion. Although no pits were found in either A516-GR70 or C1020, the cracks shown are another indication that corrosion has occurred. A516-GR70 appeared to contain more cracks than C1020, meaning more corrosion occurred in the former sample.

The conclusions were insufficient given the variability in the results may have been due to several of the limitations encountered. It was initially determined that three trials for each sample/solution combination would provide adequate results. Unfortunately, high standard deviations of corrosion rates were obtained in both HCl and carbonated water. Although results might have been different, theoretical calculations of HCl support these results. It would still be beneficial to run more tests to ensure the trends are what they appear to be. A second limitation might have been due to the different sample geometries. Two metals, A106M and C1020, were rectangular cuboids while A516 was cubic, shaped as such for ease of manufacturing. No literature was found that explored differences in results due to working electrode geometry, although different geometries have been used across multiple experiments. Lastly, there were several ASTM standards that could have been used, such as ASTM G1, which contains procedures on test specimen preparation, removal of corrosion products, and evaluation of the corrosion damage. This standard discussed three categories of cleaning samples: mechanical, chemical, and electrolytic. Samples in this experiment were mechanically cleaned using rough grind; other methods could have provided more thorough cleaning.

5.0 Conclusions

1. Weight loss results showed that HCl is much more corrosive to low carbon steel than carbonated water.
2. Corrosion rates in HCl appear to increase with increasing Si content.
3. While Si may reduce corrosion, there is no evidence that increased Si will help more than less Si.

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Appendix A: Sample Compositions

Element (weight. %)	A106M	A516-GR70	C1020
C	0.204	0.19	0.13
Mn	0.961	1.09	0.48
Si	0.94	0.19	0.02
Ni	0.02	0.13	0.02
Cr	0.02	0.17	0.04
Mo	0.02	0.05	<0.005
Ti	-	0.015	-
V	0.001	0.005	<0.005
Al	0.026	0.026	0.03
S	0.005	0.002	0.017
P	0.011	0.010	0.015
Cu	0.02	0.25	0.06
B	-	0.0001	-

Appendix B: Carbonated Water Quality Report of Inorganic Minerals and Metals

Substance	MRL	MCL	Level Found
Calcium	0.10	NR	161
Sodium	0.20	NR	11.7
Potassium	0.10	NR	1.4
Fluoride	0.100	2.0 (1.4 - 2.4)	0.16
Magnesium	0.020	NR	5.5
Bicarbonate	1.0	NR	335
Nitrate	0.010	10.00	1.5
Chloride	0.10	250.00	24.6
Copper	0.050	1	ND
pH (units)	NA	6.5 - 8.5	7.2
Sulfate	0.10	250.00	49.9
Arsenic	0.014	0.010	ND
Lead	0.005	0.005	ND
Total Dissolved Solids	1.00	500	472

MCL Maximum Contaminant Level

MRL Minimum Reporting Limit

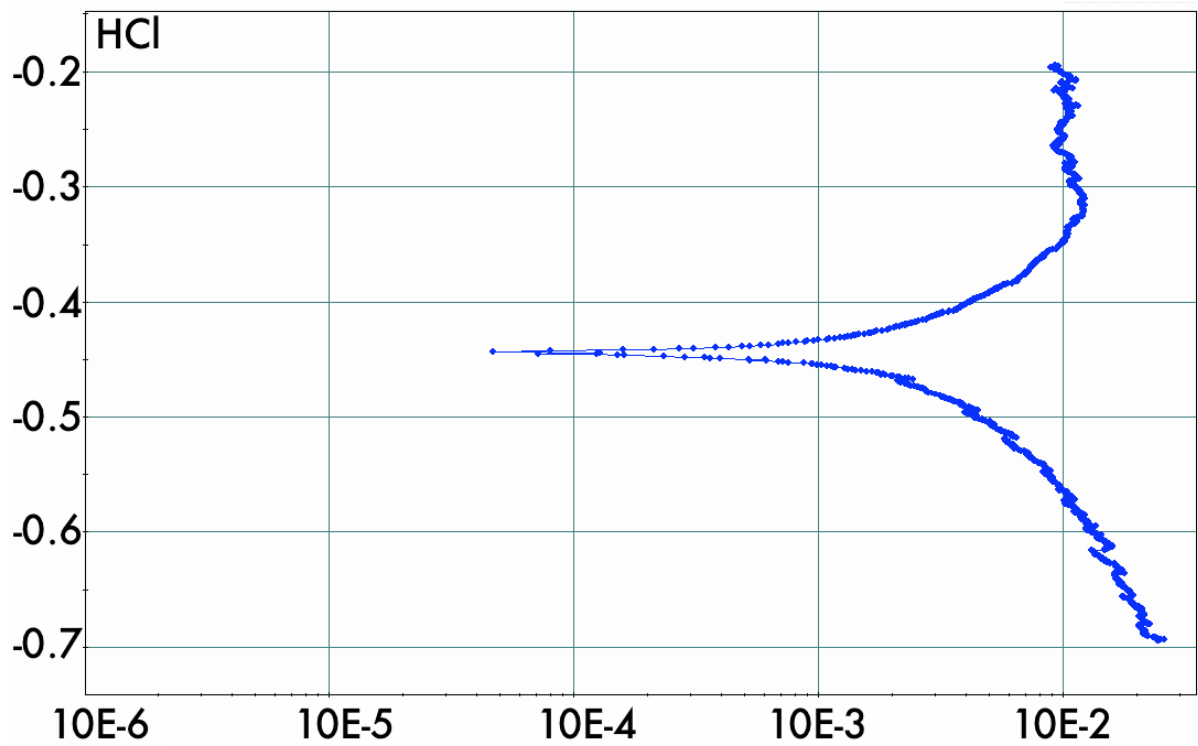
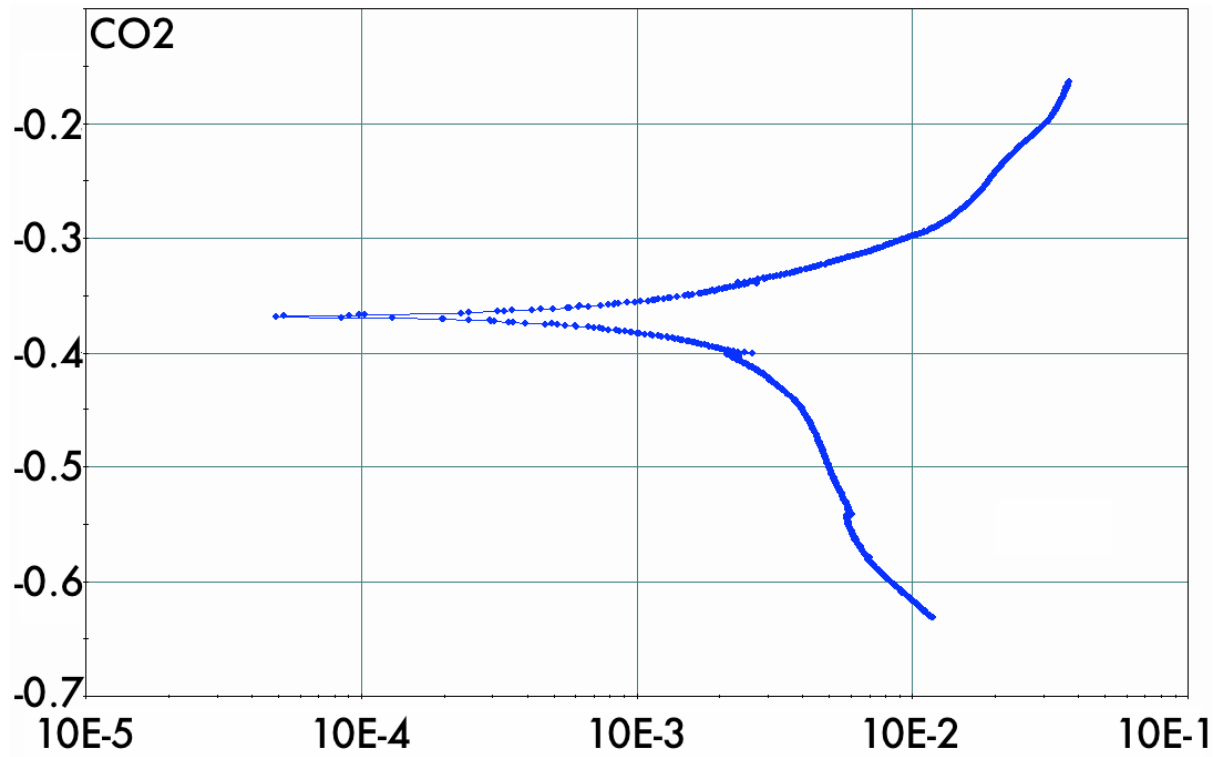
NR Not Regulated

ND Not Detected

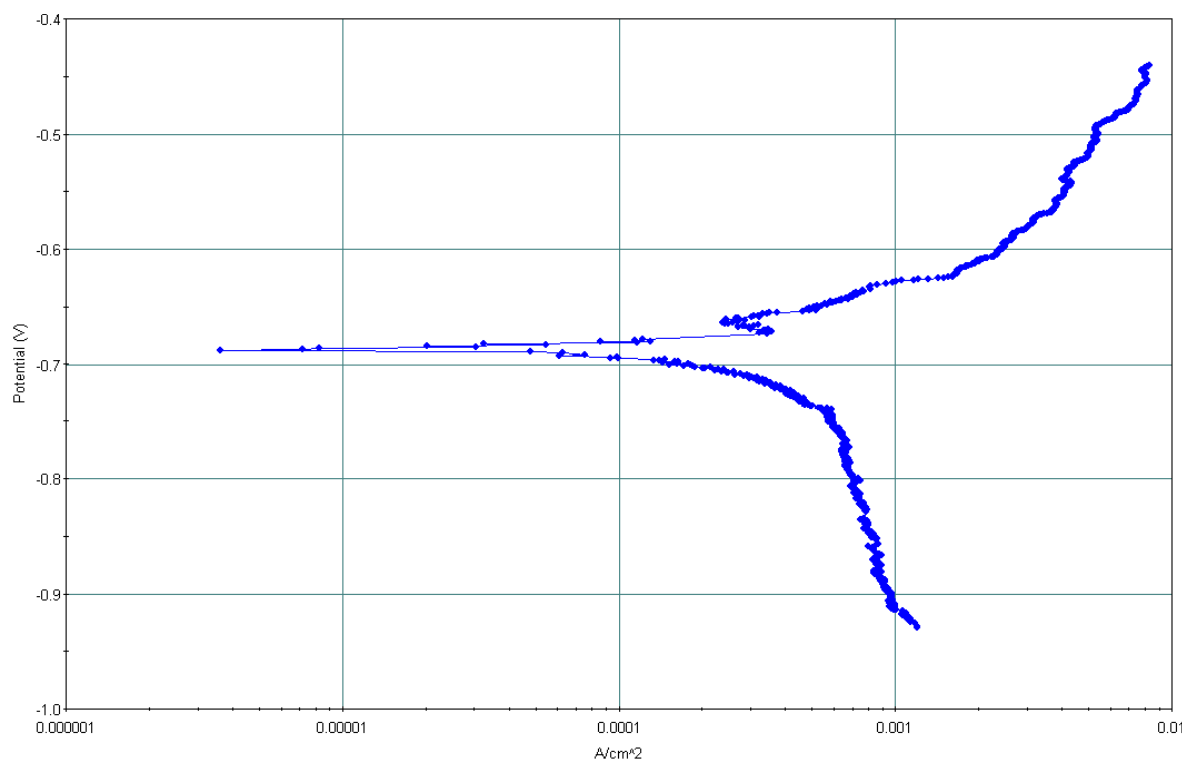
NA Not Applicable

Source: Perrier Water Quality Report, December 2010

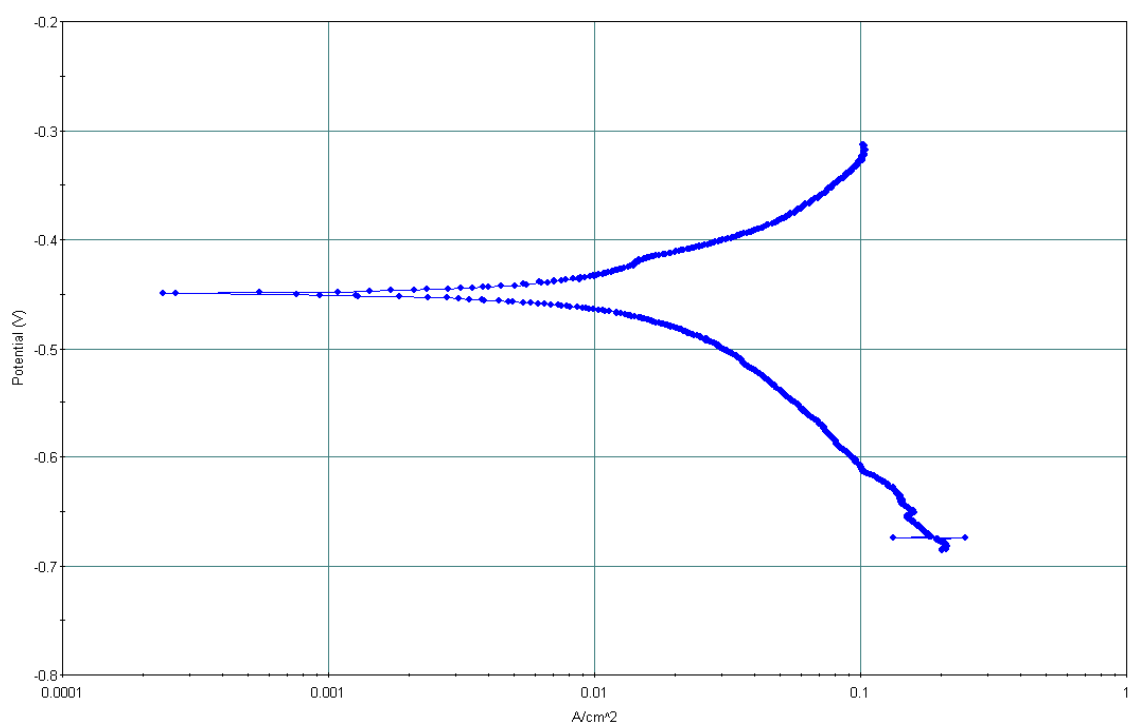
Appendix C: Potential vs. Current Density plots for each test



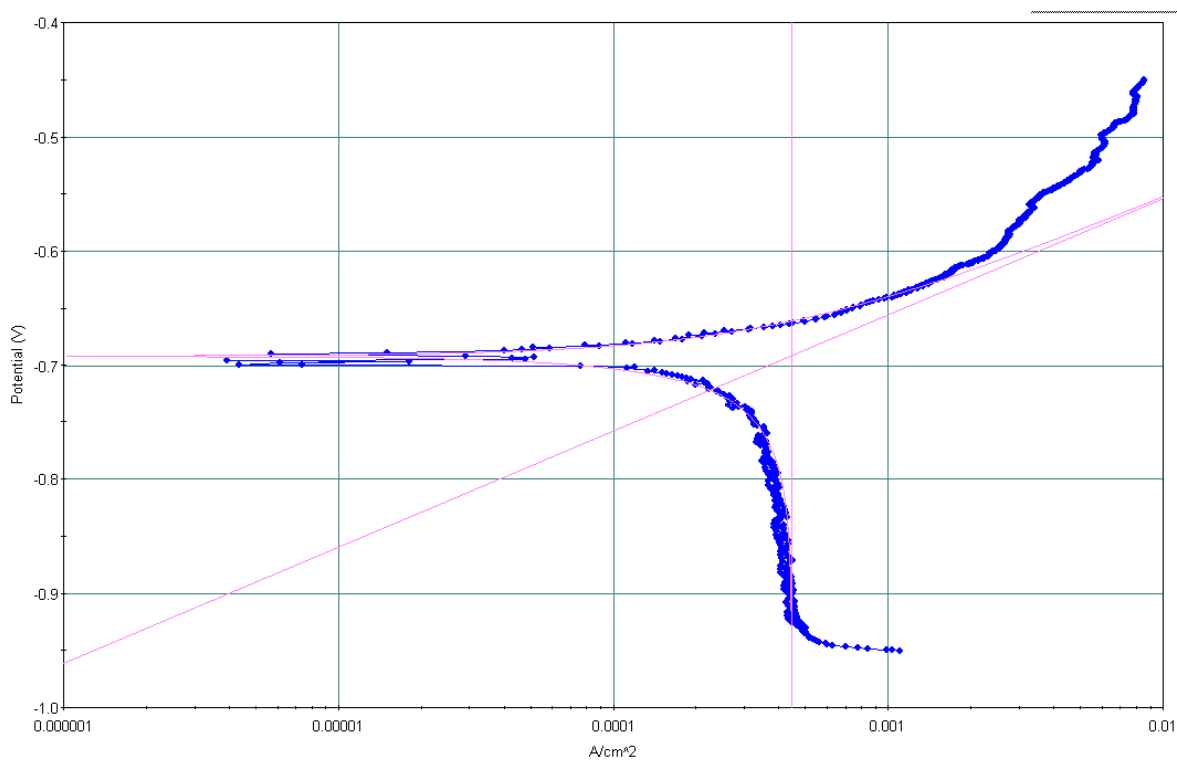
A106M, HCl



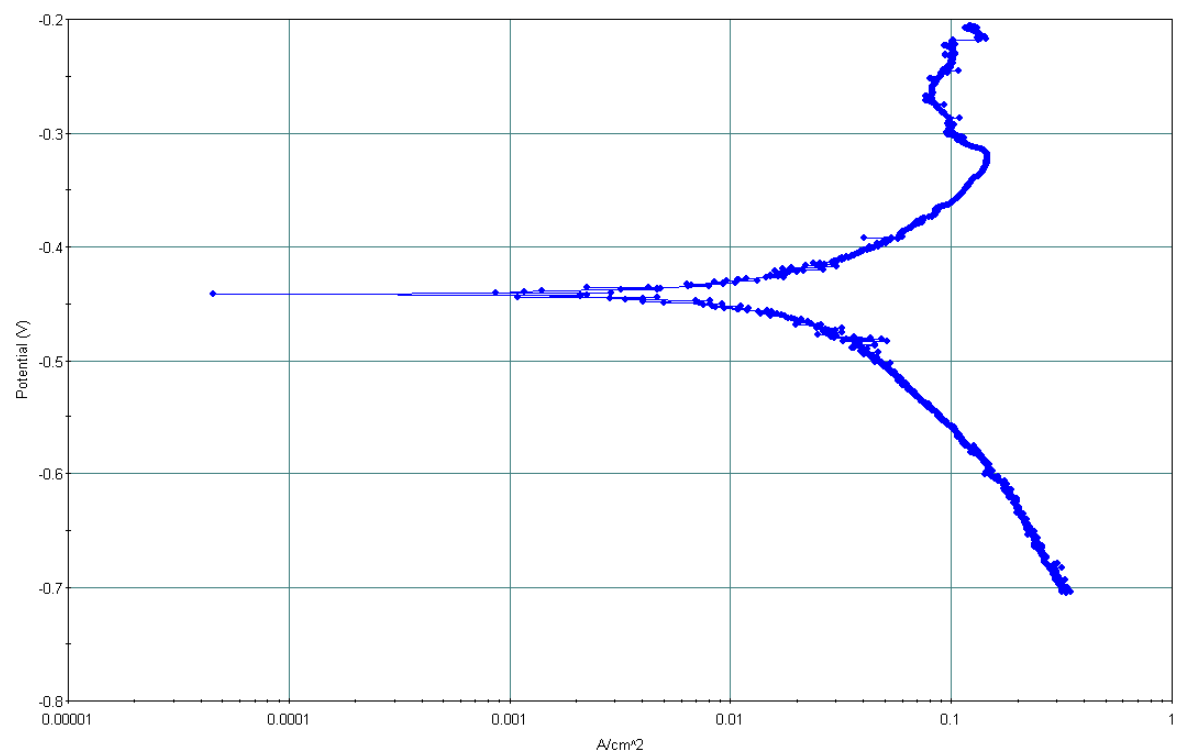
C1020, carbonated water



C1020, HCl



A516, carbonated water



A516, HCl