The Analysis of Electroplating Methods on Corrosion Resistance

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Steel is used for infrastructure, appliances, buildings, and other materials due to its tough, weldable, and durable nature; however, it is susceptible to corrosion. Zinc, on the other hand, has high corrosion resistance, though it lacks many desirable properties that steel has. By electroplating steel with zinc, chemically producing a layer of zinc around steel, the resulting material can retain the positive qualities of steel while having an additional layer of corrosion protection. The objective of this experiment was to determine which combination of factors for electroplating steel would yield the highest corrosion protection when exposed to saltwater. The experimental design was based off of a two-factor Design of Experiment (DOE), and it was analyzed with that DOE, along with an ANOVA test. Two critical factors in the electroplating process were examined: potential difference and the duration the steel was electroplated for. Each steel sample was electroplated with zinc under a specific set of conditions according to the DOE. After the steel samples were plated, they were immersed in salt water for calculation of the response variable: the change in mass per unit area from before corrosion testing to after. A partnership with DENSO allowed for surface examination of the samples before plating, after plating, and after corrosion testing with a Scanning Electron Microscope (SEM). After analyzation, it was determined that both potential difference and time were significant, while the interaction effect was not. The ANOVA test further validated the effectiveness of the variables with a rejection of the null hypothesis. It was proven that although increasing voltage and time does increase the mass and thickness of the plated layer, the quality declines. A direct relationship does not exist between the quantity and quality of an electroplated layer.

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Introduction

In the modern world, material science is growing rapidly, for materials are constantly being used for new and unique purposes. One of the biggest focuses of material science is metals. Metals have countless uses across various industries. They are used for plumbing, electronics, silverware, automobiles, airplanes, boats, rockets, military equipment, weapons, and much more. Metals have the ability to conduct electricity and are among the strongest materials in existence. While metals are often durable and highly effective in their physical properties, they are subject to a variety of physical and chemical changes. One of nature’s most effective chemical processes is corrosion. Corrosion can take a robust metal and degrade it until the point of failure. Not only does corrosion impact the integrity of a metal, but it can also have a negative impact on the environment. Large boats and ships, for example, are usually made from steel or steel alloys. As steel components corrode from salt water, sulfides present in polluted harbors, and overall galvanic corrosion, the material is weakened, and the excessive amount of metal ions released into the water can be harmful to the existing flora and fauna. Fortunately, some metals are more resistant to corrosion than others. Unfortunately, those metals often do not have the necessary properties for their purpose. This often creates a dilemma, since a certain metal desired for a critical purpose cannot effectively work if it is heavily subject to chemical changes such as corrosion. The solution? Electroplating.

Electroplating is the chemical process of taking a piece of metal and coating it with the metal ions of another metal that is usually more corrosion resistant, resilient, conductive, or cosmetically appealing. This allows for the use of powerful metals in industry that are lacking some physical or chemical properties. For example, steel is often used for infrastructure, appliances, buildings, and more because it is incredibly strong, tough, weldable, and durable; however, it is very susceptible to corrosion. I-beams, made from steel, are heavily used in architecture. Due to steel's firm and stable nature, I-beams have a cross section that looks like the letter "I", making them less than half the mass of a regular beam with a rectangular cross section and economically efficient to use. In reality, steel is an alloy of iron, carbon, and other elements, so it rusts easily because iron oxidizes easily. The following figure is a side by side comparison of new I-beams and I-beams that have rusted.

Figure 1. Effect of Corrosion on Steel ("Steel I-Beams")

Figure 1 shows new I-beams (left) and I-beams that have rusted over time (right). As corrosion progresses, the beams lose strength and stability.

It is not a question in industry whether steel should or should not be used, but it does lack in its ability to resist corrosion. Ways for solving this problem must be explored. In contrast to steel, zinc has high corrosion resistance, though it lacks many desirable properties that steel has. By electroplating steel with zinc, the resulting sample can retain the positive qualities of steel while having an additional layer of corrosion protection.

It is crucial that metals are resilient as the failure of them is harmful economically and environmentally and can put the lives of many at risk. The objective of this experiment was to find a method for electroplating steel that would yield the highest corrosion protection when exposed to saltwater, the corrosive agent used for testing. The experimental design and analyzation process were based off of a two-factor Design of Experiment (DOE). Moreover, two critical factors in the electroplating process were examined: potential difference (voltage) and the duration of time the steel was electroplated for. Each steel sample was electroplated with zinc under a specific set of conditions according to the DOE. After the steel samples were plated, they were immersed in salt water for three days for calculation of the response variable: the change in mass per unit area from before corrosion testing to after. A valuable partnership with the international automotive supplier, DENSO, allowed for detailed surface examination of the samples before plating, after plating, and after corrosion testing with a Scanning Electron Microscope (SEM). At the conclusion of experimental testing and analyzation of the response variable measured (change in mass per surface area), the descriptive statistics collected using the Scanning Electron Microscope, and the observations made throughout the duration of the research trials, it was evident that using a high voltage significantly decreases plating quality. The samples plated under the condition of a high voltage, despite different plating times, suffered from significant mass loss after corrosion testing compared to the samples that were plated at a low or standard voltage. The time of electroplating also had a significant effect on electroplating quality. The results of an ANOVA statistical test validated these findings. The conclusions are helpful for industry as they prove that the quality of the electroplating layer hits a tipping point as the voltage increases.

With new technology and innovation on the rise, industries are also focused on improving past developments. Steel and other metals and alloys have incredible qualities. They can bear heavy loads and withstand intense environmental changes. This research experiment studied methods for improving the corrosion resistance of steel through electroplating.

Review of Literature

This experiment's purpose was to determine the effect of changing potential difference and the time of electroplating on the ability for zinc plating to prevent the corrosion of plated steel. The important scientific concepts in this experiment lie within properties of metals, electroplating, and corrosion.

Electroplating is the process of coating a metal with another metal. This procedure is carried out in the presence of an electrolyte solution and a power source with positive and negative terminals. There are two metals involved in a simple electroplating process: the cathode and anode. The cathode is the metal that will be plated, and the anode is the metal that will plate onto the cathode. In this experiment, zinc was the anode, and steel was the cathode. For electroplating, both metals are placed in the same electrolyte solution, often called a "bath," as shown in Figure 4, where the cation of the salt (zinc) matches the anode (Kanani). For this experiment, the electrolyte solution was zinc nitrate.

In an electrolytic "bath," the cathode is attached to the negative terminal of the supply, and the anode to the positive. Electrons flow from negative to positive in a circuit, opposite of conventional current (McMillan). For electroplating to ensue, this is vital. The solid anode loses its electrons, traveling through the power source and negatively charging the anode. The rest of the zinc then becomes aqueous in the solution. The following half-reaction equation gives the oxidation reaction at the anode when it is zinc (Lou, Yinlun). Half reactions represent the oxidation or reduction component of a redox reaction.

$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$

Figure 2. Oxidation Half Reaction of Zinc

Figure 2 displays the half reaction of zinc during electroplating. The half reaction is an oxidation reaction because the anode loses electrons. The electrons from zinc, the anode, flow through the power source and negatively charge the cathode. The positively charged ions from the anode are then attracted to the negatively charged ions of the solid cathode, which was steel in this experiment.

$Fe^{2+}{}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$

Figure 3. Reduction Half Reaction of Steel

Figure 3, above, displays the half reaction of iron during electroplating. Steel was technically used for this experiment, but since steel is largely made of iron (atomic symbol Fe), the half reaction of iron was used for the equation to represent steel. The half reaction is a reduction reaction, because the cathode gains electrons. Once the steel is negatively charged, it attracts the positive aqueous zinc ions that are produced from zinc's half reaction (Figure 2). This completes the electroplating process as zinc forms a solid layer around the steel (Lou, Yinlun). Figure 4, below, shows the setup of the experiment.

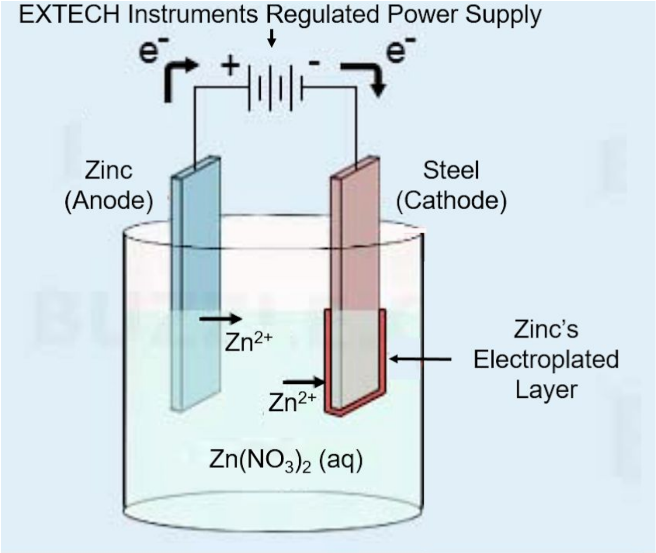


Figure 4. Experimental Setup ("Zinc Plating")

Figure 4 shows the experimental setup. Figure 2's reaction takes place at the zinc anode and Figure 3's takes place at the steel cathode. The electrons flow through the power supply to negatively charge the cathode. The positive zinc ions are then attracted.

Faraday's Law, one of the crucial aspects of this experiment, states that "The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed" ("Faraday's Laws Of Electrolysis…"). In the following equation, let Q represent mass deposited, I represent current, t represent time, and Z represent the electrochemical equivalent.

$$Q = I \times T \times Z$$

The three factors that affect plating are time, current, and the electrochemical equivalent. The electrochemical equivalent is unique for each metal, and it aids in quantifying the mass of anodic plating. While that value is constant, time and current may be altered by various experimental designs. In this experiment, the electrochemical equivalent was not considered; the electrochemical equivalent is based off of the anode used. SInce the only anode used was zinc in this experiment, the constant affected each trial to the same degree.

As aforementioned, the first factor for this experiment was the potential difference, measured in volts, of the power supply. While potential difference was the factor, current is actually what affected electroplating. Current is the rate of flow of electric charge (McMillan). The higher the current (measured in amperes), the more electrons that flow per unit of time. Current is related to potential difference, as stated by Ohm's law:

$$V = I \times R$$

In Ohm's law, let V represent potential difference, I represent current, and R represent resistance. This equation can be simply rearranged so current equals potential difference divided by resistance. For electroplating, the natural resistance of the wires and the solution are essentially constant, so resistance is negligible within the equation. Potential difference was simply easier to adjust and keep constant on the EXTECH Instruments Regulated Power Supply, which was the power source used for electroplating, so it was chosen as the factor for the experiment. However, it is technically still the current, not the potential difference, that affects electroplating. It was only possible to use potential difference since it alters current directly, as Ohm's Law states. For electroplating, an increase in current increases the plating layer thickness, since the greater flow of electrons allows electroplating to occur quicker (“Chemistry Simulations”). Because potential difference increases as current increases, an increase in potential difference leads to an increase in the mass of a plated layer on the cathode.

The second factor in this experiment was time of the electroplating process. Generally, the longer the time the metals are in the electroplating solution, the more the cathode is plated by the anode (“Chemistry Simulations”). This is simply because there is more time for the oxidation reaction to take place at the anode, and therefore, more time for the reduction reaction to occur at the cathode. In this experiment, the positive zinc ions had more time to make bonds with the negatively charged steel ions, creating a layer of greater mass.

There are numerous different methods of electroplating that are both similar and different to the method used in this experiment. This experiment used a simple electrolyte solution and a power source to facilitate the necessary redox reactions, all within one bath. Similarly, a galvanic cell has the anode and cathode separated in containers, each with a solution of the respective metal bonded with the same anion or negative polyatomic, connected with a porous disk or a salt bridge. The setup of those bridges prevents the physical solutions from mixing (Zumdahl) while still allowing the ions from the anode to travel to the cathode. This type of setup is not often used for electroplating as much as other electrolysis experiments, specifically when the desired plating metal is different from the cathode. Galvanic plating is often complex, unnecessary, and inefficient for plating many objects or parts instantaneously. Another variation of electroplating that is used quite often in industry cases is plating a metal with the same metal. There is no need for a salt in the solution, only a power source (Zumdahl).This is method is cheap, and is often only done for minor metallic reinforcements, or for decoration. One other unique method for electroplating harnesses solar energy. In a specific experiment designed by the University of Missouri, a photovoltaic device was able to power the electrolytic process, where a nail was nickel plated, and was successfully corrosion resistant (Dix). This process is much more complicated from an energy standpoint, but is quite astounding and eco-friendly; amazingly, the plated nail worked successfully for corrosion resistance. Unfortunately, that experiment did not allow for any human manipulation of current or potential difference, which would make it hard to replicate and control.

When it comes to assigning an anode, the anode should be more reactive than the cathode to accomplish the purpose of electroplating for corrosion resistance. “The most reactive elements tend to be short one or two electrons or have one or two extra” (University of California Santa Barbara). Another significant factor in the reactivity of an element is the structure of the atoms themselves. The Activity Series of Metals (Appendix A) lists metals in order of their reactivity from highest to lowest (Libretexts). The more reactive a metal is, the faster it will corrode, because it is the most likely to oxidize. The goal of electroplating is not necessarily to eliminate all corrosion, for corrosion is inescapable; the goal is to minimize the corrosion of a base metal, the cathode, by introducing a sacrificial anode that will corrode instead. Therefore, the anode must be a metal that is higher on the activity series than the cathode. Metals on the activity series commonly used as sacrificial anodes or for electroplating are aluminum, magnesium, zinc, and chromium. Common base metals used in industry are copper and steel. Steel is not on the standard activity series list because it is an alloy though it was confirmed that zinc is above iron in the activity series. The method of electroplating used in this experiment utilized cold rolled steel as a cathode and zinc as the anode. This was an appropriate selection of metals because zinc is more reactive than steel.

Metals are electroplated for various reasons, with one of the most popular being corrosion resistance. Metals are plated to increase corrosion resistance because many of the metals or metal alloys that are strong, lightweight, or cost efficient that are desirable to use in industry do not have sound anti corrosive properties. The professional contact for this research project, Derek Aluia, is the head of Materials Engineering at DENSO, an international automotive supplier. In his department, they electroplate car parts to decrease their sensitivity to thermal changes, while preventing corrosion. Many parts that go in an engine are made of or electroplated with a metal that has a high specific heat. This is to control heating of the engine, as failure to do so could result in serious problems. Derek Aluia also uses electroplating to make parts smoother; he specifically mentioned that he electroplates the rotor and other metals used for breaks. This is to decrease the friction that is present when they are rotating, while providing strong protection from corrosion for quality assurance of the metals over time.

There is frequent discussion in industry around electroplating to ensure that the products manufacturers produce and the methods they use are efficient and fulfilling their intended purpose. Experimental testing and observations are essential to the progression of this idea. Francis LaQue from the Center for Corrosion Technology conducted a study in which he placed steel plates in different atmospheric environments for a whole year and studied their corrosion. The most prevalent factors in each of the atmospheres were salt content in the air, the time the metal was kept wet, temperature, and other atmospheric pollutants. From this experiment, LaQue noted that, “samples location 80 feet from the ocean corroded six times faster than a location 800 feet from the ocean” (North Carolina State University). It is also important that the test results from this study took place after a year of exposure. The method used for corrosion analysis is similar to that used in this experiment. The zinc plated steel plates were placed in a salt solution, sodium chloride, for an extended period of time. From LaQue’s observations, it was expected that the extent of corrosion would increase with time. That is, the metal would lose more mass.

As a whole, electroplating and corrosion are the main concepts behind this experiment. Potential difference and time of electroplating were the two factors focused upon in the electroplating process, as determined by Faraday’s Law. The goal was to determine how changes in these variables affected the corrosion of zinc-plated steel. It is understood that if the electroplated layer is thicker and consistent across the cathode, the plated metal will have sufficient protection from corrosion inducing oxides, acids, sulfides, and salts. In this experiment, corrosion in the presence of a salt solution, sodium chloride, was explored.

Problem Statement

Problem:

To determine the effect of the electroplating process on the corrosion resistance of plated steel.

Hypothesis:

If steel is plated with zinc at 4.5 volts for 60 seconds, the change in mass per a specific area through the corrosion process will be the smallest, and the change in the thickness of the plated sample will be the smallest.

Data Measured:

The independent variables in this experiment were potential difference (in volts, V) and the duration of electroplating (in seconds, s). The low, standard, and high levels used for potential difference were 1.5 V, 3.0 V, and 4.5 V. The low, standard, and high levels used for time were 30 s, 45 s, and 60 s. The measured response variable used for statistical analysis was the change in mass (grams) over a specific area (cm^2) from corrosion.Qualitative descriptions of the metals before and after corrosion were collected by means of a Scanning Electron Microscope. A Design of Experiment (DOE) was be used to determine to what extent changing different factors in the electroplating process affected the corrosion resistance of plated steel. An ANOVA test was also used to compare the mean change in mass over a given area.

Experimental Design

Materials:

(2) 1 L Beaker
(23) 100 mL Beaker
5% NaCl, Sodium Chloride Solution 2.00 L
1.0 M $Zn(NO_3)_2$, Zinc Nitrate 2.00 L
10% Hydrochloric Acid Solution 100 mL
Lab Grade Acetone
Analytical Lab Balance (0.0001 g precision)
Digital Micrometer (0.001 in precision)
Distilled Water
Stamping Die (optional)
Gloves
Scanning Electron Microscope (SEM)
EXTECH Instruments Regulated Power Supply
(22) 1 in x 2 in x 22 gauge Pure Zinc Sheet Metal (Anode)
(22) 1 in x 2 in x 22 gauge Plain Steel Sheet Metal, Hillman H# 11770 (Cathode)
Silicon Gel
Teflon Tape
Alligator Clips
Ruler
Aluminum Foil
KIMTECH Kimwipes
Large Pill Containers
Large Paintbrush
Small Paintbrush
X-ACTO Knife
Snippers

Procedure:

Prepare Steel Cathode and Zinc Anode

1. Cut 1 in. x 2 in. pieces of zinc and steel using snippers and a stamping die (optional). Weigh a few samples of each metal to check that samples are of similar mass.

2. Wearing gloves, use soap and water to clean off the metals. After rinsing, chemically etch all of the metal samples, including zinc, by placing each one in 100 mL of hydrochloric acid for 1 minute. Let samples dry completely before any testing is completed.

3. Continue to wear gloves when handling samples.

Electroplating the Steel

1. Record the masses of one piece of steel and one piece of zinc with an Analytical Lab Balance.

2. Turn on the power source to the voltage required for the unique trial according to the Design of Experiment.

3. Attach one piece of steel to the negative terminal of the power source and one piece of the zinc to the positive terminal with alligator clips, as shown in the Figure 7.

4. submerge the zinc anode and steel cathode in 90 mL of 1.0 M $Zn(NO_3)_2$ solution. The metals should not be touching and the alligator clips should not be submerged in the solution. See Figure 8.

5. Allow the metals to sit in the beaker for the duration required for each respective trial. Halfway through the time, rotate both the anode and cathode by 180°.

6. Remove the zinc and the zinc-plated steel sample from the 1.0 M $Zn(NO_3)_2$ solution.

7. Allow the plated sample to sit overnight to dry. The zinc can be disposed of.

8. Repeat steps 1-7 for each factor combination in the DOE for 11 samples in total. Nine of the trials have unique combinations. Two are repeats of the standard/standard combination (S,S), that is, 3.0 volts and 45 seconds.

Acetone Wash and Initial Measurements

1. Once samples are dry, use a dry, large paintbrush to remove loosely plated zinc from the steel samples.

2. Give each sample an acetone wash to remove any more loose zinc using acetone and the kimwipes.

3. Record the mass of each sample again. Ensure that each steel sample did indeed gain mass from the electroplating. This will count as the initial mass for each sample.

Masking the Edges

1. Place each plated metal sample between two pieces of teflon tape, ensuring that there are no trapped air bubbles.

2. Use an X-ACTO knife to cut out a 1 cm x 2 cm rectangle of teflon tape on the plated side of each sample, as seen in Figure 9.

3. Seal off the edges of the cut out rectangle with a thin layer of Silicon Gel, as seen in Figure 9. The Silicon Gel can be applied using a small paint brush (optional).
4. Label all samples by marking the teflon tape.
5. Let masked samples sit overnight to allow the silicon to dry.

Testing for Corrosion

1. Fill multiple 100 mL beakers with 90 mL of 5% NaCl solution, enough for every sample/trial.
2. Place every sample in its own beaker, ensuring that all areas of the exposed region on the sample are submerged in the corrosive solution.
3. Cover beakers with foil and let them sit for three days.
4. Remove the samples from the 5% NaCl solution.
5. Carefully remove the teflon tape.
6. Repeat steps 1-3 in the *Acetone Wash and Initial Measurements* section for every sample, this time, recording the final mass.
7. Calculate the change in mass for each sample from before corrosion testing to after by subtracting the initial mass from the final mass.
8. Divide the change in mass by the area of the surface exposed, theoretically 1 cm x 2 cm, to calculate the response variable for each trial.

Using the Scanning Electron Microscope

1. Use a Scanning Electron Microscope with EDS software to record descriptive statistics of the metal samples before and after corrosion tests.

Diagram:

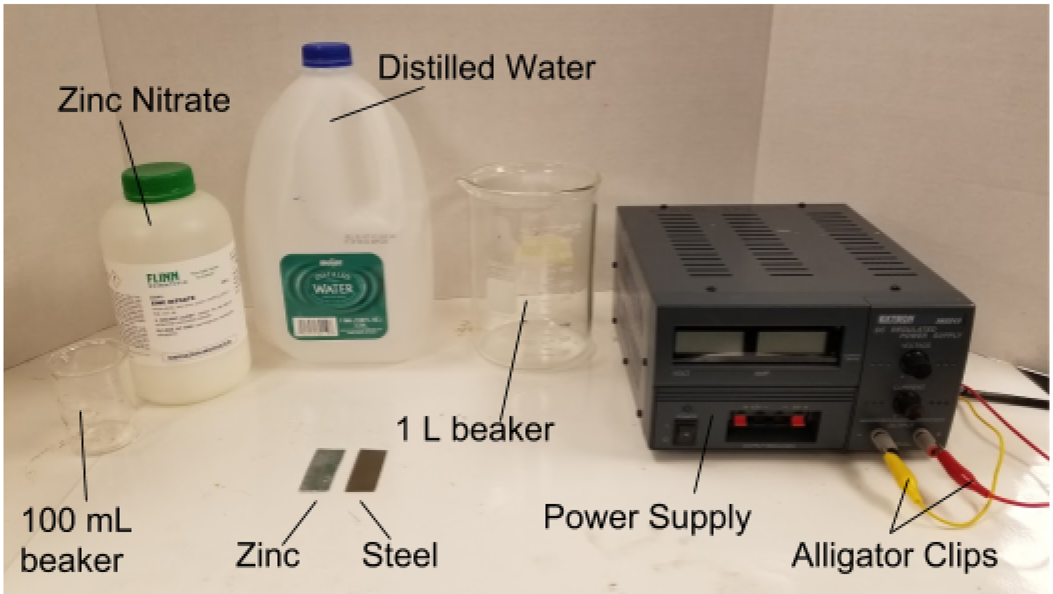


Figure 5. Electroplating Materials

Figure 5 displays the materials that were required to complete the electroplating portion of the experimental setup. Not pictured are the stamping die and snippers used to cut the metal pieces, the hydrochloric acid Solution used for chemically etching the samples, the analytical lab balance used for weighing the samples, gloves used to keep oils from gettings on samples, and the large pill containers used to organize, label, and transport samples at multiple points throughout the testing and analyzation process.

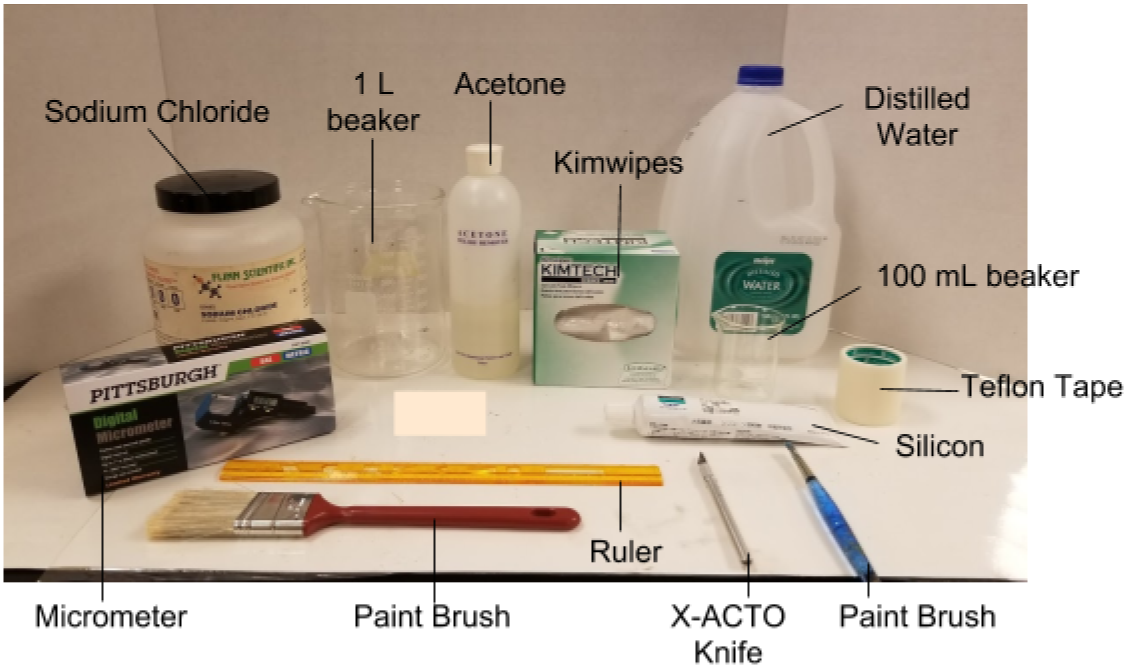


Figure 6. Corrosion Testing and Analyzation Materials

Figure 6 displays the materials required for corrosion testing and analyzation of the samples. Not pictured are the aluminum foil used to cover solutions for overnight storage and the Scanning Electron Microscope.

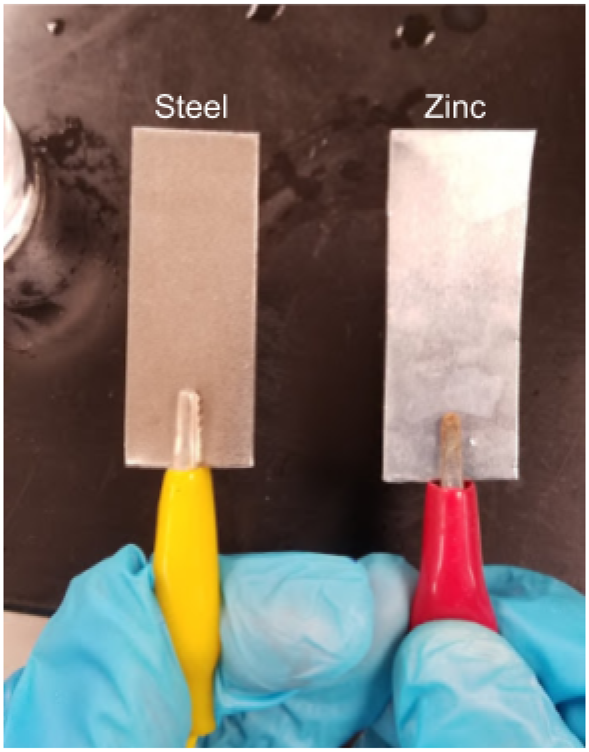


Figure 7. Attaching Alligator Clips to Steel and Zinc

Figure 7 shows how the steel and zinc samples were connected to the power source for every trial. The steel piece was connected to the negative terminal of the power source with a yellow alligator clip. The zinc was connected to the positive terminal of the power source with a red alligator clip.

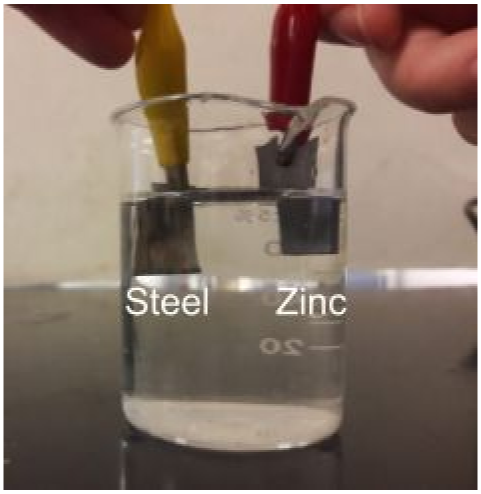


Figure 8. Electroplating Steel

In the experiment depicted in Figure 8, a solution of zinc nitrate was used as the electrolyte in the electroplating process. The cathode, steel, is connected to the negative terminal of the power source, and the anode, zinc is connect to the positive terminal of the power source.

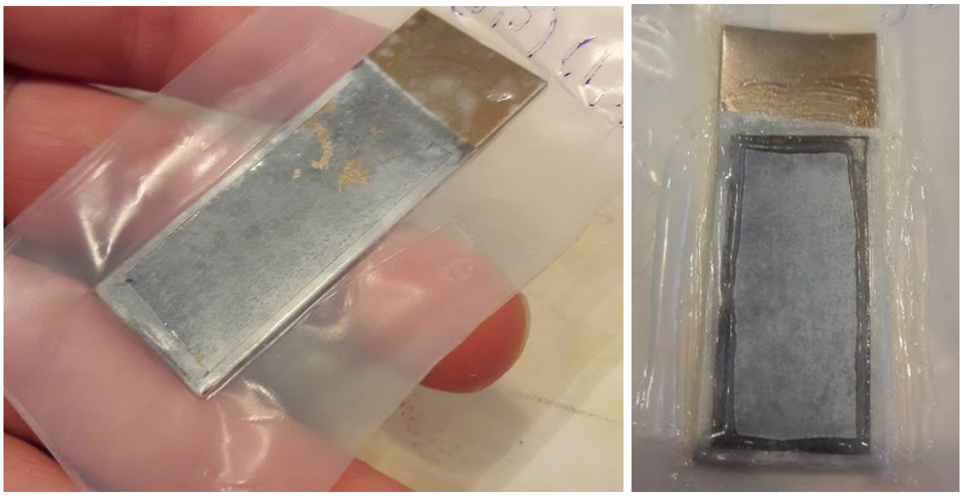


Figure 9. Denso Method

Figure 9 shows how the “Denso” method was used to tape the plated metal sample, and then how the correct surface area of teflon tape was cut out and the edges were glued off to prevent air bubbles during the corrosion testing. The silicon overlapped the teflon tape by about one millimeter.

Data And Observations

To test how electroplating steel affected its protection from corrosion, two factors were used throughout the electroplating process of this experiment. Table 1, below, shows the two factors and their three variances.

Table 1
Factors and Variables

Potential Difference (Volts)			**Time (Seconds)**		
(-)	S	(+)	(-)	S	(+)
1.5	3.0	4.5	30	45	60

The first factor was the potential difference applied, measured in volts, for the electroplating process. The second factor was time, in seconds, of the electroplating process. These numbers were determined throughout the pretrial portion of the experimental process. There were a total of nine combinations throughout this experiment, with a permutation for each variance between factor, including the low, standard, and high values.

Table 2, below, shows the final results from the experimental data, including all the factor combinations. Two DOEs were tested for the change in mass from after electroplating, to after corrosion. To calculate the “unit area,” the metal samples were taped in such a way that an exact amount of plated surface area was exposed to the saltwater solution that would corrode the zinc plating. In turn, the change in mass from before plating to after was divided by the area of the exposed plating, to find the numerical results of the experiment.

Table 2
Trials Results

DOE		**1**	**2**	**Average**
ΔMass per Unit Area Exposed (g/cm^2)	(S,S)$_1$	-0.0088	-0.0069	-0.0079
	(+,+)	-0.0258	-0.0157	-0.0208
	(+,S)	-0.0060	-0.0133	-0.0096
	(+,-)	-0.0190	-0.0104	-0.0147
	(S,+)	-0.0055	-0.0105	-0.0080
	(S,S)$_2$	-0.0246	-0.0088	-0.0088
	(S,-)	-0.0101	-0.0046	-0.0074
	(-,+)	-0.0055	-0.0065	-0.0060
	(-,S)	-0.0038	-0.0006	-0.0022
	(-,-)	-0.0007	-0.0040	-0.0024
	(S,S)$_3$	-0.0085	-0.0065	-0.0075

Table 2, above, shows the results for the two DOEs and the change in Mass per Unit Area Exposed in grams per square centimeter. Three “standard, standard” trials were ran, as denoted by (S,S) and a subscript. The second standard trial ran in the first DOE, (S,S)$_2$, as highlighted in the table, was a large outlier compared to the the other five standard trials, so that standard was exempt during analyzation to prevent skewness. With that standard removed, the total average for the standard trials was -0.0079 g/cm^2. This data set will be the data that is formally analyzed in the Data Analysis and Interpretation section. Appendix D may be used to compare the DOEs to each other.

Additionally to the change in mass per unit area, the zinc-plated steel samples were measured with a micrometer. While the initial thickness results were somewhat useful, the final results were inconsistent. Within the five used standards, the change in plating thickness was largely different. While in other experiments, this may have meant the experiment was inconsistent, that is not true for this experiment. The measurements in Table 2 were fairly consistent, while the micrometer measurements were drastically more variant. As a result, those numbers will not be reported.

Table 3
First DOE Observations

Trial	Factor Combination	Observations
1	$(S,S)_1$	Steel had small, rusty patch before plating was completed. Base zinc piece has black blotchy patterns after plating
4	(+,+)	Fairly bad corrosion on steel before plating. Plating layer was thicker on one half of the steel; thickness of the plating layers was consistent within the two differences. Base zinc appeared to oxidize consistently
5	(+,S)	Slight corrosion before plating, though fairly clean metal piece. Base zinc appeared to oxidize evenly
8	(+,-)	Bad corrosion on steel beforehand. Accidentally started timer approx. 4 seconds late. Visual plating is the same as (+,+). Base zinc oxidized evenly
10	(S,+)	Clean steel piece, even plating. Base zinc oxidized evenly
3	$(S,S)_2$	Small visual amounts of corrosion on steel beforehand. Mostly even plating layer. Base zinc oxidized evenly This trial was removed from the statistical analysis due to its nature as an outlier
6	(S,-)	Extreme corrosion on one side of steel before plating; plating was completed on the other side, which was fairly clean. Base zinc oxidized evenly

Trial	Factor Combination	Observations
7	(-,+)	Bad corrosion on bottom half before plating. Less plating on bottom half. Base zinc oxidized evenly.
2	(-,S)	Steel had some rusting across sample beforehand. Accidentally unplugged positive wore before testing; no apparent plating happened. Trial was reran. Base zinc oxidized evenly
9	(-,-)	Clean piece of steel. Even plating layer. Base zinc did not oxidize evenly
11	$(S,S)_3$	Mostly clean, slight corrosion at top. Plating was consistent across sample. Base zinc appeared to oxidize consistently

Table 3, above gives the observations for the first DOE, while Table 4, below, gives the observations for the second DOE.

Table 4
Second DOE Observations

Trial	Factor Combination	Observations
1	$(S,S)_1$	Perfect piece of steel before plating. Even plating layer. Zinc oxidized evenly
5	(+,+)	Fair corrosion on steel beforehand, but even throughout. Thick plating, but even layer. Zinc bubbled in the water during electroplating. Some zinc flakes fell straight to the bottom of the electroplating solution during plating
2	(+,S)	Perfect piece of steel before plating. Plating layer appeared thick. Zinc oxidized evenly
10	(+,-)	Clean steel piece. Rough, but even plating layer. Zinc bubbled a small amount during electroplating bubbling during plating. Fresh batch of zinc nitrate (started in Trial 7)
8	(S,+)	Fairly bad corrosion on steel beforehand, but even plating layer. Zinc oxidized evenly. Fresh batch of zinc nitrate (started in Trial 7)
6	$(S,S)_2$	Nice piece of steel. Mostly even plating, with a small concentrated area of thicker plating towards top of sample. Zinc oxidized evenly
4	(S,-)	Fairly bad corrosion on steel beforehand. Plating layer was fairly uneven. Zinc oxidized evenly

Trial	Factor Combination	Observations
3	(-,+)	Fairly even layer of small corrosion beforehand. Zinc oxidized evenly
9	(-,S)	Perfect piece of steel beforehand. Plating was extremely consistent across the sample. Zinc oxidized inconsistently. Fresh batch of zinc nitrate
7	(-,-)	Perfect piece of steel. Plating did not create a complete layer. Zinc oxidized evenly. Out of materials to rerun the trial. Used fresh batch of zinc nitrate from this trial on
11	$(S,S)_3$	Fairly bad corrosion on steel beforehand. Even plating layer. Zinc oxidized evenly. Fresh batch of zinc nitrate

Table 3 and 4 are a record of the observations from each trial. Observations were recorded on the appearance of the steel sample before it was plated, for some pieces already had some slight corrosion on them. The visual quality of the zinc coating after the sample was plated was also recorded, and the appearance of the zinc sample after it was used for electroplating was noted, for there were some differences across trials. When stating “zinc oxidized evenly,” this was meant that during the electroplating process, the zinc anode visibly was thinner, yet even, across its base piece.

Figure 10. Unauthorized Oxidation

Figure 10 shows an unexpected change in the appearance of the steel samples that occurred just minutes after they were chemically etched. All of the metal samples used in the trials, zinc and steel, were chemically etched with hydrochloric acid before use. The steel samples expressed signs of oxidation like the piece shown above. Because the change was consistent across all of the steel samples that were used, it was concluded that that this did not have any significant effect on the results; however, this is still considered “noise” in the experiment.

Figure 11. High and Low Voltage Differences

Figure 11 is a side-by-side comparison of the plating layer on a sample plated with a low voltage of 1.5 V (left) and a sample plated with a high voltage of 4.5 V (right). In all cases, samples that were plated with a low voltage had an even and consistent layer. The samples plated with a high voltage had a thick and rough layer. Although those plated with a high voltage had a thicker layer initially, most of the zinc fell off just from movement of the sample or during the acetone wash treatment that each plated sample underwent before being placed in the corrosive solution. After being cleaned, the high voltage samples ended up looking similar to the low voltage, as shown in Figure 12, below. The zinc plated onto the samples with a low voltage did not appear to fall off at all.

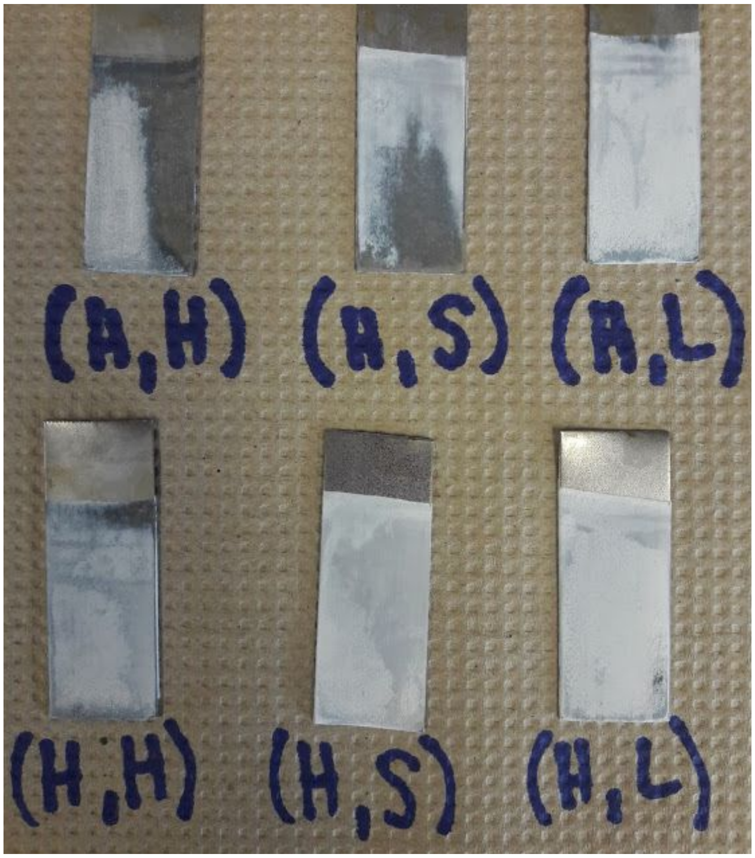


Figure 12. High Potential Difference Trials

Figure 12 displays the zinc-plated steel samples after the acetone wash treatment for all combinations of variables tested for which the potential difference was held at its high level of 4.5 volts. The top row is from the first DOE, the bottom row is the second. (Please note that “H” represents the “high” (+) level of a variable, and “L” represents the “low” (-) level). These samples had the thickest layers in general, though, as shown in Figure 11, they were the worst quality. As seen in the (+,+) and (+,S) combinations from the first DOE, the plating did not stay on entirely towards the right and bottom portions of each respective sample once the samples were cleaned.

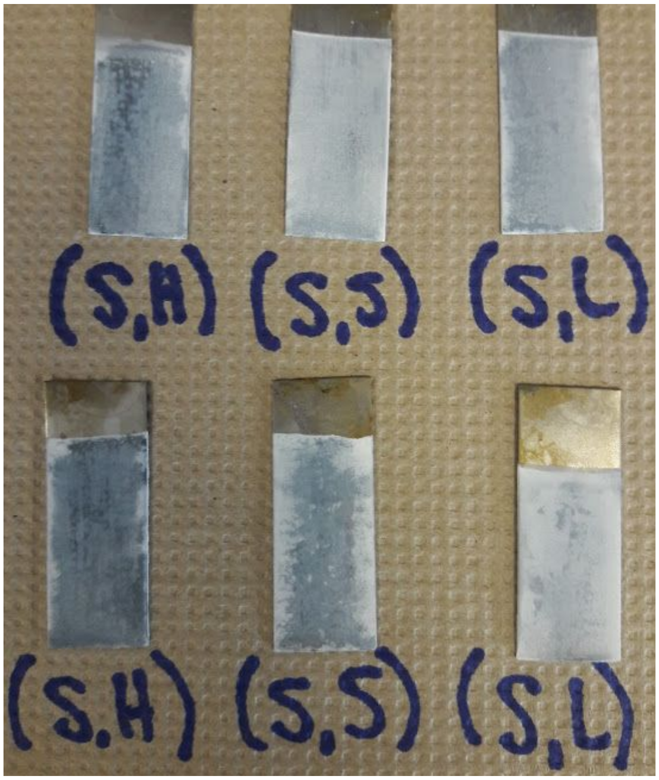


Figure 13. Standard Potential Difference Trials

Figure 13, above, shows the zinc-plated steel samples after the acetone wash treatment for all combinations of variables tested for which the potential difference was held at its standard level of 3.0 volts. These layers were visually of better quality than the samples that were exposed to 4.5 V. Also, with progression of time for the pictured samples, the thickness of the layer appears to increase.

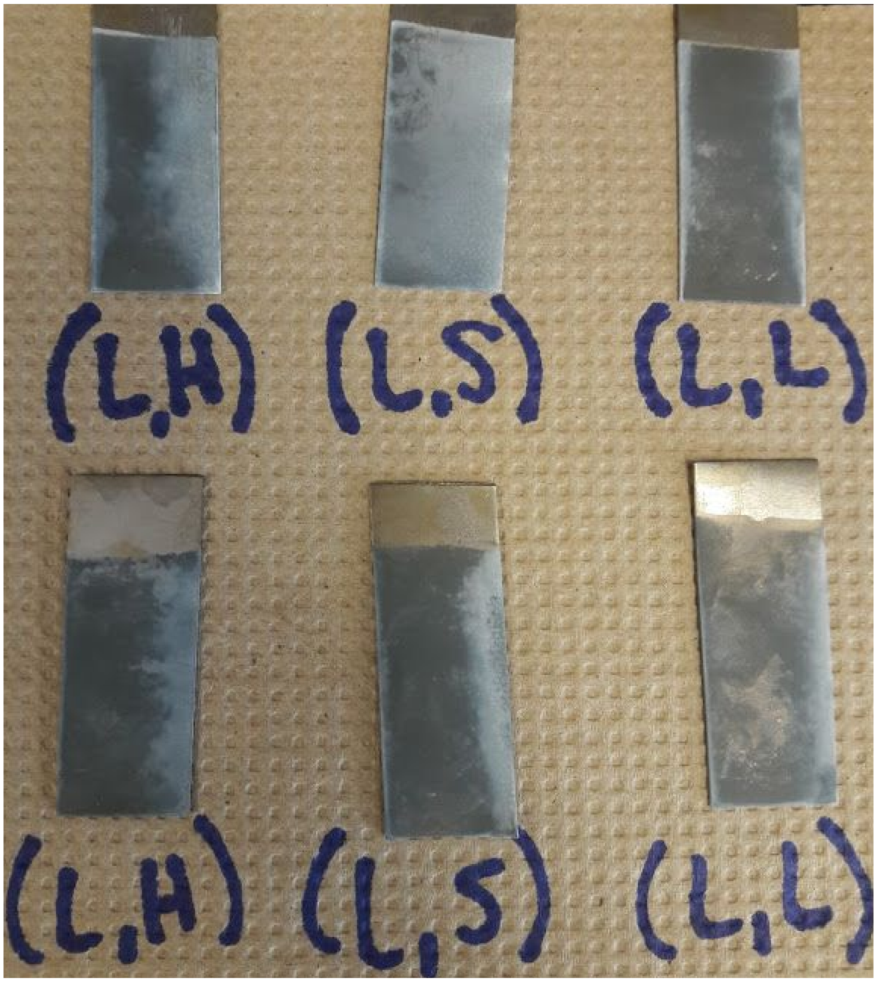


Figure 14. Low Potential Difference Trials

Figure 14, above, shows the six metal samples after the acetone wash treatment from both DOEs when the potential difference was 1.5 volts. When compared to the other samples right after electroplating, overall, these metal samples had the thinnest, but generally most consistent layers of plating. However, after the samples underwent the acetone wash treatment, the samples still had had the most consistent layer. The second (-,-) sample was a little different from the others as it had some spotty plating, with a few miniscule areas where the zinc plating was almost entirely gone after the acetone wash.

Figure 15. Error Through the Denso Method

Figure 15, above, shows some of the error that resulted in using the "Denso Method" to tape off the metals. Once the teflon tape was cut and removed, some small patches of plating came off with the tape. While considered noise, this was impossible to entirely avoid; it was countered with delicacy, though not to perfection. It was assumed that this did affect corrosion, but in an immeasurable way.

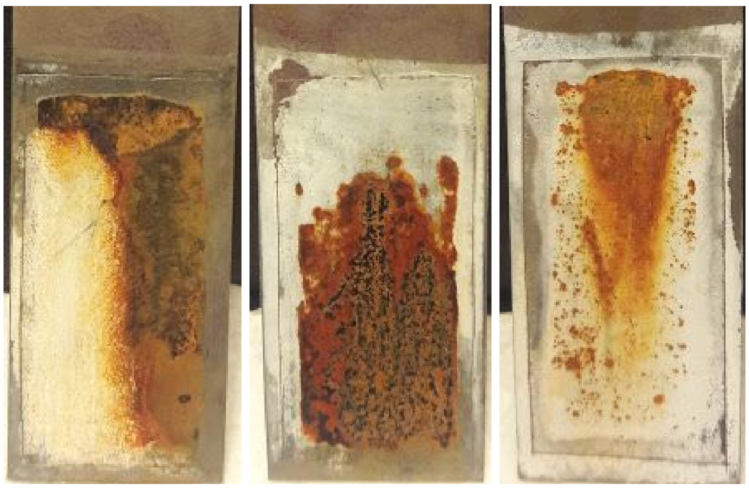


Figure 16. High Potential Difference Trials After Corrosion

Figure 16 shows the three steel samples from the first DOE that were plated with a high potential difference after the corrosion test, with the teflon tape and silicon sealings removed. Most of the corrosion and iron oxidation, rust, occurred where the layer of zinc was lacking to begin with, as comparable to the first row of Figure 12. This implies that the zinc layers worked well at not corroding.

Figure 17. Standard Potential Difference Trials After Corrosion

Figure 17, above, shows the three steel samples from the first DOE that were plated with a standard potential difference after the corrosion test. These samples can be compared to the first row of those in Figure 13.

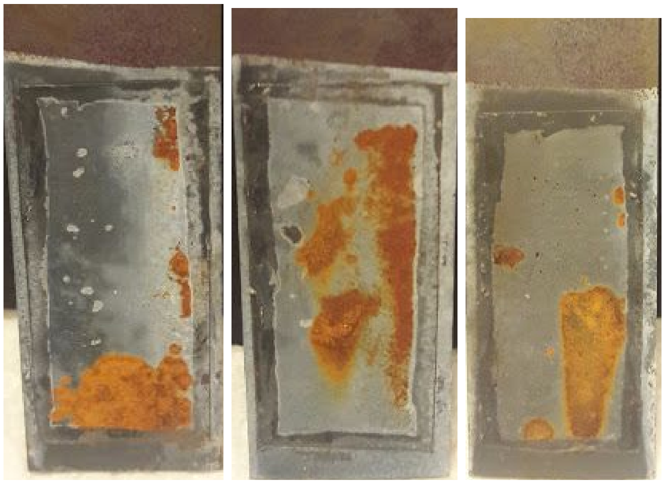


Figure 18. Low Potential Difference Trials After Corrosion

Figure 18 shows the three steel samples from the first DOE that were plated with a low potential difference after the corrosion test. These samples can be compared to the first row of those in Figure 14.

The following figures show an image after electroplating and after corrosion underneath the SEM, for each trial ran within the first DOE of the experiment. Refer to Appendix B for a comparison to steel.

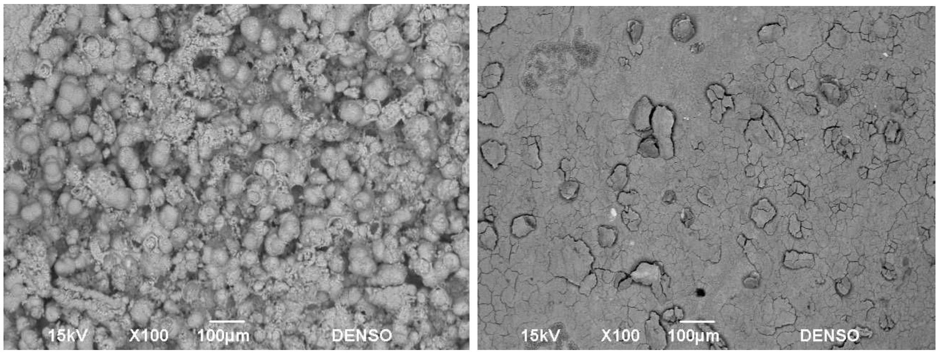


Figure 19. Combination (+,+) Before and after Corrosion

Figure 19 shows the before and after corrosion photos when the electroplating process had 4.5 V administered for one minute. (Please note that the trial photos were taken at 100x magnification, while the previous images are 750x). As clearly seen in the left photo, the electroplating layer was extremely uneven for this factor combination. The rounded particles are the zinc deposits, disconnected and very messy. After corrosion, the plating layer that originally stuck well was intact. There are many visible cracks, as the plating layer was close to cracking off. During this factor combination, it is assumed that instead of the zinc “corroding,” much of the layer simply fell off, which explains why the after corrosion image shows little corrosion.

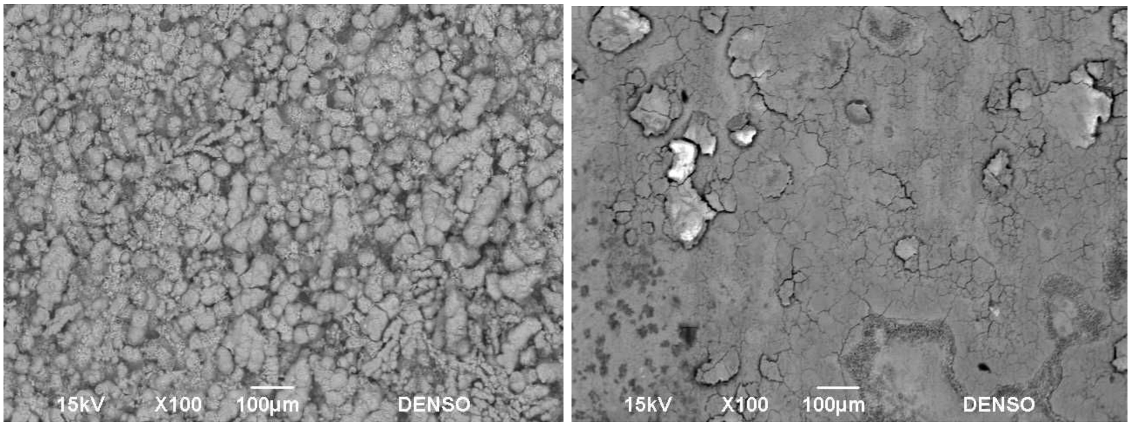


Figure 20. Combination (+,S) Before and after Corrosion

Figure 20, above, shows the before and after corrosion photos when the electroplating process had 4.5 V, for 45 seconds. As seen by the before image, this plating layer was slightly better than when the electroplating process was one minute long, though the round, uneven zinc deposits are still present. After corrosion, the zinc was clearly breaking apart in quite a few areas, but the base layer was still intact.

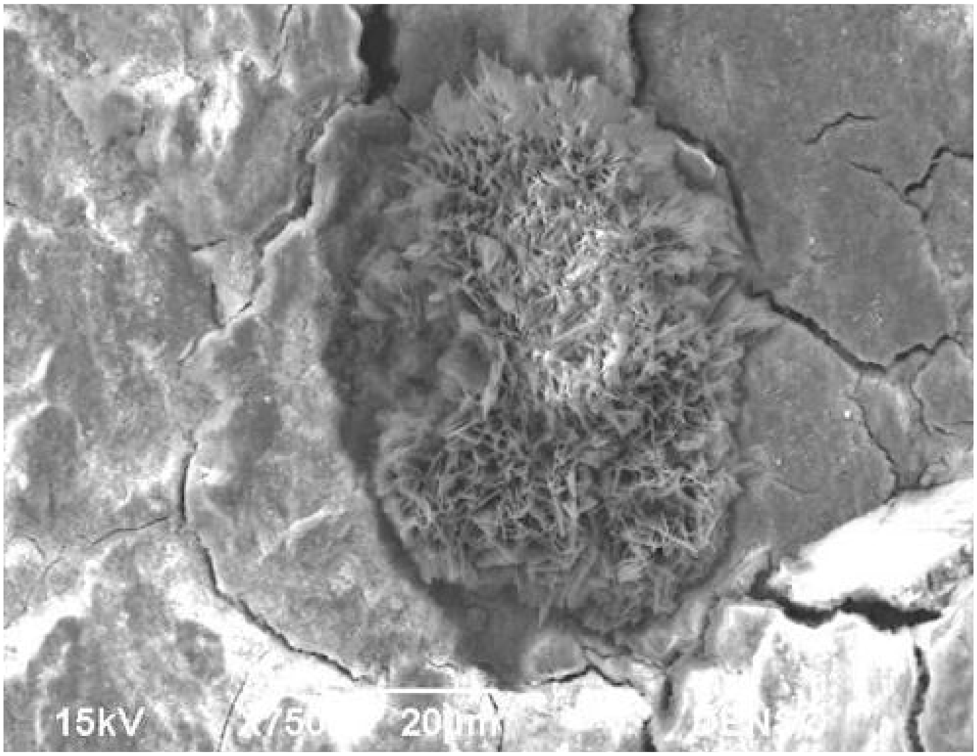


Figure 21. Irregular Structure in (+,S) After Corrosion

Figure 21, above, shows an irregular structure that appeared after corroding the (+,S) trial, of 4.5 V and 45 seconds. This image is magnified 750x, as opposed to the 100x of the other images. It was unclear exactly what this structure was; however, around this structure is the zinc plating, which is clearly breaking apart. Therefore, this was assumed to be the steel, protruding through the fractured zinc layer.

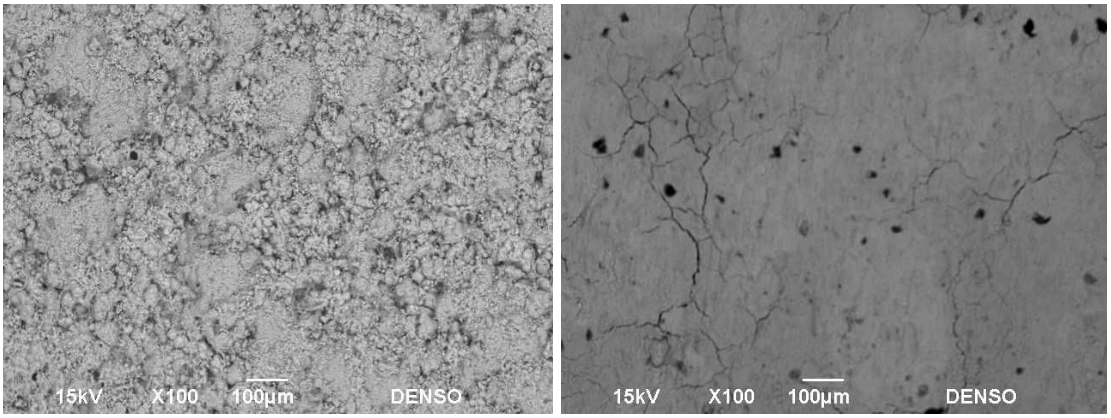


Figure 22. Combination (+,-) Before and after Corrosion

Figure 22, above, shows the before and after photos when steel was plated with zinc at 4.5 volts for 30 seconds. The before photo is similar to that of Figure 19 and 20's, where the plating layer was very spotty with many round deposits of zinc in many uneven layers. The after corrosion photo, however, shows that the plating layer that stayed intact had many less cracks and breaking points, indicating a better strength of the layer.

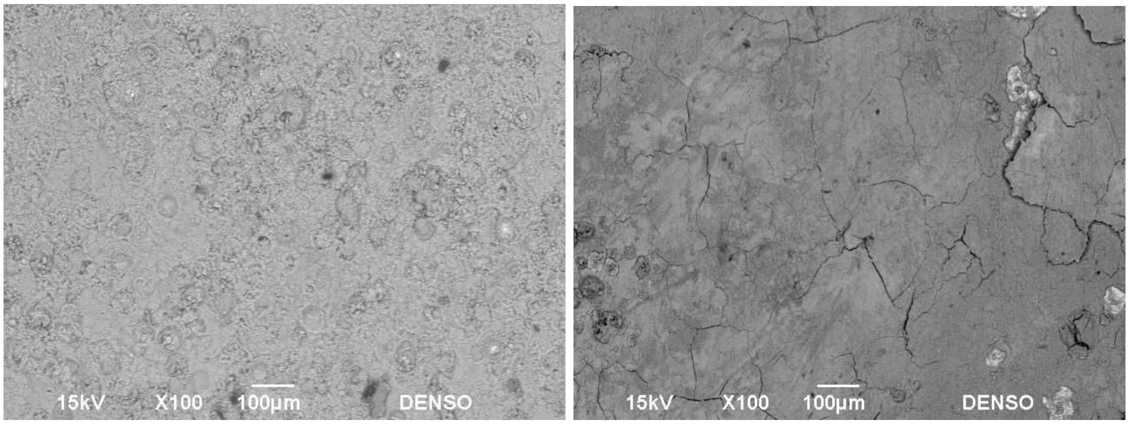


Figure 23. Combination (S,+) Before and after Corrosion

Figure 23, above, shows the before and after corrosion photos for when steel was plated with zinc at 3.0 volts for 60 seconds. After electroplating, the left photo shows that this factor combination produced a more consistent layer than all of the trials where the potential difference was 4.5 volts. After corrosion, the main zinc layer was fairly intact, with some areas breaking apart a small amount.

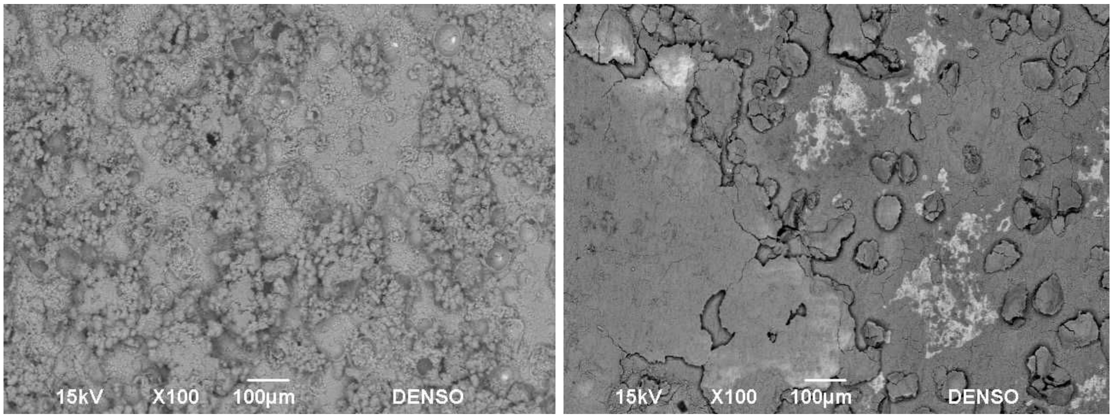


Figure 24. Combination $(S,S)_1$ Before and after Corrosion

Figure 24, above, shows the before and after corrosion photos of when steel was electroplated at 3.0 volts for 45 seconds. After electroplating, the before image actually looks less consistent than when the time was 60 seconds, which seems to contradict the pattern that was followed when the potential difference was 4.5 volts, where shorter times produced more consistent layers. The after corrosion image reveals something the other images do not; the left side of the image shows a metal layer that is clearly above the layer towards the right. Furthermore, lighter areas are seen throughout that side of the metal. This would imply that parts of the zinc layer corroded off enough to expose the steel for this combination, specifically.

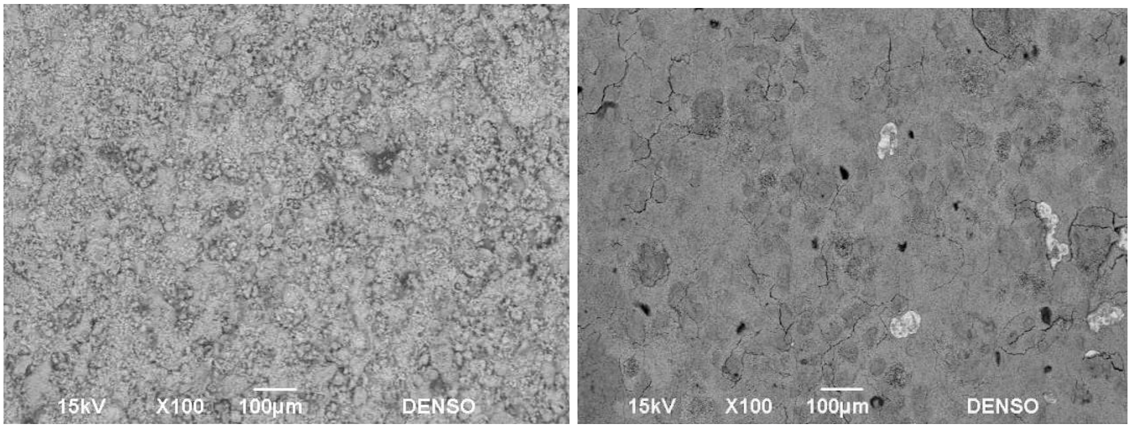


Figure 25. Combination $(S,S)_2$ Before and after Corrosion

Figure 25, above, shows the before and after corrosion images from the second trial when steel was electroplated at 3.0 volts for 45 seconds. This specific trials was removed as an outlier, and the before image gives some hints as to why the results were skewed. It had many of the round, uneven structures that the samples plated at 4.5 volts had, which would have affected the amount of corrosion that occurred. After corrosion, however, the sample shows a fairly even layer of zinc still intact, with some parts of steel visible in the lighter portions of the image.

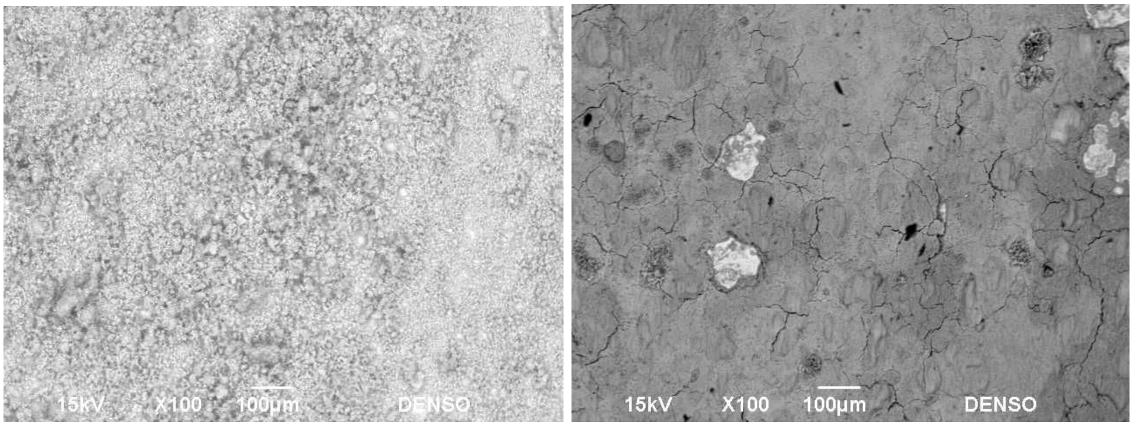


Figure 26. Combination $(S,S)_3$ Before and after Corrosion

Figure 26, above, shows the before and after corrosion images from the third trial when steel was electroplated at 3.0 volts for 45 seconds. The image after electroplating on the left shows some of the inconsistency in the layer towards the center and left, but the right side shows more consistency. After corrosion, a few small areas of zinc corroded entirely, exposing the steel, but otherwise the main layer stayed fairly intact.

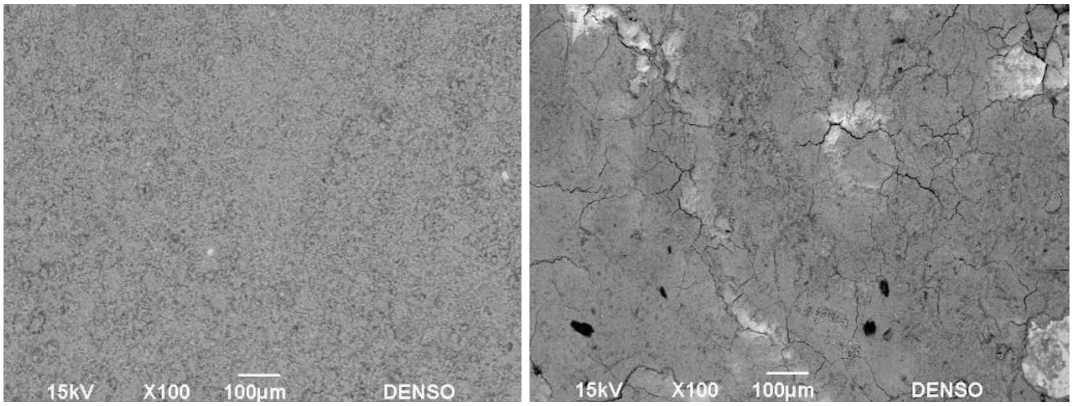


Figure 27. Combination (S,-) Before and After Corrosion

Figure 27, above, shows the before and after corrosion images from when steel was electroplated at 3.0 volts for 30 seconds. The left image shows that a fairly even layer was produced from electroplating. After corrosion, the steel was visible in some areas, and the zinc had some cracks, though it was fairly intact.

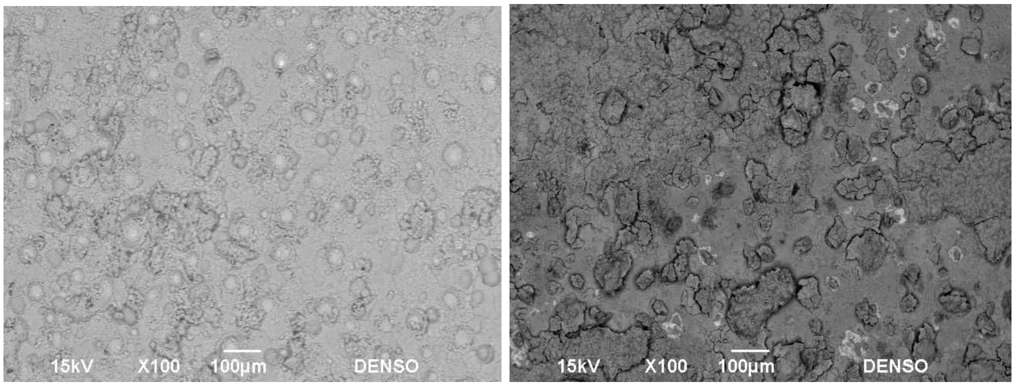


Figure 28. Combination (-,+) Before and After Corrosion

Figure 28, above, shows the before and after corrosion images from when steel was electroplated at 1.5 volts for 60 seconds. The image after electroplating shows an irregularity that was not in the trials with the other voltages. There were multiple circle-shaped deposits on the metal, which were assumed to simply be parts of the zinc that plated differently for an unknown reason. After corrosion, much of the zinc corroded, as the layer is broken up and uneven. Additionally, some steel is visible in the lighter parts of the image.

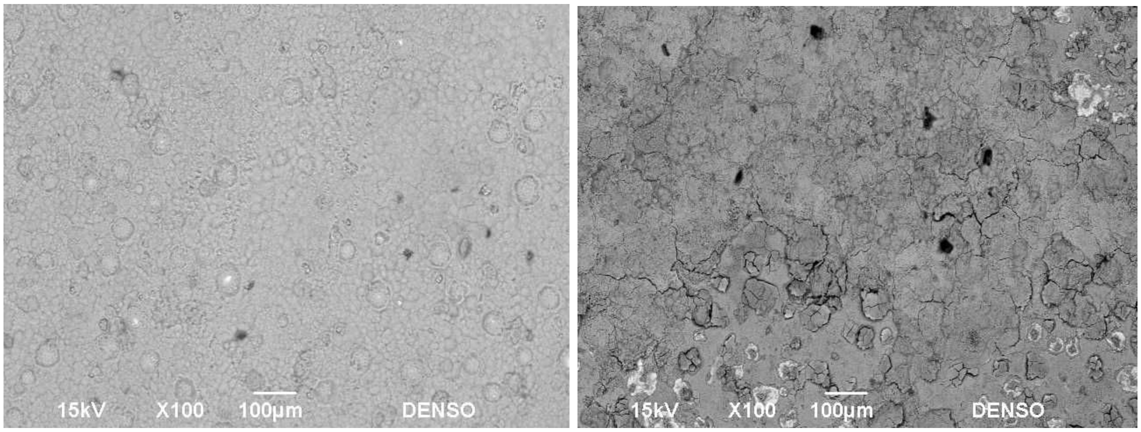


Figure 29. Combination (-,S) Before and After Corrosion

FIgure 29 shows the before and after corrosion images from when steel was electroplated at 1.5 volts for 45 seconds. The before corrosion photo shows the same circular irregularity as in Figure 28, though the rest of the layer is much more consistent. After corrosion, some steel is also visible through the zinc, and the zinc layer did corrode quite a bit.

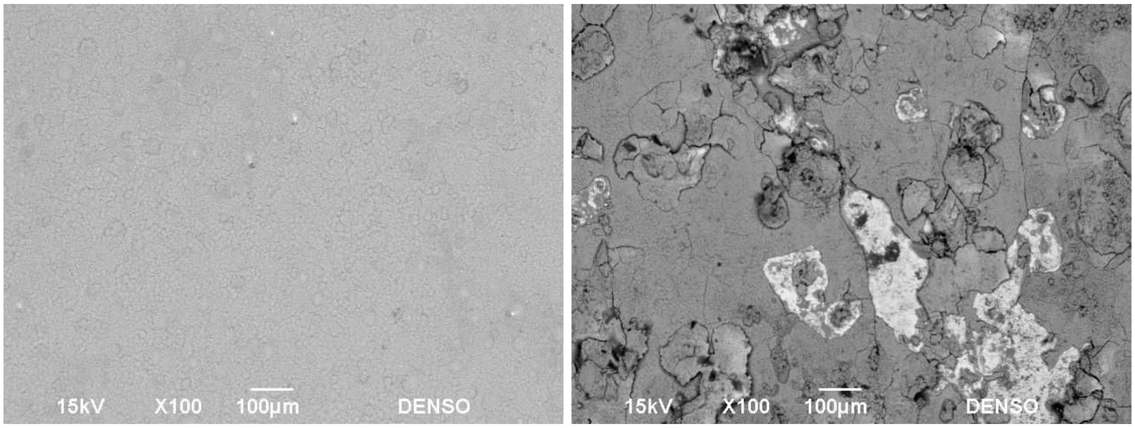


Figure 30. Combination (-,-) Before and After Corrosion

Figure 30, above, shows the zinc-plated steel sample from the (-,-) factor combination of the first DOE, which consisted of 1.5 V during electroplating, with a time of 30 seconds. On the left is the sample before corrosion. This sample appeared to be very smooth under the SEM, with a consistent layer of zinc. When compared to the after electroplating images for every other sample combination, this one produced the most consistent layer. After corrosion, the sample looks awful. The most amount of steel is visible in the lighter areas of the image, which means that, proportionally, zinc corroded the most in this factor combination when compared to the mass that plated.

Appendix C shows images of another method that was attempted to test plating thickness with the help of DENSO. No official observations were made from that method.

Data Analysis and Interpretation

The data collected and discussed in the Data and Observations section of the paper was reliable and appropriate to statistically analyze for many reasons. Controls were tested during pre-trials to understand the expected behavior of the samples during the real trials when various levels of the factors were applied. The patterns made evident in pre-trial testing were maintained across the factor combinations through the actual trials. For example, the pre-trials indicated that if the potential difference was too high, the thickness of the plating layer increased but the quality decreased dramatically and most of the plating layer fell off in corrosion testing. All of the samples that were electroplated with a high voltage, 4.5 V, and had a zinc layer that was of low quality that the samples electroplated with the low voltage, 1.5 V. Randomization was used when running the trials to reduce bias from any human ability or consistency improvements over time. Data was acquired from two run throughs of a Design of Experiment (DOE). More replication was desired, but time constraints with DENSO and limited resources restricted that ability. For the statistical analyses conducted in this section, averages of the results from both DOEs were used. This made the results more reliable.

The experiment of electroplating and corrosion was analyzed using a two factor Design of Experiment (DOE), along with an ANOVA statistical test. The DOE is a robust statistical analysis tool that measures the extent of the impact of several different factors on the response variable in the experiment, while the

ANOVA tests to see if population means are the same. Both analyzations contributed to the statistical meaning of the experiment.

Table 5
Factors and Variables

Potential Difference (Volts)			Time (Seconds)		
(-)	S	(+)	(-)	S	(+)
1.5	3.0	4.5	30	45	60

From Table 5, above, there were a total of nine factor combinations, including the low (-), standard (S), and high (+) values.

Design of Experiment

Below, Table 6 shows the results for the two DOEs and the change in Mass per Unit Area Exposed in grams per square centimeter. The average value for each combination of factors was used for the statistical analysis.

Table 6
Trials Results

DOE		1	2	Average
ΔMass per Unit Area Exposed (g/cm^2)	(S,S)$_1$	-0.0088	-0.0069	-0.0079
	(+,+)	-0.0258	-0.0157	-0.0208
	(+,S)	-0.0060	-0.0133	-0.0096
	(+,-)	-0.0190	-0.0104	-0.0147
	(S,+)	-0.0055	-0.0105	-0.0080
	(S,S)$_2$	----------------	-0.0088	-0.0088
	(S,-)	-0.0101	-0.0046	-0.0074
	(-,+)	-0.0055	-0.0065	-0.0060
	(-,S)	-0.0038	-0.0006	-0.0022

Doe		**1**	**2**	**Average**
ΔMass per Unit Area Exposed (g/cm^2)	(-,-)	-0.0007	-0.0040	-0.0024
	$(S,S)_3$	-0.0085	-0.0065	-0.0075

As noted in the Data and Observations, the $(S,S)_2$ factor combination in the first DOE was removed from the analyzed data due to it being an outlier.

Table 7, below, reorganizes the data from Table 7 using the averages, combining all (S,S) into one average.

Table 7
Organization of factors

		Time (s)			**Row Totals**	**Row Means**
		(+)	S	(-)		
Potential Difference (V)	(+)	-0.0208	-0.0096	-0.0147	-0.0451	-0.0150
	S	-0.0080	-0.0079	-0.0074	-0.0233	-0.0078
	(-)	-0.0060	-0.0022	-0.0024	-0.0106	-0.0035
	Column Totals	-0.0348	-0.0197	-0.0245	-0.1584	----------
	Column Means	-0.0116	-0.0066	-0.0082	----------	-0.0088

Table 7, above, organizes the DOE results into totals and means. The value -0.0088 is $\bar{x}$, which represents the mean of the sum of the column and the row means, the metals samples lost 0.0088 grams per square centimeter exposed to the saltwater solution during the corrosion process.

To analyze the data, a DOE was utilized. The design of experiment was used only to test the effect of the five traditional factor combinations, including (+,+), (+,-), (-,+), (-,-), and (S,S). The other combinations will be incorporated into other statistical analyses.

Below, the following tables and figures give the effects of the single factors, potential difference and time, and the interaction effect.

Table 8
Effect of Potential Difference

Potential Difference	
(-) (1.5 V)	(+) (4.5 V)
-0.0060	-0.0208
-0.0024	-0.0147
Avg. = -0.0042	Avg. = -0.0178

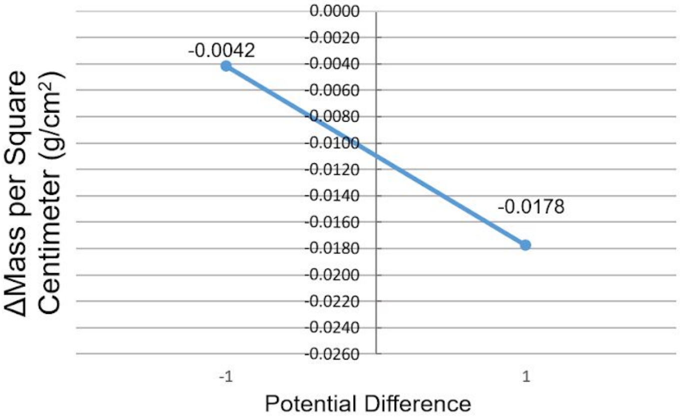


Figure 31. Effect of Potential Difference

Table 8, and Figure 31, above, show the effect of changing potential difference from 1.5 volts to 4.5 volts, excluding the standard trials where the potential difference was 3.0 volts. The change in mass per square centimeter increased greatly in the negative direction, with a numerical effect of -0.0136. This value was found by taking the difference of the averages when the potential difference was high (4.5 V) and low (1.5 V) as shown in Table 8.

Table 9
Effect of Time

Time	
(-) (30 s)	(+) (60 s)
-0.0147	-0.0208
-0.0024	-0.0060
Avg. = -0.0086	Avg. = -0.0134

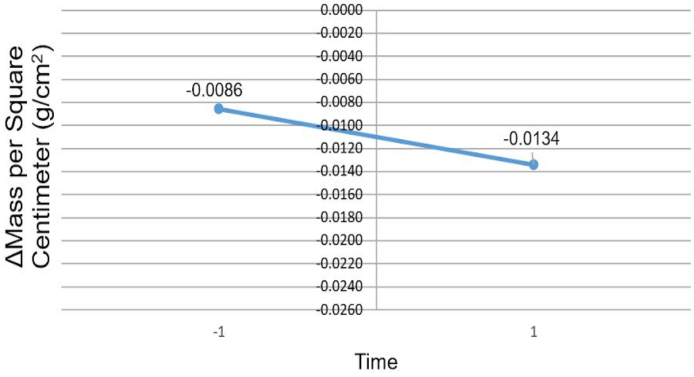


Figure 32. Effect of Time

Table 9 and Figure 32, above, show the effect of time, as it changed within the trials from 30 seconds to 60 seconds, excluding the standard trials where the time was 45 seconds. The change in mass per square centimeter increased slightly in the negative direction, with a numerical effect of -0.0048. This value was found by taking the high (60 s) average of trials from the low (30 s) as shown in Table 9. While this number is relatively large in the context of this experiment, its magnitude appears much smaller than the effect of potential difference.

Table 10
Interaction Effect

			Potential Difference	
			(-)	(+)
Time	Solid Segment	(+)	-0.0060	-0.0208
	Dotted Segment	(-)	-0.0024	-0.0147

Table 10, above, shows the interaction effect between potential difference and time. This table corresponds with Figure 33, below.

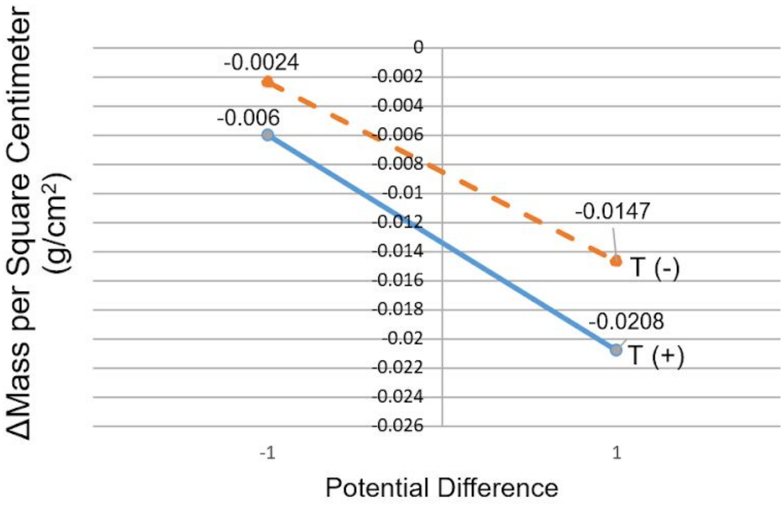


Figure 33. Interaction Effect of Potential Difference and Time

Figure 33 shows the interaction effect of potential difference and time, and correlates to Table 10. As both segments move from left to right, the potential difference changed from 1.5 volts to 4.5 volts. The dotted segment represents the trials where the electroplating process was 30 seconds long, as denoted by T (-), and the solid segment represents trials where the electroplating process was 60 seconds long, as denoted by T (+). Both of the segments appear to be parallel to each other, which impresses that, statistically, there is no interaction between time and potential difference. Additionally, the graph shows that the metal samples that were exposed to the electroplating solution for 60 seconds (solid segment) lost more mass on average than 30 seconds (dotted segment). These samples visibly had a thicker layer directly after electroplating, and the masses after electroplating supported that; however, they also were the least consistent layers, as they corroded and fell off the steel the most.

The numerical interaction effect was found to be -0.0013. This was found by taking the slope of the dotted segment, and subtracting it from the slope of the solid segment.

Below, Figure 34 graphs the standard trials of this experiment.

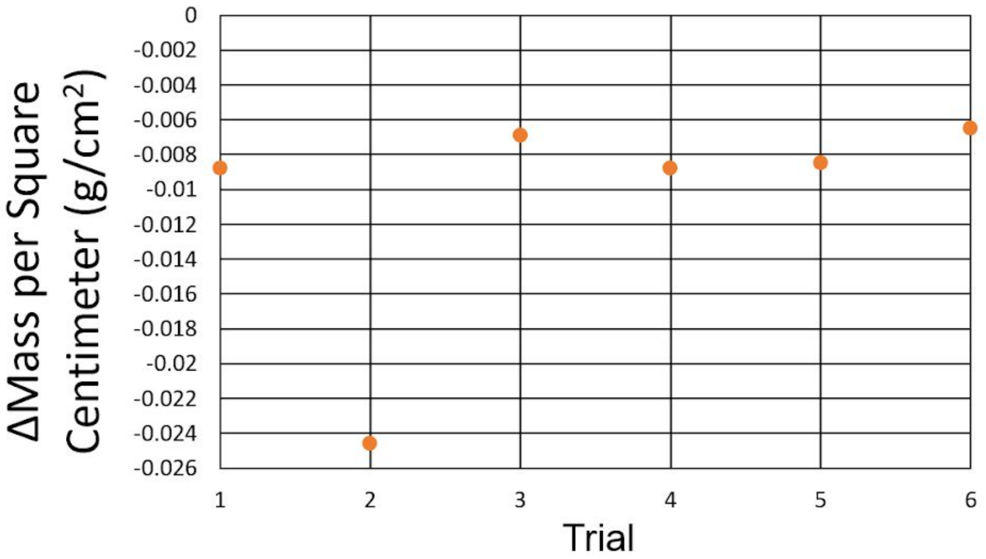


Figure 34. Dot Plot of Standards

Figure 34 is a dot plot of the results from from all six (S,S) combinations that were tested. The first three standards, 1-3, correspond to the three standards that were tested in the first DOE, and the second three standards, 4-6, correspond to those tested in the second DOE (refer to Table 6). As aforementioned in the Data and Observations, the second standard tested in the first DOE, represented by trials 2 above, was an outlier, so it was not used when computing the range of standards or when running any of the statistical tests. The range of standards was found to be 0.0023. This small range indicates that the data collected is reliable and can be used for statistical analyses and that the results of those analyses are a good representation of the true populations.

In the following line plot, let P represent the effect of potential difference, let T represent the effect of time, and let PT represent the interaction effect between potential difference and time.

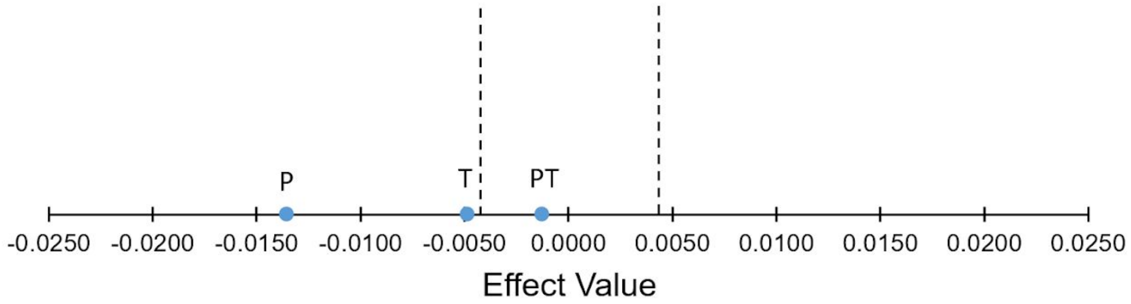


Figure 35. Line Plot of Effects.

Figure 35, above, gives a line plot of effect. This graph was used to determine the significance of the factors in the experiment. The “fences” were found by taking ±2 times the range of standards, which was 0.0023. The factors outside the fences are statistically deemed to be significant within the experiment. As the graph shows, both the single factor effects were deemed significant, and the interaction effect was not significant. For time, despite the effect value being just outside the fences, it was still determined significant; when viewing the images of the samples for corrosion under the SEM (refer to Data and Observations), there were numerous visible differences when time varied between trials. For the interaction effect, Figure 33 clearly indicated that there was a minimal relationship between the two factors due to the lines being almost parallel, so it was logical that the interaction effect was statistically insignificant.

The parsimonious prediction equation can be used to test the theoretical result of a test. It eliminates any insignificant factors, for they are statistically negligible. Below, Figure 36 shows the parsimonious prediction equation for this experiment.

$$y \;=\; \text{"}grand\ average\text{"} \;+ \tfrac{factor\ 1\ effect}{2} * Factor\ 1 + \tfrac{factor\ 2\ effect}{2} * Factor\ 2 \;+\; \text{"}noise\text{"}$$
$$y \;=\; -0.0097 \;+ \tfrac{-0.0136}{2} * Potential\ Difference \;+ \tfrac{-0.0048}{2} * Time \;+\; \text{"}noise\text{"}$$

Figure 36. Parsimonious Prediction Equation

Figure 36, above, shows the Parsimonious Prediction Equation for this experiment. The grand average excluded (S,-), (S,+), (+,S), and (-,S), but included all the others. The following equation is an example of how the equation may be used to predict a value.

$$y \;=\; -0.0097 \;+ \tfrac{-0.0136}{2} * (1) \;+ \tfrac{-0.0048}{2} * (-1) \;+\; \text{"}noise\text{"}$$
$$y \;=\; -0.0141 \;+\; \text{"}noise\text{"}$$

FIgure 37. Parsimonious Prediction Equation Example

Figure 37 uses the factor combination of (+,-), when potential difference is 4.5 volts and time is 30 seconds, as a theoretical prediction of the actual value. The experimental value of this factor combination was -0.0147 g/cm^2, which is close to the predicted value, even with any unauthorized noise.

The individual effects of potential difference and time were significant. The effect of potential difference was -0.0136. This means that as the voltage moves from the low level to the high level, the change in mass per square centimeter is expected to decrease by -0.0136 g/cm^2**.** The effect of time was -0.0048. This means that as the time goes from the low level to the high level, the change in mass per square centimeter is expected to decrease by -0.0048 g/cm^2.

ANOVA Statistical Test

The ANOVA statistical test compares means of three or more populations. It does not just measure how far apart the sample means are from each other, but it measures how far apart they are relative to the variability between individual observations. An ANOVA was appropriate for analyzing the response variable in this experiment because each factor combination represents an independent population. As aforementioned, the Design of Experiment analysis tested the extent to which each independent variable affected the response variable measured. The ANOVA was useful in determining if the variation between the factor combinations was significant. An ANOVA test was conducted on the data expressed in Table 7. Each factor different combination counted as one independent population, so there were nine independent populations: (+,+), (+,S), (+,-), (S,+), (S,S), (S,-), (-,+), (-,S), and (-,-).

There are three main assumptions that must be met for an ANOVA to correctly report the statistical relationships between the individual populations. The assumptions and a detailed explanation of their parallel to the experiment is outlined below.

1. There must be “I” independent Simple Random Samples (SRSs), one from each of I populations where I = # of different populations. In terms of this experiment, there were nine independent populations - one for each factor combination. The Simple Random Sample for each population consists of all of the results reported for that factor combination from all of

the DOEs that were run. There were results representative of each population tested, therefore this assumption was met.

2. Each population must have a normal distribution. Although a distribution could not be graphed for each independent population due to a small sample size, the consistency evident in the graph and range of standards, (refer to Figure 34), implies that the results represent independent populations with normal distributions. However, this assumption technically was not met.
3. All populations must have the same standard deviation, and that value is unknown. The nine independent populations do not have the same standard deviations; nevertheless, this assumption is considered to be met, because an ANOVA is not sensitive to violations of this assumption when all samples have the same size, which in this case they do, or similar sizes.

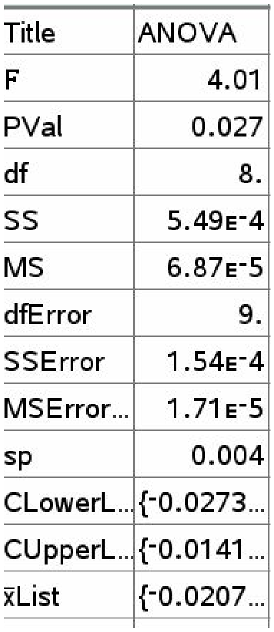
Because the second assumption for the ANOVA to work was not technically met, the results must be taken with some caution. Because the standards plot shows consistency, however, the results are likely valid due to the consistency of the results, as shown by the standards.

The null and alternative hypotheses for the test are stated below.

H_0: $\mu_{(+,+)} = \mu_{(+,S)} = \mu_{(+,-)} = \mu_{(S,+)} = \mu_{(S,S)} = \mu_{(S,-)} = \mu_{(-,+)} = \mu_{(-,S)} = \mu_{(-,-)}$
H_a: $\mu_{(+,+)} \neq \mu_{(+,S)} \neq \mu_{(+,-)} \neq \mu_{(S,+)} \neq \mu_{(S,S)} \neq \mu_{(S,-)} \neq \mu_{(-,+)} \neq \mu_{(-,S)} \neq \mu_{(-,-)}$

Above are the hypotheses for the ANOVA test where H_0 is the null hypothesis and H_a is the alternative hypothesis. If ΔMass per Unit Area Exposed (g/cm^2) is the "output," then, in words, the null hypothesis states that the mean outputs of all nine factor combinations are equal to each other. Likewise, yet contrastingly, the alternative hypothesis states that the mean outputs from the nine independent populations are not equal to each other. The results from the ANOVA test follow in Table 11.

Table 11
ANOVA Results



Title	ANOVA
F	4.01
PVal	0.027
df	8.
SS	5.49E-4
MS	6.87E-5
dfError	9.
SSError	1.54E-4
MSError…	1.71E-5
sp	0.004
CLowerL…	{-0.0273…
CUpperL…	{-0.0141…
x̄List	{-0.0207…

Table 11, above, gives the results for an ANOVA test run on this experiment. The ANOVA incorporates all nine factor combinations, including the ones where the standards mix with the high and low variances, unlike the Design of Experiment. The degree of freedom, abbreviated to df in the table, was eight, for it is one less than the number of independent populations, nine. The ANOVA test produced an F value of 4.01. That number corresponds to a p-value, PVal, which was 0.027. The F value was calculated by dividing the Mean Square Group (MS) value, $6.87*10^{-5}$, by the Mean Square Error (MSError) value, $1.71*10^{-5}$. The Mean Square Group represents the variation among sample means between each population. The Mean Square Error represents the variation among individuals in all samples of each population. Appendix E outlines how the MS and MSError were calculated.

The null hypothesis was rejected, because the p-value was less than the alpha level, α, of 0.05. Statistically, there is evidence that the independent populations have different outputs. In other words, there was only a 2.7% chance of getting the results that occurred by chance alone if the null hypothesis was true.

After analyzing the results from both statistical analyses, the significance of the experimental factors were determined. The DOE stated that both potential difference and time significantly affected the response variable, which was ΔMass per Unit Area Exposed (g/cm^2). In a similar manner, the ANOVA produced a p-value less than the alpha level, α, of 0.05 that led to the rejection of the null hypothesis which stated that the means of the independent populations were equal. While the ANOVA confirmed the means for each factor combination were different, the DOE showed the factors that made those means different, and to what extent they were effective.

Conclusion

The purpose of this experiment was to determine the effect of the electroplating process on the corrosion resistance of zinc-plated steel. The experiment was designed to test and measure the extent of the effect of altering potential difference and duration of the electroplating process on the corrosion resistance of zinc-plated-steel. To test this, a Design of Experiment (DOE) was utilized for the electroplating process under nine variable combinations (refer to tables 1-4), and all those combinations were placed under the same conditions for corrosion testing.

The hypothesis of this experiment stated that “If steel is plated with zinc at 4.5 volts for 60 seconds, the change in mass per a specific area through the corrosion process will be the smallest, and the change in the thickness of the plated sample will be the smallest.” After experimenting and using multiple statistical analyses, the hypothesis was rejected. On average, zinc-plated steel under the hypothesized conditions lost more zinc, -0.0208 grams per square centimeter, than any other variable combination when exposed to the corrosive solution. Furthermore, while the numerical results for the change in thickness of the plated samples prior to corrosion resulted in inconsistencies and were unusable, the qualitative observations conclude that the samples that suffered the greatest mass loss also suffered the largest decrease in plating thickness.

As stated in the Review of Literature, current is simply the flow of electrons in a circuit. As the current is increased, the flow of electrons increases.

As also explained in the Review of Literature, potential difference was manually easier to manipulate than current, so it was used as the factor instead of current, for Ohm's law allows that substitution to work. For electroplating, this allows an anode to plate a larger quantity of itself onto the cathode at higher potential differences than lower ones in a specific quantity of time. That held true in this experiment. When the potential difference was 4.5 volts, which made the current a larger value due to a direct relationship between the two, a greater mass of the zinc anode plated the steel cathode; this is because zinc's electrons flowed at a faster rate through the power source's wires, which allowed more plating to occur. The time worked in tandem with current, as it simply allowed more time for electroplating to occur. As longer durations resulted in a thicker layer with a greater mass.

As concluded from the Data Analysis and Interpretation, potential difference and time both had a significant effect on the experiment, but the interaction effect did not. Since Faraday's Law includes current (related to potential difference) and time, stating that they are crucial in determining the mass of plating through electroplating, it was expected that both potential difference and time were significant on their own, and they were. However, the interaction effect between potential difference and time was not significant due to their proportion. The interaction effect graph showed that the rate of change of the change in mass per surface area was the same when time and potential difference were increased. As potential difference increased from 1.5 volts to 4.5

volts, changing the time increased the amount of plating in a linear manner. Thus, there was no statistical “interaction” between the two factors.

While Faraday’s law did hold true, higher potential differences and times plated larger quantities, the thicker layers were visibly uneven, as seen in Figure 11, and many edges and loose areas fell off before the corrosion process even occurred and while the samples were in the corroding solution. The Scanning Electron Microscope images also confirmed that the higher voltage and time trials had disordered plating layers, compare Figure 22 to Figure 30, while the lower times and voltages had much more even layers. The numerical results for the experiment showed that larger potential differences and times generally had larger losses in mass than the lower values. While this seems to numerically contradict Faraday’s Law, his law was only applicable to the actual mass of electroplating, and it was irrelevant to the corrosion aspect of the experiment. The results displayed the effect of taking the extreme of electroplating factors; for electroplating, 4.5 volts is often considered “extreme,” and a lower potential difference like 3.0 volts is more common. The results showed that an increased potential difference and time, simply to produce a larger mass in the same time as a lower potential difference, will produce an uneven, weak layer. Those plating layers may just fall off without any corroding liquids, or even by simply blowing on them.

This experiment showed what Faraday’s law cannot demonstrate: a layer of greater mass does not necessarily make it better for corrosion protection. This finding correlates with the findings reported in the article “*Zinc Electrodeposition from Acetate Solutions*.” It was discovered that there is a limit at which an increase in current (and consequently, potential difference) will stop increasing the density of the anode buildup (Krishnan). At that point, there is too much atomic motion for the plating to occur evenly, and most of the anodic ions do not cathode. While 4.5 volts was not that limit, it began to reach it. Pre-trials showed that even though plating would still occur at higher potential differences, the layers were extremely uneven and fell off in the solution. As such, 4.5 volts was considered an extreme value for potential difference.

Although the experimental design was improved from pretrial testing and and partnership with the professional contact, there was a fair amount of noise and error in the experiment. There were slight changes in the concentration of the electrolyte solution, as noted in the observations, because more solution was made halfway through trials. Also, because of this and the overnight storage of the solution, the aeration of the solution used in each trial may have fluctuated. This was not measurable; however, it is known that an increase in the aeration of the electrolyte used for electroplating does increase the amount of oxides deposited onto the cathode (Aluia). These are both small sources of possible error. Most of the error, however, did come from setting up the DENSO method with the teflon tape. When pulling the cut teflon tape off the samples, small bits of plating would sometimes come off, as shown in Figure 15. In turn, those areas would corrode more than any other, resulting in inconsistencies within the plating laters. Additionally, there was no way to look at each metal under the exact same position before and after corrosion under the Scanning Electron Microscope (SEM). In an attempt to counteract this, the “most consistent plating” area was used for the SEM after electroplating, and the “most corroded” area was used after corrosion, which was assisted by Mr. Aluia. Since one area of plating may have been compared with another area, it was impossible to declare all qualitative aspects of plating solely with the SEM.

Further studies indicate multiple ways to improve on this experiment’s design. There were a few ideas suggested by Mr. Aluia that were not implemented in this experiment due to time constraints and resource availability, which may improve this experiment in future testing. It was advised to expose the metal samples in a specific volume of the electroplating solution in a ration with the area of the exposed metals to the corrosion solution; however, more zinc nitrate would have been needed, so the maximum volume of the solution with the given resources was used. For the corrosion process, the metals visibly showed corrosion after only two days, so they were then removed. Since zinc and steel corrode at different rates, the samples were removed from the salt solution before the steel had the opportunity to corrode. If the samples were in the solution for any longer, it would have been difficult to account for when zinc finished corroding, and when steel began; the rates of corrosion would have altered, and the results would have skewed. In another experiment, allowing the samples to corrode until they are completely deteriorated would be immensely useful as another way to model benefits of plating.

Current researchers are using electrochemistry to improve material design. At DENSO, Mr. Aluia displayed a few zinc-plated objects. An alternator rotor in cars is commonly zinc plated, so modeling the atmosphere it is exposed to would accurately model the plating's effect for that situation. Adding nitrates to a saltwater solution would also effectively model ocean water, which was the inspired idea for this experiment. “Design engineers in the aerospace industry are...challenged to improve...function of components used in commercial and military aircraft. Parts used in these aircraft must withstand high stress corrosive conditions with long-term use, and must meet highly demanding cycle life specifications” (Able Electropolishing). Electroplating and electropolishing, an electrochemical process used to remove metallic ions from a metal part, are both used for increasing corrosion resistance and long-term fatigue resistance of metal parts. For example, Able Electropolishing is using electrochemistry to fix critical parts in aircrafts that are failing prematurely, reduce the noise produced by gears grinding in electric motors, remove microcracks on metal surfaces, and improve the lifespan of metal parts. Although the process of electropolishing is similar, it is technically the opposite of electroplating; however, the relationships between potential difference and time are the same. Using that information, electroplating and electropolishing are both useful methods for polishing metals and creating quality metals.

Acknowledgements

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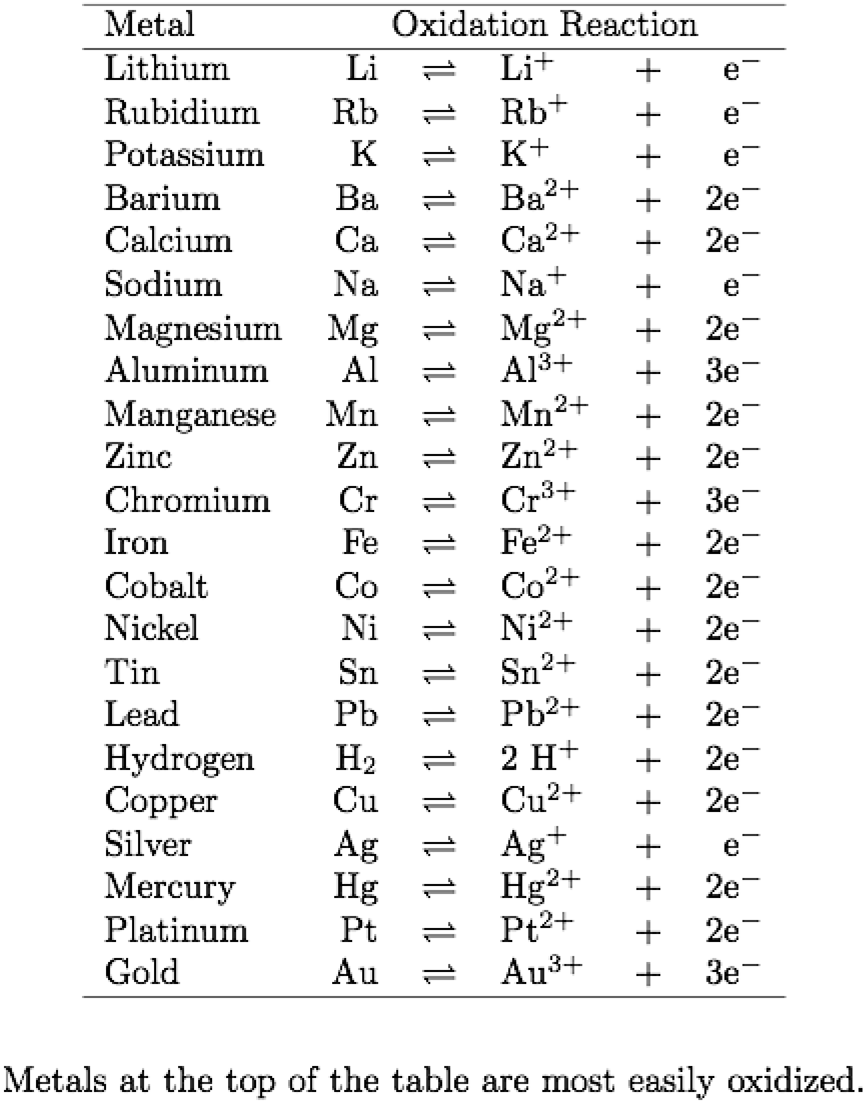
Appendix A: Activity Series of Metals



Metal	Oxidation Reaction				
Lithium	Li	$\rightleftharpoons$	Li^+	$+$	e^-
Rubidium	Rb	$\rightleftharpoons$	Rb^+	$+$	e^-
Potassium	K	$\rightleftharpoons$	K^+	$+$	e^-
Barium	Ba	$\rightleftharpoons$	Ba^{2+}	$+$	$2e^-$
Calcium	Ca	$\rightleftharpoons$	Ca^{2+}	$+$	$2e^-$
Sodium	Na	$\rightleftharpoons$	Na^+	$+$	e^-
Magnesium	Mg	$\rightleftharpoons$	Mg^{2+}	$+$	$2e^-$
Aluminum	Al	$\rightleftharpoons$	Al^{3+}	$+$	$3e^-$
Manganese	Mn	$\rightleftharpoons$	Mn^{2+}	$+$	$2e^-$
Zinc	Zn	$\rightleftharpoons$	Zn^{2+}	$+$	$2e^-$
Chromium	Cr	$\rightleftharpoons$	Cr^{3+}	$+$	$3e^-$
Iron	Fe	$\rightleftharpoons$	Fe^{2+}	$+$	$2e^-$
Cobalt	Co	$\rightleftharpoons$	Co^{2+}	$+$	$2e^-$
Nickel	Ni	$\rightleftharpoons$	Ni^{2+}	$+$	$2e^-$
Tin	Sn	$\rightleftharpoons$	Sn^{2+}	$+$	$2e^-$
Lead	Pb	$\rightleftharpoons$	Pb^{2+}	$+$	$2e^-$
Hydrogen	H_2	$\rightleftharpoons$	$2\ H^+$	$+$	$2e^-$
Copper	Cu	$\rightleftharpoons$	Cu^{2+}	$+$	$2e^-$
Silver	Ag	$\rightleftharpoons$	Ag^+	$+$	e^-
Mercury	Hg	$\rightleftharpoons$	Hg^{2+}	$+$	$2e^-$
Platinum	Pt	$\rightleftharpoons$	Pt^{2+}	$+$	$2e^-$
Gold	Au	$\rightleftharpoons$	Au^{3+}	$+$	$3e^-$

Metals at the top of the table are most easily oxidized.

Figure 1. Activity Series

Figure 1, above, gives the reactivity series for metals. The higher the metals on this chart, the more reactive. In this experiment, zinc is plating Copper. SInce zinc is more reactive, it will successfully plate Copper.

Appendix B: Steel Under the Scanning Electron Microscope

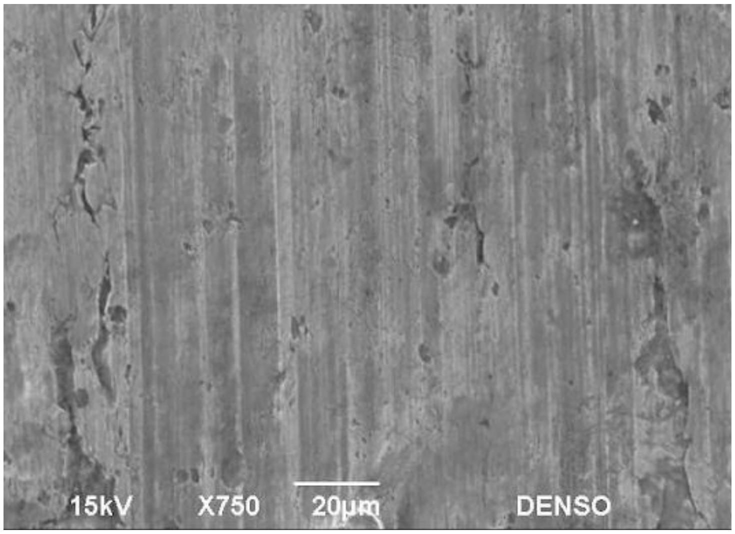


Figure 1. Steel Under the Scanning Electron Microscope

Figure 1, above, shows the steel under the Scanning Electron Microscope (SEM). The most notable quality of this steel is the brittleness, and lack of consistency. This image may be used for visual comparisons at the molecular level. There is a surface pattern of vertical lines at the molecular level. This indicates the direction in which the steel was rolled or polished. This pattern is not visible to the human eye.

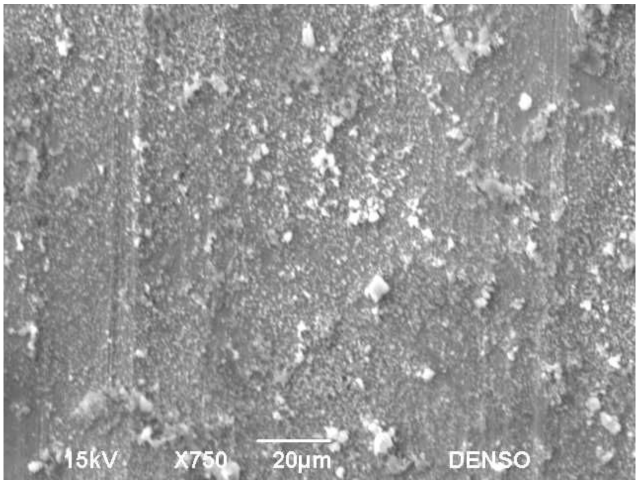


FIgure 2. Steel After Corrosion

Figure 2, above, shows a piece of steel magnified 750x after being corroded in saltwater. This image was used to identify and compare if steel ever began to visibly corrode through a zinc layer during pre-trials.

These images must be carefully considered for multiple reasons; they are magnified 750x, rather than 100x, as each factor combination is within the Data and Observations. Additionally, the corrosion conditions of Figure 2 were not recorded; this was mistakenly done early in the experiment, and there were no materials or time to corrode another piece of steel exactly as the other combinations were corroded.

Appendix C: Mounting Plated Samples

In addition to the formal method of measuring the change in mass per surface area, DENSO aided in attempting to mount the samples to check the plated samples' cross sections, and measure that thickness.

FIgure 1. Mounted Samples

Figure 1 shows three of the zinc-plated steel samples. These samples were mounted in a plastic holder that was then filled in with plastic granules. High temperature and pressure were used to melt and compress the granules to form a solid circular block containing the samples. Although the block was polished with fine diamond sandpaper discs to obtain a clean mirror finish as pictured above, the plating layers chipped off and were unmeasurable under a microscope.

Appendix D: DOE

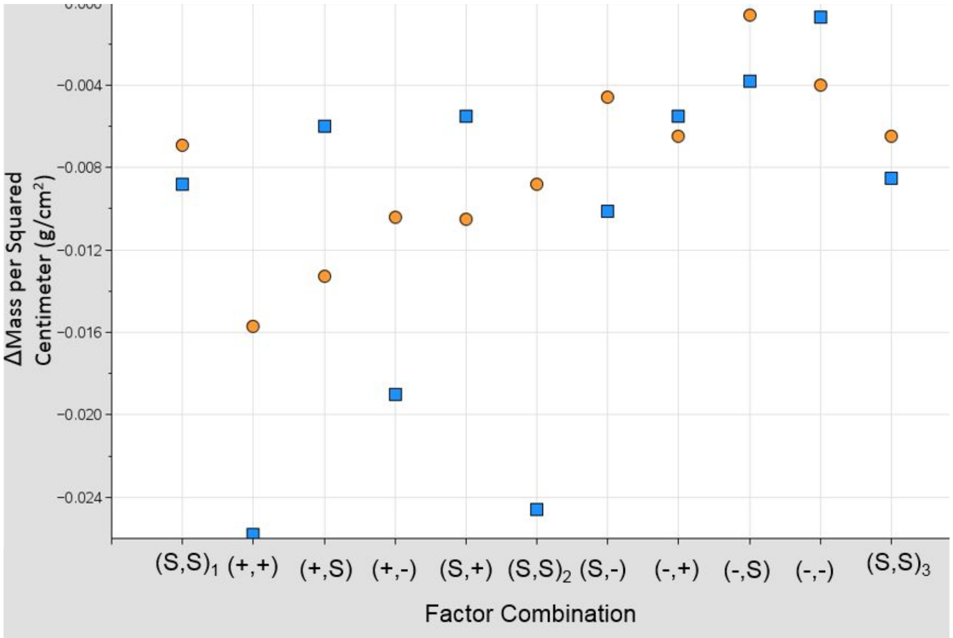


Figure 1. Dot plot of DOE 1 and DOE 2

Figure 1 is a dot plot of the results from this experiment. The squares represent the results from DOE 1, and the circles represent the results from DOE 2. The scale of this graph goes from 0.0000 at the top of the graph, to -0.0260 g/cm^2, as the graphs within the Data Analysis and Interpretation are. The purpose of this graph is to check for consistency within the trials.

As noted previously, $(S,S)_2$ within the first DOE was a large DOE, so it was removed. The (+,+) trials were the only trials that had large variance between them, and that was likely due to the low-quality plating layer that was created through that factor combination. In fact, that variance actually demonstrates the effect of using a high potential difference, as opposed to the (-,+) trials where the potential difference was lower and the results were much more consistent. This was one of the reasons the stats tests were still able to run well.

Appendix E: Calculating Mean Square Group and Mean Square Error

The following equations showing the steps for calculating the Mean Square Group. This is a measure of the variation among sample means between each population.

$$MS = \frac{n_1(\overline{x}_1-\overline{x})+n_2(\overline{x}_2-\overline{x})+n_3(\overline{x}_3-\overline{x})+n_4(\overline{x}_4-\overline{x})+n_5(\overline{x}_5-\overline{x})+n_6(\overline{x}_6-\overline{x})+n_7(\overline{x}_7-\overline{x})+n_8(\overline{x}_8-\overline{x})+n_9(\overline{x}_9-\overline{x})}{I-1}$$

$$MS = \frac{2(-0.0208+0.0088)+2(-0.0097+0.0088)+2(-0.0147+0.0088)+2(-0.0080+0.0088)+2(-0.0080+0.0088)+2(-0.0074+0.0088)+2(-0.0060+0.0088)+2(-0.0022-0.0088)+2(-0.00235+0.0088)}{9-1}$$

$$MS = 6.8669 * 10^{-5}$$

This equation calculates the MS value which represents the Mean Square Group in the ANOVA test. It is used to along with the Mean Square Error (See below) to calculate the F value.

The following equations show the steps for calculating the Mean Square Error. This is a measure of the variation among individuals in all samples of each population.

$$MSError = \frac{(n_1-1)s_1^2+(n_2-1)s_2^2+(n_3-1)s_3^2+(n_4-1)s_4^2+(n_5-1)s_5^2+(n_6-1)s_6^2+(n_7-1)s_7^2+(n_8-1)s_8^2+(n_9-1)s_9^2}{N-I}$$

$$MSError = \frac{(5.1005*10^{-5})^2+(2.6645*10^{-5})^2+(3.698*10^{-5})^2+(1.25*10^{-5})^2+(7.8125*10^{-5})^2+(1.5125*10^{-5})^2+(0.05*10^{-5})^2+(0.512*10^{-5})^2+(0.5445*10^{-5})^2}{18-9}$$

$$MSError = 1.7122 * 10^{-5}$$

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